DEVELOPMENT OF A GENERALIZED KINETIC MECHANISM FOR PHOTOCHEMICAL SMOG

Thesis by

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To Vickie, my wife, who has both encouraged and endured.

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ABSTRACT

In this dissertation a generalized kinetic mechanism for photochemical smog is formulated and validated. There are two basic objectives for pursuing this work. First, kinetic mechanisms are a critical component of airshed simulation models whose uses include the evaluation of alternative control strategies for photochemical smog. Second, kinetic mechanisms provide a means of understanding the chemistry of smog formation. In addition to developing the kinetic mechanism, extensive consideration is given here to further experimental studies of the kinetics of elementary reactions and to procedural aspects of smog chamber experiments which will aid in reducing uncertainty in future mathematical simulation studies.

The most important feature of the kinetic mechanism which is presented in Chapter I lies in its general nature; that is, the mechanism has been written so as to be applicable to a large number of hydrocarbons--and, ultimately, the entire atmospheric hydrocarbon mix--rather than just a specific hydrocarbon such as propylene. The rationale for the lumping procedure is described in detail. By design the resultant mechanism takes advantage of the general features typical of smog formation to maintain at a minimum the number of reactions and species included while at the same time retaining a high degree of detail, especially as concerns the chemistry of the inorganic species. In essence a careful balance between compactness of form and accuracy of prediction is sought. The mechanism is then validated using n-butane-NO_x, propylene-NO_x, and n-butane-propylene-

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 NO_{χ} smog chamber data at 13 different sets of initial reactant concentrations and a wide variety of hydrocarbon to NO_{χ} ratios.

Several sources of potential uncertainty in the predictions of the mechanism are discussed. Of these the two most serious--and the two most amenable to correction--are gaps in our knowledge of rate constants and mechanisms of key elementary reactions and effects related to smog chamber systems which either alter or incorrectly monitor the course of smog formation in controlled experimental studies. These sources of uncertainty along with recommendations for future studies to minimize them are the topics of Chapters II and III.

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I. DEVELOPMENT AND VALIDATION OF A GENERALIZED KINETIC MECHANISM FOR PHOTOCHEMICAL SMOG

The formulation of a kinetic mechanism of general validity for atmospheric photochemical reactions is an endeavor beset by several inherent difficulties:

- (i) There is a multiplicity of stable chemical species present in the atmosphere. Most of these exist at very low concentrations, thereby resulting in major problems in detection and analysis. A number, in fact, probably remain unidentified.
- (ii) There is a large variety of unstable species (highly reactive, short-lived intermediates) in the atmosphere.
 These species cannot yet be measured because of their extremely low concentrations and high reactivities.
- (iii) Among the stable and unstable species, there are literally hundreds of potential chemical reactions that may be occurring.

However, while we must admit to only a limited knowledge of atmospheric reaction processes, it remains essential that we attempt to formulate quantitative descriptions of these processes which are suitable for inclusion in an overall airshed simulation model. The general considerations of, the progress toward, and the remaining problems in the development and validation of a generalized mechanism for atmospheric photochemical reactions that is to be included in an

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overall airshed model are the subjects of this chapter.

A. Review of the Photochemical Smog System and Current Photochemical Kinetic Mechanisms

A large number of experimental programs have been carried out over the past two decades with the aim of increasing our knowledge of the process by which photochemical smog forms. In 1961 Leighton published an accurate and, it now appears, reasonably complete description of the photochemistry of air pollution. Since that time additional kinetic and mechanistic studies of elementary reactions thought to be important in smog formation have served to further refine our understanding of the overall process. By 1969 the picture had become sufficiently complete so as to make feasible the initial formulation and validation of kinetic mechanisms for the mathematical simulation of smog formation observed under controlled laboratory conditions.

1. The Nature of the Photochemical Smog System

The general features of the concentration-time behavior of the photochemical smog system are shown in Figure 1. These data were obtained by Altshuller et al. (1967). Although the experimental data in Figure 1 involve only the single hydrocarbon propylene, propylene photooxidation in the presence of NO_X manifests the major characteristics of photochemical smog. The rate of decrease of both propylene and NO does not reach a substantial value immediately after the lights are turned on, suggesting an induction period. After the apparent induction period NO is rapidly oxidized to NO_2 . The concentration of NO



FIGURE 1. Concentration-Time Behavior of Photochemical Reactants and Products in Smog Chamber

reaches a low value which persists throughout the latter stages of the reaction. At about the time the NO_2 concentration reaches a maximum, measurable O_3 formation begins to take place. The subsequent loss of NO_2 is attributable to formation of organic pernitrates (e.g., peroxyacetylnitrate (PAN)) and nitric acid. Additional stable organic products such as formaldehyde (HCHO) and acetaldehyde (CH₃CHO) also form in the propylene-NO_y system.

It has been observed that the peak amount of 0_3 produced over a fixed time of irradiation increases rapidly, goes through a maximum, and finally decreases as one performs a series of controlled experiments in which the initial hydrocarbon concentration is held constant and the total initial concentration of NO_x is increased.

Although the data shown in Figure 1 are indicative of the concentration behavior in atmospheric photochemical smog, a number of factors may serve to make the chemical behavior in a smog chamber differ from actual atmospheric chemistry:

- (i) Wall effects which may be present in a chamber cannot presently be related to ground level surface effects in the atmosphere,
- (ii) Most smog chamber experiments reported to date have not included oxides of sulfur or aerosols in the initial mixture. In most cases, these two classes of species are present in the atmosphere,
- (iii) Concentration levels employed in smog chamber experiments are often higher than atmospheric levels, and

(iv) The intensity and distribution of artificial radiation employed in a chamber may not be representative of solar radiation.

In spite of these potential problems, smog chamber studies are a necessity in understanding the chemistry of the smog system. This is so because it is virtually impossible to isolate chemical reaction effects from those of transport and diffusion in the atmosphere.

2. The Nature of Photochemical Kinetic Mechanisms

The object of developing a kinetic mechanism for photochemical smog is to enable the prediction of both smog chamber reaction phenomena, such as is illustrated in Figure 1, and atmospheric reaction phenomena. There are some general considerations which are important in developing such a mechanism. First, the mathematical description of the mechanism (in terms of the number of species included) must not be overly complex, as computation times for the overall airshed model within which the mechanism is to be imbedded are likely to be excessive. On the other hand, an overly simplified mechanism may omit important reaction steps, and thus be inadequate to describe atmospheric reactions over a range of conditions. A major requirement, then, is that the mechanism predict the chemical behavior of a complex mixture of many hydrocarbons, yet that it include only a limited degree of detail. <u>Thus, the mechanism must strike a careful</u> balance between compactness of form and accuracy of prediction.

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A kinetic mechanism, once developed, must be validated. This procedure is commonly conceived as consisting of two parts: validation in the absence of transport processes and validation in their presence. In practical terms we are speaking, respectively, of comparison of the model's predictions with data collected in smog chamber experiments and with data collected at contaminant monitoring stations in an airshed. When we speak of validation of a kinetic mechanism here, we are referring to the comparison between predictions and experiment based on smog chamber studies.

To provide a framework for the discussion of kinetic mechanisms, we will first consider the highly generalized kinetic scheme given below.

 $NO_{2} + h\nu \stackrel{1}{\rightarrow} NO + 0$ $0 + O_{2} + M \stackrel{2}{\rightarrow} O_{3} + M$ $O_{3} + NO \stackrel{3}{\rightarrow} NO_{2} + O_{2}$ $O_{3} + Hydrocarbons \stackrel{4}{\rightarrow} Stable Products + Radicals$ Radicals + Hydrocarbons $\stackrel{5}{\rightarrow} Stable Products + Radicals$ Radicals + NO $\stackrel{6}{\rightarrow} Radical + NO_{2}$ Radicals + NO $\stackrel{7}{\rightarrow} Stable Products$ Radicals + Radicals $\stackrel{8}{\rightarrow} Stable Products$

[&]quot;Radicals" include both O-atoms and OH radicals, the principal radical oxidizers of hydrocarbons.

The reactions that take place in the generation of photochemical smog, as exemplified by the above mechanism, can be classified as follows (in the terminology of chain reactions):

- (i) Initiation reactions those that provide free radicals to induce chain reactions, e.g., $NO_2 + hv \rightarrow NO + O^*$
- (ii) Branching reactions those in which there is a net increase in radical species, e.g., 0 + HC → Products + Radicals, where more than one radical results
- - Radical + HC \rightarrow Product + Radical (iv) Termination reactions - those that remove free radicals

through the formation of stable end products, e.g., reactions 7 and 8.

Let us now examine the behavior of this highly generalized mechanism to see if it is capable of predicting the qualitative features of the photochemical smog system, in particular the rapid rate of conversion of NO to NO_2 and the effect of varying initial reactant concentrations on O_3 formation. In the discussion that follows, we denote

^{*}This reaction is not the only initiation reaction that occurs in the generation of smog. Photolysis of nitrous acid, alkyl nitrites and aldehydes also provide free radicals. For simplicity, and because NO₂ photolysis is the most important initiation reaction, we have omitted others in this generalized mechanism.

the total concentration of radicals as [R] and that of hydrocarbons as [HC]. We can write a material balance on the total concentration of free radicals in the following manner:

$$\frac{d[R]}{dt} = a[NO_2] + b[HC][R] - c[NO_2][R] - d[R]^2$$

where the terms on the right hand side have the following significance:

The symbols a,b,c,d represent the combination of appropriate rate constants and stoichiometric coefficients.

We can identify two limiting cases of interest:

(i) Near t = 0 when [R] = 0, i.e.,

$$\frac{d[R]}{dt} = a[N0_2]$$

From this we can see that initially the concentration of free radicals increases at a rate proportional to the NO_2 concentration. Presumably, most of these radicals are oxygen atoms.

(ii) When the total radical population reaches a steady state

(ss), d[R]/dt = 0. At this point

$$0 = a[NO_2] + b[HC][R] - c[NO_2][R] - d[R]^2$$

For case (ii) we can examine the effect on $[R]_{ss}$ of the relative

concentrations of NO_2 and HC. When $[\mathrm{NO}_2]$ >> [HC] ,

$$\frac{d[R]}{dt} = 0 \simeq a[NO_2] - c[NO_2][R]_{ss}$$

or $[R]_{SS}$ is a constant a/c, dependent only on the photolysis rate of NO₂ and the rate of termination with NO₂. When the rate of production by chain branching, b[HC][R] equals the termination rate with NO₂, c[NO₂][R], the steady state radical concentration is

$$[R]_{ss} = [a[N0_{2}]/d]^{1/2}$$

Finally, when $[HC] >> [NO_2]$,

$$\frac{d[R]}{dt} = 0 \simeq b[HC][R] - d[R]^2$$

so that $[R]_{ss} = b[HC]/d$.

Summarizing, at steady state the limits of total free radical concentrations are

$$\frac{a}{c} \leq [R]_{ss} \leq \frac{b[HC]}{d}$$

$$(high NO_2)$$
 $(1ow NO_2)$

Using these relationships, Johnston et al. (1970) have estimated that actual concentrations may be:

c[NO ₂] b[HC]	10	1	0.1
[R] _{ss} ,ppm	1.1×10 ⁻⁴	2 × 10 ⁻³	3.6×10^{-2}

Leighton (1961) estimated that in photooxidation of an olefin such as propylene, NO is converted to NO_2 at a rate of 0.04 ppm min⁻¹ by reactions of the type 6. This rate is consistent with the steady state radical concentrations just calculated. For example, using $[R] = 10^{-3}$ ppm, [NO] = 0.1 ppm and a rate constant for reaction 6 of 500 ppm⁻¹min⁻¹, the rate of conversion of NO to NO_2 is 0.05 ppm min⁻¹.

Aside from predicting the rapid conversion of NO to NO_2 , a mechanism must also be capable of simulating the effect of different initial reactant ratios on product formation in the smog system. Let us consider the two cases of low and high NO_2 concentrations. The photochemical smog process is initiated by NO_2 with the rate of increase of the total radical population depending on the initial concentration of NO_2 . The maximum concentration of NO_2 occurs when the rate of conversion of NO to NO_2 just equals the rate of termination of radicals by NO2. If this maximum concentration of NO2 is low (i.e., low total initial NO_{χ}), the concentration of radicals reaches very high values. The radicals rapidly convert NO to NO2, allowing ozone to form. As we increase the total initial NO_x , and hence the NO_2 concentration at its maximum, the amount of 0_3 formed should increase up to a point. That point is the one at which radical removal by NO_2 is at least as fast as chain branching, i.e., $b[HC] \simeq c[NO_2]$. As we continue to increase the initial NO_x , and hence the NO_2 , the steady state radical concentration continues to decrease, as we have seen. The result is that the rate of ozone formation slows down. Nevertheless, if we wait long enough there will be a significant accumulation of 0_3 . Thus, if we consider 0_3 formation only over a fixed time of irradiation, it will seem that increasing initial NO is a beneficial policy with respect to O₃ formation, when, in fact, what has really happened is that we have not waited long enough for the reaction to go to completion.

We can also examine the effect of initial reactant ratios on the maximum amount of 0_3 formed during an irradiation. Consider first an experiment in which the concentration of initial NO_x (NO + NO_2) is large compared to initial HC. Note that the relative amounts of NO and NO_2 will serve only to govern the time needed to convert the NO to NO_2 and should not affect the ultimate maximum O_3 concentration attained. In this case the hydrocarbon is expended before all the NO is converted to NO₂. Since an appreciable amount of NO remains after the hydrocarbon is depleted, no significant 03 concentration can be reached. Consider next the opposite limit, namely $[NO_x]_o << [HC]_o$. Now the NO is rapidly converted to NO_2 with little expenditure of HC. As [NO] becomes small, 0_3 can accumulate. However, because of the large concentration of HC, the reaction of 0_3 and HC will prevent $[0_3]$ from becoming too large. Finally, the intermediate case of $[HC]_{o} \simeq$ $[NO_x]_0$ can be expected to yield the largest O_3 concentration. Thus, if one considers the maximum O_3 concentration achieved, regardless of the time of irradiation, as a function of $[HC]_0/[NO_x]_0$, one will get a curve which exhibits a maximum.

We have seen that the simplified mechanism presented early in this section can account for several of the qualitative features of the photochemical smog system. However, the mechanism is inadequate for quantitative predictions of concentration-time behavior in smog chamber systems and the atmosphere for two basic reasons:

- (i) Several important inorganic reactions involving NO, NO_2 , H_2O and CO need to be included, and
- (ii) The mechanism lacks detail in the treatment of hydrocarbon and radical species.

In attempting to construct a mechanism capable of accurate prediction, each of these points must be carefully considered.

We now present a very brief survey of the important inorganic and hydrocarbon reactions in the photochemical smog system. Numerous reviews of these reactions are available (Leighton, 1961; Altshuller and Bufalini, 1971; Johnston et al., 1970), so that we will consider here only those elements of the chemistry important to the development of a kinetic mechanism.

a. Inorganic Reactions

The reactions in the system of NO_x , air, H_2O and CO have received much attention. A survey of rate constant values reveals the following reactions to be of greatest importance:

$$\begin{array}{c} \mathsf{NO}_2 + \mathsf{hv} \stackrel{1}{\to} \mathsf{NO} + \mathsf{O} \\ \mathsf{O} + \mathsf{O}_2 + \mathsf{M} \stackrel{2}{\to} \mathsf{O}_3 + \mathsf{M} \\ \mathsf{O}_3 + \mathsf{NO} \stackrel{3}{\to} \mathsf{NO}_2 + \mathsf{O}_2 \end{array} \end{array} \right\} \mathsf{The} \ \mathsf{NO}_2 - \mathsf{NO} - \mathsf{O}_3 \ \mathsf{Cycle} \\ \mathsf{O} + \mathsf{NO} \stackrel{3}{\to} \mathsf{NO}_2 + \mathsf{O}_2 \\ \mathsf{O} + \mathsf{NO} + \mathsf{M} \stackrel{4}{\to} \mathsf{NO}_2 + \mathsf{M} \\ \mathsf{O} + \mathsf{NO}_2 \stackrel{5}{\to} \mathsf{NO} + \mathsf{O}_2 \\ \mathsf{O} + \mathsf{NO}_2 + \mathsf{M} \stackrel{6}{\to} \mathsf{NO}_3 + \mathsf{M} \end{array} \right\} \mathsf{Important} \ \mathsf{Reactions} \ \mathsf{of} \ \mathsf{O} \\ \mathsf{with} \ \mathsf{Inorganic} \ \mathsf{Species} \\ \mathsf{O} + \mathsf{NO}_2 + \mathsf{M} \stackrel{6}{\to} \mathsf{NO}_3 + \mathsf{M} \end{array} \right\} \mathsf{Important} \ \mathsf{Reactions} \ \mathsf{of} \ \mathsf{O} \\ \mathsf{NO}_2 + \mathsf{NO}_2 + \mathsf{M} \stackrel{6}{\to} \mathsf{NO}_3 + \mathsf{M} \end{array}$$

$$\begin{array}{c} 0_{3} + N0_{2} \stackrel{7}{\rightarrow} N0_{3} + 0_{2} \\ N0_{3} + N0_{2} \stackrel{9}{\rightarrow} 2N0_{2} \\ N0_{3} + N0_{2} \stackrel{9}{\rightarrow} N_{2}0_{5} \\ N_{2}0_{5} \stackrel{10}{\rightarrow} N0_{2} + N0_{3} \\ N_{2}0_{5} + H_{2}0 \stackrel{10}{\rightarrow} 2HN0_{3} \end{array} \right) The Chemistry of N0_{3}, \\ N_{2}0_{5} + H_{2}0 \stackrel{10}{\rightarrow} 2HN0_{3} \\ N0 + HN0_{3} \stackrel{12}{\rightarrow} HN0_{2} + N0_{2} \\ HN0_{2} + HN0_{3} \stackrel{12}{\rightarrow} H_{2}0 + 2N0_{2} \end{array} \right) Reactions of HN0_{3} with Inorganic Species \\ N0 + N0_{2} + H_{2}0 \stackrel{14}{\rightarrow} 2HN0_{2} \\ 2HN0_{2} \stackrel{15}{\rightarrow} N0 + N0_{2} + H_{2}0 \\ HN0_{2} + hv \stackrel{16}{\rightarrow} 0H + N0 \end{array} \right) Chemistry of HN0_{2} \\ OH + N0_{2} + M \stackrel{17}{\rightarrow} HN0_{3} + M \\ OH + N0 + M \stackrel{18}{\rightarrow} HN0_{2} + M \\ OH + N0 + M \stackrel{18}{\rightarrow} HN0_{2} + M \\ OH + C0 + (0_{2}) \stackrel{19}{\rightarrow} C0_{2} + H0_{2} \\ H0_{2} + N0 \stackrel{20}{\rightarrow} 0H + N0_{2} \end{array} \right) Important Reactions of OH \\ with Inorganic Species \\ Mo_{2} + hv \stackrel{21}{\rightarrow} 20H \\ \end{array}$$

We shall discuss several of these reactions further in Chapter II, considering the degree of study they have received, the rates at which they proceed, and the uncertainty associated with the individual reaction rate constants.

b. Hydrocarbon Reactions

We first wish to make a fundamental distinction between types of mechanisms, based on the treatment of hydrocarbon and free radical reactions. The first type is that written for the photooxidation of a specific hydrocarbon. This is the type we ordinarily envision, one in which each species in each reaction represents a distinct chemical entity. The second type is the lumped mechanism, one which contains certain fictitious species which represent entire classes of reactants.

In many chemical systems the number of species is often extremely large. In addition, there is usually a significant range of reactivities of the species in systems of this type. Certain species may not be present in measurable concentrations and many rate constants may not be known accurately. As a result, quantitative predictions of reaction rates may be highly uncertain. In such a case, one is unable to deal with each species separately; rather, one may partition the species into a few classes (called lumped classes), and then consider each class as an independent entity. This idea has already been illustrated in the highly simplified general mechanism cited earlier, in which all hydrocarbons and free radicals were represented by HC and R, respectively.

General lumping theory in chemical kinetics has been the subject of several recent investigations. Wei and Kuo (1969a, 1969b) have presented a general lumping analysis of monomolecular, first order reacting mixtures. Hutchinson and Luss (1970), Luss and Hutchinson (1971), and Golikeri and Luss (1972) have studied the lumping of reaction mixtures consisting of a large number of parallel, independent

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and irreversible nth order reactions. In contrast to the work of Wei and Kuo, which was directed toward the determination of conditions under which exact lumping was possible, the studies of Luss have been concerned with the problem of predicting a priori the maximum error involved in lumping and with the type of species that should be lumped together to ensure that the prediction error is less than some given bound.

No theory has yet been developed that is concerned with the lumping of large sets of coupled, bimolecular reactions, such as occur in the generation of photochemical smog. We outline here some of the more important questions that must be addressed if we are to effectively model atmospheric photochemical reactions.

- (i) In the photochemical smog system the large number of hydrocarbons and free radicals makes lumping a necessity in developing a practical kinetic mechanism. However, which hydrocarbons should be lumped together and what criterion should be used to establish groupings? For example, should the lumping be carried out according to hydrocarbon class, such as paraffins, aromatics, olefins, etc., with respect to reactivity with 0, 0₃ and OH· regardless of class, or with regard to the number of free radical products?
- (ii) Which free radicals should be lumped together and what criterion should be used to establish groupings? For example, should the lumping be carried out with respect

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to radical class such as alkyl, acyl, alkoxyl, etc., with respect to most probable chain length, or with respect to reactivity?

- (iii) How are the lumped rate constants and stoichiometric coefficients to be determined?
- (iv) Is the order of the reaction of the lumped hydrocarbon species the same as the individual reaction being represented?

The one guideline that does generally apply is that lumping should be carried out such that a balance is achieved between accuracy of description of the underlying processes and compactness of the mechanism. Let us now consider some of the alternatives for lumping in photochemical smog systems.

Given a distribution of atmospheric hydrocarbons, we must first identify and tabulate the reactions in which they may participate. Photochemical decomposition of primary hydrocarbon pollutants is unimportant, except perhaps for aldehydes; we must therefore focus our attention on thermal reactions. Of the active species that we have mentioned thus far, those capable of reacting with hydrocarbons include 0, 0_3 , and OH. In this discussion we divide the primary hydrocarbons according to the classes--olefins, paraffins, aromatics, and aldehydes--and examine the reactions of each with the three oxidants. While these groupings are certainly not inclusive of all classes of hydrocarbons in the atmosphere, they comprise the major portion. The two basic aspects of an individual reaction that we will

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consider are: (i) the product distribution, and (ii) the rate constant.

(1) Atomic Oxygen - Hydrocarbon Reactions

The principal products of 0 atom hydrocarbon reactions are summarized below:

olefin $0 + c = c \rightarrow R \cdot + Rco^*$ paraffin $0 + RH \rightarrow R \cdot + OH \cdot$ aromatic $0 + O - R \rightarrow R \cdot + OH \cdot$ aldehyde $0 + RCHO \rightarrow RcO + OH \cdot$

(2) Ozone-Hydrocarbon Reactions

Only olefins, among the four hydrocarbon groupings we are considering, are attacked readily by ozone in the vapor phase. The so-called Criegie mechanism for 0_3 addition to olefins can be summarized as

$$0_3 + c = c \rightarrow c = 0 + c - 0 - c$$
 (Zwitterion)

The products are thus a carbonyl and an unstable intermediate called a zwitterion, the subsequent reactions of which are not very well known. Possible decomposition reactions of the zwitterion are

^{*}If one of the carbon atoms on the double bond is external, both $H\dot{C}O$ and $R\dot{C}O$ can form.

$$R_{1}R_{2}CO0 \Rightarrow R_{1}R_{2} + CO_{2}$$

$$HRCO0 \Rightarrow ROH + CO$$

$$HRCO0 \Rightarrow RO \cdot + H\dot{C}O$$

$$HRCO0 \Rightarrow R\dot{C}O + OH \cdot$$

In addition, the zwitterion may participate in reactions with 0_2 , NO, or NO₂:

$$\begin{bmatrix} c - 0 - 0 + A \rightarrow \end{bmatrix} c = 0 + A0$$
 (A = 0₂, N0, or N0₂)

If this reaction predominated we would expect a yield of two carbonyl compounds per olefin. Actually, a yield between 1 and 1.4 is observed. In general, then, a stable carbonyl and two free radicals are formed through the $0_3^$ olefin reaction. We might note, however, that the dynamics of this class of reactions are still not fully understood. We shall return to 0_3 -olefin reactions in Chapter II where we discuss reactions needing further experimental investigation to elucidate product distributions.

(3) Hydroxyl Radical - Hydrocarbon Reactions

Hydroxyl radicals react with hydrocarbons either by abstracting a hydrogen atom or by addition. For paraffins the reaction is known to be

$$RH + OH \cdot \rightarrow R \cdot + H_2O$$

At this time there are no reported product data for

OH/olefin or OH/aromatic reactions, although it is known that the propylene reaction proceeds via addition to the double bond to form a radical. If this is the case with other olefins, we would expect one free radical as a product,

$$C = C + OH \cdot \rightarrow R \cdot *$$

Aldehyde/OH reactions also yield one free radical,

HCHO + OH•
$$\rightarrow$$
 H₂O + HCO

c. Free Radical Reactions

As we have just seen, the reactions of 0, 0_3 , and OH• with hydrocarbons yield the following classes of free radicals: R•, RCO, RO•, where R can be a hydrogen atom, an alkyl group, or an alkyl group containing an alcohol functional group. We must now trace the most likely reactions of these species with the others in the system. Consider R•, RCO, and OH• as typical products. Both R• and RCO will most probably react with 0_2 by

$$R \circ + 0_2 \rightarrow R0_2 \circ$$

$$RC0 + 0_2 \rightarrow RC00 \circ$$

These peroxy radicals will undergo a variety of reactions, the most important of which are with NO and NO_2

The actual structure of this radical would be HO- $\dot{\zeta}$ - $\dot{\zeta}$.

$$ROO \cdot + NO \rightarrow NO_{2} + RO \cdot$$

$$RCOO \cdot + NO \rightarrow NO_{2} + RCO \cdot$$

$$"O \qquad 0$$

$$RCOO \cdot + NO_{2} \rightarrow RCOONO_{2}$$

$$HO = 0$$

The two new radicals formed will then probably react in the following manner:

$$RO \bullet + O_2 \rightarrow RCHO + HO_2 \bullet$$
$$RCO \bullet \rightarrow R \bullet + CO_2$$
$$\bigcup_{i=1}^{i} O_2 \rightarrow RO_2 \bullet$$

The likely history of typical alkyl and acyl radicals in chain propagation reactions can thus be depicted as

$$\frac{0}{0} \stackrel{0}{\rightarrow} RCO0 \stackrel{NO}{\rightarrow} RCO \stackrel{U}{\rightarrow} RCO \stackrel{U}{\rightarrow} O_2 \stackrel{U}{\rightarrow} O_2 \stackrel{VO}{\rightarrow} O_2 \stackrel{VO}{\rightarrow} RO \stackrel{O2}{\rightarrow} HO_2 \stackrel{NO}{\rightarrow} OH \stackrel{O2}{\rightarrow} HO_2 \stackrel{VO}{\rightarrow} OH \stackrel{VO}{\rightarrow} HC$$

We see that, during the lifetimes of R• and \dot{RcO} , many molecules of NO can be converted to NO_2 (of course, each step in the sequence competes with other propagation and termination reactions). When NO concentration becomes sufficiently low, one possibility is that the peroxyacyl radicals will react with NO_2 to give peroxy acyl nitrates. The alkoxyl radicals may also react with NO_2 at this point to yield alkyl nitrates.

Now the problem of representing hydrocarbon and free radical reactions should be somewhat clearer. In a complex mixture of hydrocarbons, such as is observed in the atmosphere, we might divide the total hydrocarbon population into n lumped hydrocarbon species, HC_1, HC_2, \dots, HC_n . Each of these may potentially react with 0, 0₃, and OH, yielding varying numbers and types of free radicals depending on the class of hydrocarbon participating in the reaction. Thus, a careful analysis of lumping alternatives is a necessary step in the development of a generalized kinetic mechanism. In Section IBl we undertake such an analysis. However, before going to this, we present a brief synopsis of currently available kinetic mechanisms for photochemical smog reactions. This review should be of aid to the reader in assessing the extent to which current mechanisms adequately treat the details of the inorganic and hydrocarbon chemistry. With this background, it is relatively easy to identify those areas in need of further development.

3. Current Photochemical Kinetic Mechanisms

It is only in the last ten years that general kinetic mechanisms have been postulated to describe photochemical smog chemistry. The mechanisms that have been proposed can be classified as either specific (written for photooxidation of a specific hydrocarbon) or lumped (written for one or more species involving lumped reactants) and include the following:

Specific Mechanisms

Westberg and Cohen (1969)	isobutylene
Behar (1970)	propylene
Hecht and Seinfeld (1972)	propylene
Niki et al. (1972)	propylene
Demerjian et al. (1973)	propylene <u>trans</u> -2-butene isobutene,

n-butane, and formaldehyde

Lumped Mechanisms

Eschenroeder and Martinez (1972) Wayne et al. (1971) Hecht and Seinfeld (1972)

Specific mechanisms, while often quite complex (e.g., the Hecht and Seinfeld propylene mechanism contains 81 reactions), can play an important role as an aid in understanding the fundamental chemistry of the photooxidation process. However, for none of the specific mechanisms listed above has there been reported a program of validation over a range of initial reactant concentrations. Thus, all five can only be considered at this point as detailed chemical

Three lumped mechanisms, nearly identical in structure, were developed at an early stage by Eschenroeder (1969), Friedlander and Seinfeld (1969) and Behar (1970). (Eschenroeder's mechanism, slightly modified, is substantially the same as, or superior to, those of Friedlander and Seinfeld and Behar). For the obvious reasons of simplicity and convenience, it would be desirable to adopt such mechanisms for general use. However, these mechanisms not only omit steps now known to be important, but they were never successfully validated over a range of initial conditions. All three have since been either abandoned or modified.

speculations for the specific hydrocarbon system.

Assuming, however, that validated versions of specific mechanisms are available, these mechanisms would still not be suitable for inclusion in an urban airshed model. The main reason for this centers on the philosophy underlying the development of such mechanisms. The decision to develop and implement a specific mechanism implies the desire to represent reaction processes as accurately as is feasible. Thus, a relatively large number of reaction steps must be incorporated in a description of the dynamics of consumption of a particular hydrocarbon, such as propylene. Reaction dynamics will, however, vary for the many hydrocarbon species present in the atmosphere. If, for example, thirty to forty steps are required to describe propylene kinetics, and fifty hydrocarbon species, each having unique dynamics, are believed to exert a significant impact on atmospheric reaction processes, one is faced with an intractable representation of the system. Alternatively, adoption of a detailed representation of the reactions of a single species (for example, propylene) which may, upon development, be applied to a single, generalized hydrocarbon is tantamount to constructing a mechanism having many of the representational deficiencies of a lumped kinetic scheme and, in addition, introduces a substantial parameter estimation problem.

Each of the three lumped mechanisms listed above is currently in use in programs of mathematical modeling of photochemical smog in the Los Angeles basin. Detailed discussions of each are readily available in the original references. (A reprint of the paper describing the formulation and initial validation of the Hecht and Seinfeld

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mechanism can be found in Appendix A.) We note, however, that the mechanisms of Eschenroder and Martinez and Hecht and Seinfeld are very similar. Table I presents a comparison of the two mechanisms. The EM differs from the HS mechanism in the treatment of HNO_3 and HNO_2 , the inclusion of CO, and the treatment of HO_2 .

While the EM and HS mechanisms are quite similar, the third in current use, that of Wayne et al., given in Table 2, adopts an inherently different approach. The mechanism is based on the photooxidation of propylene, and its application to atmospheric photochemistry is presumably based on the assumption that the mixture of atmospheric hydrocarbons behaves as a binary mixture of propylene and a second, relatively unreactive, hydrocarbon. This assumption is in contrast to that inherent to the EM and HS mechanisms, i.e., that the atmospheric hydrocarbon mixture can be represented by two lumped hydrocarbon species, one more reactive than the other, neither of which represents a specific hydrocarbon. Because of the inclusion of detailed propylene chemistry in the Wayne mechanism, many specific radical species have been included, whereas only one lumped radical species (aside from 0 and OH[•])^{*} appears in the EM and HS mechanisms. In the validation exercises reported, the two lumped hydrocarbons in the EM and HS mechanisms have been specified on the basis of reactivity. As we shall see, when hydrocarbons are lumped on this basis, it is difficult to ascribe precise values to the generalized stoichiometric coefficients.

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If CO is present, HO₂• is retained as a separate species in the HS mechanism.

and Eschenroeder-Martinez
EM
$NO_2 + hv + NO + O$
$0 + 0_2 + M + 0_3 + M$
$O_3 + NO \xrightarrow{3} NO_2 + O_2$
$OH \cdot + NO_2 + M \rightarrow HNO_3 + M$
NO + NO ₂ $\stackrel{H_2O}{\stackrel{\rightarrow}{_5}}$ 2HNO ₂
$HNO_2 + hv \stackrel{6}{\rightarrow} OH \cdot + NO$
$OH \cdot + NO + M \rightarrow HNO_2 + M$
$0 + HC \stackrel{8}{\rightarrow} b_1(RO_2)$
$OH + HC \rightarrow b_2(RO_2)$
$O_3 + HC \stackrel{10}{\rightarrow} b_3(RO_2)$
$RO_2 + NO \stackrel{11}{\rightarrow} NO_2 + d(OH)$
$RO_2 + NO_2 \stackrel{12}{\rightarrow} c(PAN)$

cht-Sainfald (US) and Eachan TABLE 1 4 20 . . T1.

TABLE 2. Wayne et al. Mechanism

$$NO_{2} + hv + NO + O$$

$$O + O_{2} + M + O_{3} + NO_{2} + O_{2} + M$$

$$O_{3} + NO + O_{2} + O_{3} + O_{3} + O_{2} + O_{3} + O_{3} + O_{2} + O_{3} + O_{3} + O_{2} + O_{3} + O_{2} + O_{3} + O_{2} + O_{3} + O_{2} + O_{3} + O_{2} + O_{3} + O_{2} + O_{3} + O_{2} + O_{2} + O_{3} + O_{2} + O_{3} + O_{2} + O_{3} + O_{2} + O_{3} + O_{2} + O_{3} + O_{2} + O_{3} + O_{3} + O_{2} + O_{3} + O_{$$

TABLE 2. (Continued) Wayne et al. Mechanism

$$C_{3}H_{6} + 0 \stackrel{22}{+} CH_{3} + C_{2}H_{3}O$$

$$C_{3}H_{6} + 0_{3} \stackrel{23}{+} HCHO + C_{2}H_{4}O_{2}$$

$$C_{3}H_{6} + 0 + 0_{2} \stackrel{24}{+} HCHO + C_{2}H_{4}O_{2}$$

$$C_{3}H_{6} + 0_{2} \stackrel{25}{+} CH_{3}O + C_{2}H_{3}O$$

$$C_{3}H_{6} + CH_{3}O_{2} \stackrel{26}{+} CH_{3}O + CH_{3}CHO$$

$$C_{3}H_{6} + CH_{3}O_{2} \stackrel{27}{+} CH_{3} + CH_{3}O + C_{2}H_{3}O$$

$$C_{2}H_{3}O + M \stackrel{28}{+} CH_{3} + CO + M$$

$$CH_{3}O + NO_{2} \stackrel{29}{+} CH_{3}ONO_{2}$$

$$C_{2}H_{3}O + O_{2} + NO_{2} \stackrel{30}{+} C_{2}H_{3}O_{3}NO_{2}$$

$$DUMHC + 0 \stackrel{31}{+} CH_{3} + C_{2}H_{3}O$$

$$HCHO + hv \stackrel{32}{+} H + H + CO$$

$$NO_{2} + NO_{3} + H_{2}O \stackrel{33}{+} 2HNO_{3}$$

.

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The chief advantage of generalized mechanisms is the compact mathematical representation which lumping affords. Unfortunately, each of the three mechanisms suffer several shortcomings. In particular, they share the disadvantages of

- (i) Oversimplifying the representation of the atmospheric hydrocarbon mix. The individual hydrocarbons present in polluted air basins differ widely in reactivity, and the "average" reactivity of this mixture of organics changes continuously throughout the day. An attempt to describe this complex behavior with one or two lumped classes of hydrocarbons in a kinetic mechanism may be inadequate.
- (ii) Depending on the arbitrary selection of an "adjustable" parameter. The EM (or the HS) mechanism requires the specification of the parameter d (or ε in the HS) for the reaction RO₂ + NO \rightarrow NO₂ + fraction (OH). This reaction, of course, is fictitious (inasmuch as it is not an actual, elementary reaction) and is employed as a mathematical artifact to reduce the number of species which must be calculated in the mechanism. The Wayne mechanism contains an implicit parameter (let us call it α) which represents the propylene concentration equivalent in "reactivity" in parts per million to one ppm of a hydrocarbon mixture.

 α ppm propylene \equiv 1 ppm hydrocarbon

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This approach is fallacious conceptually because propylene does not cause NO to be oxidized (and O₃ to be formed) by the same mechanisms as do alkanes and aromatics.*

- (iii) Generating predictions that are strongly dependent upon the specification of uncertain parameters. The predictions of the EM (or the HS) mechanism are very sensitive to b_2 and d (or β and ϵ in the HS), and of the Wayne mechanism, to α . As we just pointed out, the parameters d, ϵ , and α are exceedingly difficult to specify a priori; hence, confidence in the predictions of these mechanisms for cases not explicitly validated is poor.
- B. Formulation and Validation of a New Lumped Mechanism

In the two years since the EM, HS, and Wayne mechanisms were developed, significant advances have been made in our knowledge of the mechanisms and rate constants of the individual reactions contributing to smog formation. It therefore appears that a new kinetic mechanism can now be developed which avoids many of the shortcomings of the three existing mechanisms. In particular, a new mechanism should be rigorous in its treatment of inorganic reactions (because of

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In the case of propylene, NO is oxidized primarily through longlength free radical chains initiated when propylene is oxidized; in the case of alkanes, the hydrocarbon oxidation reaction is slow, and it is the photooxidation of secondary products, primarily aldehydes, which oxidizes NO. Aromatics such as toluene are also oxidized slowly; nevertheless, products of the hydrocarbon oxidation are primarily responsible for the oxidation of NO by free radical chains thought to be shorter than those for propylene.

their importance), sufficiently detailed to distinguish between the reactions of various classes of hydrocarbons and free radicals, free of poorly defined adjustable parameters, and as compact as possible.

In the following section, we present a systematic analysis of hydrocarbon and radical lumping in order to illustrate the various levels of complexity that might be included in a mechanism and to identify the decisions which must be made in constructing a lumped mechanism. Based upon our conclusions and realizing the shortcomings of the preceding mechanisms we propose a new lumped mechanism.

1. Lumping of Hydrocarbons

Consider first the question of the lumping of hydrocarbons. Our objective is to form a small number of groups of lumped hydrocarbon species which will represent the mixture of hydrocarbons present in the atmosphere. Alternative criteria are available by which to form the hydrocarbon groupings, for example:

- (i) Lump hydrocarbons based on class (olefins, aromatics, paraffins, etc.),
- (ii) Lump hydrocarbons based on reactivity with individual oxidants, such as $0, 0_3$, or OH_{\bullet} .

Let us discuss the implications of each of these two lumping criteria. Consider criterion (i), the lumping of hydrocarbons by class. For example, let

 $HC_1 = olefins$ $HC_2 = aromatics$ $HC_3 = paraffins$ $HC_4 = aldehydes$

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Although the mechanisms for the oxidation of these four classes of hydrocarbons by 0, OH, and 0_3 have not yet been resolved in detail, the likely product distributions are:

$$HC_{1} + \begin{cases} 0 \stackrel{k_{1}}{\rightarrow} R \cdot + R\dot{C} \\ 0_{3} \stackrel{k_{1}}{\rightarrow} R\dot{C} 0 + R 0 \cdot + RCH 0 \\ k_{1} \\ 0H \cdot \stackrel{k_{1}}{\rightarrow} R \cdot \\ \end{cases}$$

$$HC_{2} + \begin{cases} 0 \xrightarrow{k_{2}} R \cdot + 0H \cdot \\ k_{2}' \\ 0_{3} \xrightarrow{k} not \text{ important} \\ K_{2}' \\ 0H \cdot \xrightarrow{k} R \cdot + H_{2}0 \end{cases}$$

$$HC_{3} + \begin{cases} 0 \xrightarrow{k_{3}} R \cdot + 0H \cdot \\ k_{3}' \\ 0_{3} \xrightarrow{} not important \\ k_{3}'' \\ 0H \cdot \xrightarrow{} R \cdot + H_{2}0 \end{cases}$$

OH adds to the double bond of olefins forming an alcohol-like free radical,

which we have assumed to react in the same fashion as an alkyl radical. This is not exactly true, as this free radical decomposes in a different manner than R_{\cdot} in subsequent reactions. Specifically, RCHOHCH₂ is thought to react to form one additional aldehyde (Niki, et al., 1972). We have, therefore, included HC₄ as a product of the OH-HC₁ elementary reaction in Table 4 to correct for this anomaly.

$$HC_{4} + \begin{cases} 0 \stackrel{k_{4}}{\rightarrow} R\dot{C}0 + 0H \cdot \\ 0_{3} \stackrel{k_{4}}{\rightarrow} not \text{ important} \\ 0H \cdot \stackrel{k_{4}''}{\rightarrow} R\dot{C}0 + H_{2}0 \\ k_{4}''' \\ hv \stackrel{k_{4}'''}{\rightarrow} RC \cdot \stackrel{*}{\rightarrow} H \cdot + C0 \\ \\ 0 \end{bmatrix}$$

Since the number of free radical products resulting from 0, 0_3 , and OH• attack on each lumped species is essentially the same for all individual hydrocarbon members of each lumped grouping (i.e., OH. attack on all paraffins is expected to yield one a_{ky} radical) the number and type of free radical products in each step shown above can be specified with some certainty. On the other hand, within each lumped species there is a distribution of rate constants for the reactions with 0, 0_3 , and OH . For example, within HC₁ there is a wide spectrum of rate constants for olefin-O reactions. Therefore, the rate constants for 0, 03, and OH reactions with each lumped species must be taken as average values which reflect in some manner the relative amounts of different individual species within each lumped species. Since the differing reactivities of the individual components comprising a grouping will lead to their disappearance at different rates throughout the course of photooxidation, the effective rate constants for reaction of the lumped species with 0, 03, and OH must also vary

*If HC₄ is HCHO, HC• (which decomposes to H• + CO) rather than RC• forms. 0

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during the course of the reaction. In summary, then, lumping of hydrocarbons by class will allow rather definite assignment of stoichiometric coefficients but will necessitate rate constants which reflect the average reactivity of the individual species within each lumped species as a function of time.

We now consider criterion (ii), the lumping of hydrocarbons by reactivity. The first question we face in this case is--reactivity with respect to what? The three obvious choices are reactivity (rate constant) with 0, 0_3 , and OH \cdot . Perhaps the most logical species among the radicals 0, 0_3 , and OH upon which to base the reactivity grouping is that species which is most responsible for hydrocarbon disappearance in photooxidation experiments. Computed rates of hydrocarbon disappearance by 0, 0_3 , and OH generally confirm that the OH-rate is the most important of the three, except at the very beginning of the photooxidation when the O-atom rate is predominant.

Table 3 presents rate constants relative to that of propylene for the reactions of several hydrocarbons with 0, 0_3 , and 0H, together with the relative reactivities of these hydrocarbons based on NO-NO₂ conversion rates observed experimentally (Altshuller and Cohen, 1963; Glasson and Tuesday, 1970). We see that the OH-hydrocarbon rate constants correlate quite well with reactivities for all classes of hydrocarbons listed in the table. On the other hand, 0-atom and 0_3 rates correlate with reactivities only for the olefinic compounds. For the aromatics, aldehydes, and alkanes, the 0-atom and 0_3 rate constants are small compared with the measured reactivities. Since the most important role played by 0H is that of generating organic free

TABLE 3

Relative Rate Constants and "Smog Reactivity"*

Compound	Relative Rate Constants			** Reactivity	
<u>Olefins</u>	0	0 ₃	ОН		
Propylene	1.0	1.0	1.0	1.0	
Ethylene	0.2	0.3	0.1	0.3	
Isobutene	4.4	1.7 ~ 2	2.5	1	
Trans-2-Butene	4.9	2.8 ~ 36	4.2	4	
2-Methy1-2-Butene	14	2.4	7.1	6	
Tetramethylethylene	18	3.9 ~ 62	8.6	17	
Aromatics					
Benzene	.007		≤ 0.05	0.1	
Xylene		< 0.2	1.1	1	
Aldehydes			,		
Formalde hyde	0.05		0.9	0.7	
Aceta1dehyde	.15	-	0.9	0.7	
Proprional dehyde	∿.2		1.8	2	
Alkanes					
n-Butane	.008		0.24	0.2	

*Source of Table: Niki et al. (1972).

**Based on the rate of conversion of NO to NO_{2}

radicals for conversion of NO to NO₂, it would appear that lumping of hydrocarbons with respect to their OH reaction rate constant would be the most consistent with measured hydrocarbon reactivities. Suppose, for example, that we elect to divide the hydrocarbon mixture into three classes based on their OH rate constant:

HC₁
$$k < 1000 \text{ ppm}^{-1}\text{min}^{-1}$$

HC₂ $1000 < k < 5000 \text{ ppm}^{-1}\text{min}^{-1}$
HC₃ $k > 5000 \text{ ppm}^{-1}\text{min}^{-1}$

On this basis each group would contain all classes of hydrocarbons, with the rate constants for reaction with OH defined by the composition of the grouping. Rate constants for reaction with O and O_3 , however, would not necessarily correlate with the grouping based on the OH rate and would have to be determined in a manner similar to the case of lumping with respect to hydrocarbon class. However, during the main course of the reaction, the hydrocarbons within each group would be consumed at roughly the same rate so that the reactivity and stoichiometry of the group would not be expected to change with time. In the late stages of the photooxidation, O_3 -hydrocarbon reactions become quite important. This raises a potential problem for lumping on the basis of the OH rate.

While rate constants can be determined relatively accurately, the number and types of free radical products within each lumped group would vary because each group would contain hydrocarbons of all classes. This would necessitate the adoption of stoichiometric coefficients which reflect the individual makeup of each lumped group.

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To illustrate the forms of lumped reactions following the scheme based on OH-reactivity, let us assume we have N groups, as, for example, the three defined above, HC_1 , HC_2 , HC_3 . The reactions with 0, 0_3 , and OH can be written:

$$HC_{i} + \begin{cases} 0 \xrightarrow{k_{i}} \alpha_{i1}R \cdot + \alpha_{i2}R\dot{C}0 + \alpha_{i3}OH \cdot \\ k_{i}' \\ 0_{3} \xrightarrow{\beta_{i1}}R\dot{C}0 + \beta_{i2}R0 \cdot + \beta_{i3}RCH0 \\ k_{i}'' \\ OH \xrightarrow{k_{i1}'} \gamma_{i1}R + \gamma_{i2}R\dot{C}0 \end{cases}$$

i = 1,2,...,N

where α_{ij} , β_{ij} , and γ_{ij} are stoichiometric coefficients which reflect the individual compositions of the HC_i, i = 1,2,...,N . For example, if HC₁ consisted entirely of olefins we might expect $\alpha_{i1} = \alpha_{i2} = 1$ and $\alpha_{i3} = 0$. Thus the stoichiometric coefficients are not to be considered as freely adjustable parameters, but rather as parameters whose values are fixed because of the choice of hydrocarbons comprising each lumped species HC_i.

Let us summarize the advantages and disadvantages of the two alternative hydrocarbon lumping criteria. For lumping by hydrocarbon class:

Advantages -

- (i) The definition of the lumped species depends only on the type of hydrocarbon (i.e., olefin, aromatic, alkane, etc.).
- (ii) Since the products of 0, 03, and OH reactions with
 various hydrocarbon classes are essentially the same

within each class, the number and type of free radical products would be well defined for each class (assuming the products are indeed known).

Disadvantages -

- (i) The rate constants for reaction with 0, 0₃, and OH vary for the individual components in each lumped species necessitating the computation of "average" rate constants.
- (ii) The relative distribution of the hydrocarbons in each lumped species will change throughout the course of the photooxidation necessitating a change in "average" rate constants with time.

For lumping by hydrocarbon reactivity (with OH):

Advantages -

- (i) The definition of the lumped species would correspond closely to the role played by the individual hydrocarbons comprising it in the conversion of NO to NO₂.
- (ii) Since the reactivity of each lumped species is roughly invariant in time, rate constants and stoichiometric coefficients for the lumped OH-HC reaction would not require adjustment during the course of the reaction.

Disadvantages -

 (i) Each grouping would contain hydrocarbons of all classes, making it difficult to account for the distribution of free radicals produced as a result of reactions with 0, 0₃, and OH. (ii) In the late stages of the photooxidation, ozonolysis reactions assume a level of importance equal to or greater than that of OH. A lumping on the basis of OH reactivity may no longer reflect the reactivity distribution of the total mixture at that stage.

Neither mode of hydrocarbon lumping appears overwhelmingly superior to the other. Nevertheless, lumping by hydrocarbon class seems to offer several advantages over lumping by reactivity. First, fewer stoichiometric coefficients need be specified in the former method, thereby leading to fewer unspecified parameters. Second, rate constant values for hydrocarbon-OH reactions are in many cases not known precisely enough to permit a clear distinction to be made among hydrocarbons as to reactivity class. Third, atmospheric measurements are made according to hydrocarbon class, and lumping by class would enable direct comparisons of mechanism predictions with atmospheric data. For these reasons, we will subsequently employ hydrocarbon lumping by class in our development of a general mechanism.

2. Lumping of Radicals

The second aspect of the overall lumping problem is the representation of free radicals. The two extremes in the representation of radicals are the specific mechanisms in which no lumping is used (each radical species is a distinct entity) and the qualitative mechanism employed earlier in which all free radicals were combined into a single species R. The first limit is unrealistic from a computational point of view and also in light of our incomplete knowledge

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of free radical rate constants. In contrast, the other limit does not afford us the ability to distinguish the effect of different hydrocarbon mixtures on the concentration/time behavior of a specific system. Therefore, we seek a basis for the lumping of radicals that lies somewhere between these two extremes.

A detailed study of free radical reactions in photochemical smog (Leighton, 1961) indicates that radicals of similar structure usually undergo similar reactions at roughly comparable rates. This suggests that the most detailed representation of radicals would involve having separate species for each radical class. The classes of radicals involved have already been introduced. They are

R۰	alkyl
RĊO	acyl
R00 •	peroxyalkyl (including HO ₂ •)
RÇ00 •	peroxyacy]
RC0 •	acylate
RO •	alkoxyl (including OH)

In Section IA2 we listed several of the most probable reactions involving these radicals that would take place in a hydrocarbon- NO_x -air system. We also illustrated typical histories of acyl and alkyl radicals in such a system. Based on these likely reactions, we wish to propose a lumping scheme which is consistent with the probable chain lengths of each radical (and thus the conversion rate of NO to NO_2).

- (i) Alkyl radicals We assume that alkyl radicals quickly add 0₂ to form peroxyalkyl radicals. Thus R00•, and not R•, need specifically enter into the mechanism.
- (ii) Acyl radicals We assume that acyl radicals, like alkyl radicals, quickly add O₂ to form peroxyacyl radicals.
 Thus, RCOO•, and not RCO, need specifically enter into the mechanism.
- (iii) Peroxyalkyl radicals These radicals undergo reaction with NO to form NO₂. Thus, they remain in the mechanism.
 Because of the importance of HO₂ we remove it from the class R•, and treat it as a separate species.
- (iv) Peroxyacyl radicals Like ROO \cdot , these can react with both NO and NO₂. They are included in the mechanism.
 - (v) Acylate radicals These radicals result from reaction of NO and peroxyacyl radicals. We assume that they decompose quickly to form alkyl radicals (hence, peroxyalkyl radicals) and CO₂. Thus, they are not included in the mechanism.
- (vi) Alkoxyl radicals These radicals result from reaction of peroxyalkyl radicals with NO and from ozonolysis of olefins, and enter into reactions with NO and NO₂ forming stable products. The most important member of this class is the hydroxyl radical. Because of the extreme importance of OH, it seems desirable to remove OH from the RO class and retain each in the mechanism.

Summarizing, the radicals which appear to be of sufficient importance to warrant separate treatment are:

ROO• (excluding HO₂•) RCOO• Ö RO• (excluding OH•) OH• HO₂•

3. Formulation of a Lumped Mechanism

The purpose of this section is to develop a lumped kinetic mechanism based on the combined conclusions reached thus far in this chapter. In particular, we will employ the lumping scheme suggested for hydrocarbon and the categorization of radicals just presented.

We first rewrite the hydrocarbon reactions so as to correspond to the preferred lumping criterion, namely by hydrocarbon class:

$$HC_{2} + 0H \cdot \rightarrow ROO \cdot + H_{2}O$$

$$HC_{3} + 0 \rightarrow ROO \cdot + 0H \cdot$$

$$HC_{3} + 0H \cdot \rightarrow ROO \cdot + H_{2}O$$

$$HC_{4} + 0 \rightarrow RCOO \cdot + 0H \cdot$$

$$HC_{4} + 0H \cdot \rightarrow \beta RCOO \cdot + (1 - \beta) HO_{2} \cdot + H_{2}O$$

The parameters α and β can be specified with a high degree of confidence. α is the fraction of carbons attached to the double bond in a mono-olefin which are not terminal carbons on the chain; thus, it can be specified a priori. Consider the O-HC₁ reaction for propylene and 2-butene which respectively contain external and internal double bonds.

$$0 + CH_{3}CH = CH_{2}$$

$$CH_{3}CH_{2}CH^{*} \longrightarrow CH_{3}CH_{2} + \dot{C}H_{3}$$

$$CH_{3}CH_{3}^{*} \longrightarrow CH_{3}CH_{2} + \dot{C}H_{3}$$

$$CH_{3}CH_{3}^{*} \longrightarrow CH_{3}CH_{2} + \dot{C}H_{3}$$

$$0 + CH_{3}CH = CHCH_{3} \longrightarrow CH_{3}CH_{2}CH_{3} \longrightarrow CH_{3}CH_{2} + CH_{3}\dot{C}H_{2}$$

If we now assume that alkyl and acyl radicals react rapidly with 0_2 and that CHO decomposes into CO + HO₂ in the presence of 0_2 , these reactions can be rewritten in our generalized notation as

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and

$$0 + CH_3CH = CHCH_3 \longrightarrow RO_2 + RCOO$$

Now, if we further assume that 0 will react with equal probability at either carbon attached to the double bond, $\alpha = 1/2$ for propylene and $\alpha = 1$ for 2-butene. By the same reasoning α can be shown to be 0 for ethylene. β is the fraction of total aldehydes which are not formaldehyde. During smog chamber studies of the propylene-NO_X system, equal quantities of formaldehyde and higher aldehydes are observed to form; thus, $\beta = 1/2$. In the case of toluene, Altshuller et al. (1970) have observed that only 15% of the aldehydes are formaldehyde, so $\beta = .85$ in this case.

The reactions of the inorganic species and the radical species ROO•, RCOO•, and RO• have already been outlined. We then assemble all U the inorganic, hydrocarbon, and free radical reactions into a generalized lumped mechanism, as is summarized in Table 4.

The most complete mathematical representation of the kinetics of this mechanism would be a description of the time-varying behavior of each reactant and product (exclusive of 0_2 , $C0_2$, and H_20 which are not followed) with a differential equation. But because the computing time required to integrate the mechanism numerically increases at a rate



A Lumped Kinetic Mechanism for Photochemical Smog

$NO_2 + h_v$	1 →	NO + 0]
0 + 0 ₂ + M	2 →	0 ₃ + M	The NO ₂ -NO-O ₃ Cycle
0 ₃ + NO	3 ≯	N0 ₂ + 0 ₂	J
0 + NO + M	4 →	N0 ₂ + M)
0 + NO ₂	5 ≯	NO + 0 ₂	Important Reactions of 0 with Inorganic Species
0 + NO ₂ + M	6 ≯	N0 ₃ + M	
0 ₃ + N0 ₂	7 →	$N0_3 + 0_2$)
NO ₃ + NO	8 ≯	2N02	
$NO_3 + NO_2$	9 →	N205	The Chemistry of NO_3 , N_2O_5 , and HNO_3
N205	10 →	$N0_{2} + N0_{3}$	
$N_{2}O_{5} + H_{2}O_{5}$	11 →	2HNO ₃	J
NO + HNO ₃	12 →	$HNO_2 + NO_2$	Reactions of HNO, with
$HNO_2 + HNO_3$	13 →	H ₂ 0 + 2NO ₂	JInorganic Species
NO + NO ₂ + H ₂ O	14 →	2HN02)
2HN0 ₂	15 →	$N0 + N0_2 + H_20$	Chemistry of HNO ₂
HNO ₂ + hv	16 →	OH + NO	

$$TABLE 4. (Continued)$$

$$OH + NO_{2} \stackrel{17}{+} HNO_{3}$$

$$OH + NO + M \stackrel{18}{+} HNO_{2} + M$$

$$OH + CO + (O_{2}) \stackrel{19}{+} OO_{2} + HO_{2}$$

$$HO_{2} + NO \stackrel{20}{+} OH + NO_{2}$$

$$HO_{2} + NO \stackrel{21}{+} 2OH$$

$$HO_{2} + NO \stackrel{21}{+} 2OH$$

$$Photolysis of H_{2}O_{2}$$

$$HC_{1} + O \stackrel{22}{+} ROO + \alpha RCOO + (1-\alpha)HO_{2}$$

$$HC_{1} + O \stackrel{22}{+} ROO + \alpha RCOO + (1-\alpha)HO_{2}$$

$$HC_{1} + O \stackrel{23}{+} RCOO + RO + HC_{4}$$

$$HC_{2} + O \stackrel{24}{+} ROO + HC_{4}$$

$$HC_{2} + OH \stackrel{24}{+} ROO + HC_{4}$$

$$HC_{3} + O \stackrel{27}{+} ROO + OH$$

$$HC_{3} + OH \stackrel{29}{+} ROO + H_{2}O$$

$$HC_{4} + hv \stackrel{29}{+} \beta ROO + (2-\beta)HO_{2}$$

$$HC_{4} + OH \stackrel{30}{+} \beta RCOO + (1-\beta)HO_{2} + H_{2}O$$

$$\frac{1}{0}$$

$$RCOO + NO + O_{2} \stackrel{34}{+} ROO + NO_{2} + CO_{2}$$

$$\frac{1}{0}$$

$$RCOO + NO + O_{2} \stackrel{34}{+} ROO + NO_{2} + CO_{2}$$

$$\frac{1}{0}$$

$$RCOO + NO_{2} \stackrel{4}{+} HO_{2} + HC_{4}$$

$$RCOO + NO_{2} \stackrel{4}{+} HO_{2} + HC_{4}$$

$$RCOO + NO_{2} \stackrel{4}{+} HO_{2} + HC_{4}$$

$$Reactions of Organic Free Radicals with NO, NO_{2}, and O_{2}$$

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$$\begin{array}{c} \text{RO} + \text{NO}_2 & \stackrel{35}{\rightarrow} & \text{RONO}_2 \\ \text{RO} + \text{NO} & \stackrel{36}{\rightarrow} & \text{RONO} \end{array} \end{array} \\ \begin{array}{c} \text{HO}_2 + \text{HO}_2 & \stackrel{37}{\rightarrow} & \text{H}_2\text{O}_2 + \text{O}_2 \\ \text{HO}_2 + \text{ROO} & \stackrel{38}{\rightarrow} & \text{ROOH} + \text{O}_2 \\ & 2\text{ROO} & \stackrel{39}{\rightarrow} & \text{ROOR} + \text{O}_2 \end{array} \end{array} \end{array} \end{array} \end{array} \\ \begin{array}{c} \text{Peroxy Radical Recombina-tion Reactions} \end{array}$$

proportional to the square of the number of differential equations, we are interested in minimizing that number. One way of accomplishing this is to apply the steady-state approximation for those species which reach their equilibrium concentrations on a time scale short relative to that of the majority of reactants and products. Mathematically, this means that the concentration-time behavior of those species assumed to be in steady-state is described by an algebraic rather than a differential equation.

In our validation experiments we have assumed four species to be in pseudo steady-state: 0, OH, RO, and NO₃. The validity of this approximation for the first three species has been established by comparing the concentrations predicted when the approximation is invoked to those predicted when the species are represented by a differential equation. We have found in these comparisons that agreement is excellent, maximum discrepancies in concentration being on the order of 0.01% over a 400 minute simulation. This test shows conclusively that the steady-state approximation is accurate for O, OH, and RO. When we tried to perform an identical test for NO₃ we found that the concentration predicted by a differential equation was negative at startup². Thus a meaningful test as to the validity of the steady-state approximation could

[&]quot;We have used the technique of Gear (1971) to solve the system of coupled differential equations.

^{**}This reflects the fact that NO₃ forms chiefly after the NO₂ peak by reaction 7. As there is no O₃ present initially, numerical roundoff error at the first time step results in negative NO₃ concentrations.

not be made. We are, however, reasonably confident that the approximation is "good" in this case as well.

 Comparison of the Lumped Mechanism to the Simplified HS and EM Mechanisms

Given the lumped mechanism we can now examine the assumptions inherent in the HS and EM mechanisms of Table 1. Both the HS and EM mechanisms have provisions for two lumped hydrocarbon species, usually specified to be of "high" and "low" reactivity. In each all the peroxy radicals are combined into the single species RO₂.

The main result of the reaction of atomic oxygen with lumped species is the formation of peroxy radicals, represented by

$$HC + 0 \rightarrow \alpha RO_2$$

Notice that production of hydroxyl radicals from O-atom reactions with paraffins and aromatics has been neglected in this step.

The ozone-hydrocarbon reactions are assumed to yield peroxy radicals and aldehydes,

$$0_3 + HC \rightarrow \gamma RO_2 + \gamma' RCHO$$

In the new mechanism it is assumed that a peroxyacyl and an alkoxy radical form rather than the peroxyalkyl radical.

The OH-hydrocarbon reactions are assumed to yield peroxy radicals and a small quantity of aldehydes,

$$HC + OH \rightarrow \beta RO_2 + \beta' RCHO$$

The remaining organic reactions are

$$RO_2 \cdot + NO \rightarrow NO_2 + \varepsilon OH \cdot$$

 $RO_2 + NO_2 \rightarrow PAN$

By comparison of the first reaction with the more correct reactions,

 $ROO \cdot + NO \rightarrow NO_2 + \varepsilon OH \cdot + (1-\varepsilon) RO \cdot$ $RCOO \cdot + NO \rightarrow NO_2 + ROO \cdot$

we see that regeneration of ROO. has been neglected in the conversion of NO to NO $_2$ by peroxyalkyl and peroxyacyl radicals. Thus, the $\,\varepsilon\,$ in the HS and EM mechanisms cannot be interpreted as the fraction of RO2 that is HO2 as it is in the more correct reactions, but rather only as an empirical parameter. As a result, the original stoichiometric coefficients α , β and γ cannot be assigned the actual values that would be expected from the chemistry of the individual species. Rather, the α , β , γ and ϵ become a set of parameters governing the chain length (the average number of free radical reactions, or propagation steps, that occur as a result of each This lack of direct correspondence of the initiation reaction). generalized stoichiometric coefficients in the HS and EM mechanisms to actual stoichiometric coefficients is the chief weakness of the two mechanisms. By virtue of its increased detail, the new lumped mechanism in Table 4 circumvents this shortcoming as the stoichimetries are derivable directly from the underlying chemistry of each elementary reaction.

C. The Data Base and Sources of Experimental Uncertainty

The significance of the validation results for a kinetic mechanism is to a large degree dependent upon the diversity and reliability of the experimental data base. We were fortunate in being able to obtain chamber runs for this study involving both low and high reactivity hydrocarbons, as well as a simple mixture. Moreover, the ratio of HC/NO_X was varied over a wide range for each reactant system. In this section we describe the data base provided by the Division of Chemistry and Physics of the Environmental Protection Agency (EPA) for validation purposes. We examine in some detail the importance of accurately specifying certain experimental variables, notably light intensity and water vapor concentration. We discuss the degree to which wall effects may influence observed chamber results. Finally, we comment on the accuracy and specificity of the analytical instrumentation used to monitor pollutant concentrations and on the reproducibility of the experiments.

1. Data Base

The data base used in this validation study is that supplied by the Division of Chemistry and Physics of EPA. It is comprised of three hydrocarbon-NO_x systems:

- (i) n-Butane-NO_x at three different HC/NO_x ratios
- (ii) Propylene-NO_x at four different HC/NO_x ratios
- (iii) n-Butane-Propylene-NO_X at six different HC/NO_X ratios

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^{*}These topics are discussed further in Chapter III.

All but two of the chamber runs were made between February and May of 1967 by the staff of the Chemical and Physical Research and Development Program at the National Center for Air Pollution Control in Cincinnati, Ohio (Altshuller et al., 1967,1969; Bufalini et al., 1971). The remaining two runs (457 and 459) were carried out in March 1968. The initial conditions of the experiments are given in Table 5.

2. Light Intensity

Radiation intensity is one of the most important parameters in a smog chamber experiment, for it governs the photolysis rate of NO₂ (reaction 1), the reaction which initiates and sustains the smog formation process. Irradiation of the smog chamber was carried out through the use of two banks of externally mounted fluorescent lamps, 148 lamps of three different types. Under normal operation, these lamps have an expected lifetime of 1000 hours, but throughout the program they were operated at a 25% overvoltage to increase radiation intensity. Over-load operation results in a more rapid deterioration of the lamps; consequently, approximately 1/7 of the lamps were replaced after every 100 hours of operation.

The average first order "rate constant" for NO_2 disappearance in nitrogen, k_d^* , was determined by the experimenters to be 0.40 min⁻¹, but was not redetermined during the ten-month period over which the

It can be shown that

$$k_{d} \sim \frac{2k_{3}}{k_{2}(M) + k_{3}} k_{a}\phi$$

where

(continued)

data provided to us were taken. We have assumed, in accordance with the results of Schuck et al. (1966), that k_1 , the overall photolysis rate of NO₂, is equal to 2/3 k_d , or 0.266 min⁻¹. Finally, we have estimated that, due to inaccuracies in the determination of k_d , in the factor of 2/3 relating k_d to k_1 , and in the estimation of irradiation intensity, k_1 has an uncertainty bound of $\pm 0.10 \text{ min}^{-1}$.

3. Water Vapor in the Chamber

Another parameter which is thought to be important in smog chamber runs is the water concentration. Water enters into the smog kinetics via reactions 11 and 14, nitric and nitrous acid production. The latter is important since photolysis of nitrous acid produces OH radicals which, in turn, initiate further reactions. The humidifier control of the inlet air stream to the chambers was set to generate 50% relative humidity at $75^{\circ}F$, but, during very cold, dry weather, relative humidities of only 30% were achieved. The humidity of the inlet air stream was checked only once or twice during the elevenmonth study.

(Continued)

 $\phi = \text{dissociation efficiency} \\ 0 + \text{NO}_2 + \text{M} \xrightarrow{k_2} \text{NO}_3 + \text{M} \\ & & & \\ 0 + \text{NO}_2 \xrightarrow{k_3} \text{NO} + \text{O}_2 \\ \end{array}$

Thus, k_d is, in essence, a lumped parameter representing the combined rates of all NO_2 reactions in an oxygen-free atmosphere. Unfortunately, the use of k_d leads to difficulties in presenting the kinetics, as the combined reaction which it represents is not first order. However, since the only available data for light intensity in these chamber experiments are based on the validity of k_d as a rate constant, we use it here to estimate k_1 .

TABLE 5

Initial Conditions Associated with the Experimental Chamber Data

EPA Run	(N0 ₂)*	(NO) [*]	(n-Butane) [*]	(Propylene) <mark>*</mark>
306**	0.03	0.30	1.60	
314	0.02	0.29	3.17	
345	0.12	1.28	3.40	
318	0.06	1.12		0.51
325	0.04	0.32		0.45
329	0.06	0.26		0.24
459	0.06	1.14		0.78
307	0.05	1.23	3.06	0.36
333	0.08	1.25	3.41	0.23
348	0.08	1.23	3.39	0.50
349	0.03	0.31	3.25	0.44
352	0.07	0.27	3.29	0.26
457	0.05	1.11	3.29	0.81

* Initial concentrations in units of parts per million (ppm)
**0.12 ppm of aldehyde also present initially

4. Wall Effects

An effect of particular concern in smog chamber studies is the influence of surfaces on chemical dynamics, and thus on observed reaction kinetics. Of major importance in this regard is the possibility of direct loss of material to the walls. Of lesser concern is the possibility of chemical interactions occurring between pollutants on the walls and material in the gas phase. Although it is possible that some low reactivity organics such as carboxylic acids and ketones can be found on the walls as a result of hydrogen bonding with adsorbed water, we focus our attention in this discussion on species which have been clearly identified on the walls of a small smog chamber (Gay and Bufalini, 1971)--nitric acid, nitrates, and nitrites. We begin then by discussing the reactions of the most important oxides of nitrogen, NO and NO₂, and examining the possibility of the interaction of each with the walls. In the process we also give attention to various mechanisms that might account for the appearance of HNO₃ on the walls.

a. NO and NO_2

Even in so-called dry systems it is reasonable to assume that an adsorbed layer of water will be found on the walls of the smog chamber. This is certainly the case for the experiments under consideration in this study, as the chamber was intentionally humidified during all runs. Thus one possible explanation for the appearance of nitrate and nitrite on the walls would be dissolution of NO and NO₂ in the adsorbed water layer. Nitric oxide can be eliminated in this regard because of its extremely low solubility in water; NO₂, however,

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dissociates in water by the following reactions (Hill, 1971):

$$6NO_2 + 3H_2O \stackrel{\ddagger}{} 3HNO_3 + 3HNO_2$$
$$3HNO_2 \stackrel{\ddagger}{} HNO_3 + 2NO + H_2O$$

The rate of loss of NO_2 in this manner is dependent upon the amount of water adsorbed, the rate of dissolution of NO_2 , and the magnitude of rate constants for the dissociation reactions. In the experiments under consideration, however, NO_2 losses via this mechanism can be neglected because, within experimental error, all of the NO_x initially present can be accounted for at the time of the NO_2 peak as NO_2 , NO_3 , and NO and NO_2 lost by sampling and dilution up to the time of the peak. We might then conclude that no significant amounts of NO or NO_2 were lost directly to the walls during the smog chamber experiments.

b. N₂05

After the $\rm NO_2$ peak occurs, and as $\rm O_3$ begins to accumulate, $\rm N_2O_5$ forms by the reactions

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
$$NO_3 + NO_2 \stackrel{>}{\neq} N_2O_5$$

 $\mathrm{N_2O_5}$ will undergo hydrolysis to form nitric acid by the reaction

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

If the hydrolysis takes place in the adsorbed layer of water on the wall, HNO₃ will form directly on the walls. However, both the water concentrations in smog chambers (63% relative humidity (RH) at 25⁰C is

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equivalent to 20,000 ppm H_2^{0}) and the rate constants for the primary reactions in nitric acid formation in the gas phase (Table 6) are large enough that the loss of NO_x after the NO_2 peak may be fully ascribed to the formation of nitric acid in the gas phase.

It remains unclear, however, as to whether N_2O_5 hydrolyzes in the gas phase or on the walls. As we have noted, the water concentration during these chamber runs was quite high. As the stationary state concentration of nitric acid^{*} would also have been high, actual HNO₃ concentrations in these experiments were always far from saturation. Thus there would have been a strong tendency for N_2O_5 , whether it were found in the gas phase or on the wall, to hydrolyze rather than to decompose, forming NO₂ by the reactions

> $N_2O_5 \stackrel{\neq}{=} NO_2 + NO_3$ $NO_3 + NO \rightarrow 2NO_2$

However, even if these reactions were favored due to the formation of N_2O_5 , the rate of formation of NO_2 would still be low since NO is depleted at this stage of the smog reactions. Thus, in light of the various considerations presented, we conclude that reactions involving N_2O_5 at the walls would have little if any effect on the course of the overall smog reactions.

Leighton (1961), p. 193, calculates that the stationary state concentration of HNO₃ is 3,000 ppm for initial conditions of 0.10 NO₂ , 0.10 O₃ , 0.01 NO , and 63% RH at 25° C.

c. HNO₃

Nitric acid is very soluble in water because of strong hydrogen bonding. Thus, it is highly likely that a nitric acid molecule in the gas phase that is involved in a collision with the wall would dissolve. The rate of loss of HNO_3 from the gas phase, then, is probably transport-limited and will depend to some degree on the rate of stirring in the chamber. Unfortunately, detection of HNO_3 in the gas phase has until now proven to be a difficult task, perhaps because the acid is lost to the walls of the sampling tubes.

d. Other Chemical and Catalytic Effects of the Walls

It would be highly beneficial to gain some insight into the degree to which interactions occur between pollutants on the walls and material in the gas phase. Unfortunately, our knowledge concerning such phenomena is limited, and we can only speculate. We thus offer the following comments:

- (i) It is expected that, for a chamber having a small surface to volume ratio, such as the one employed in the experimental studies utilized in this effort^{*}, the influence of the walls on NO oxidation rates is small. The effect would be additionally reduced in reactant systems for which the time to the NO₂ peak is relatively short (i.e., two hours or less).
- (ii) As we concluded earlier, we expect that the presence or absence of wall effects would result in no detectable

^{*}Approximately 1 ft⁻¹; the chamber has an internal surface area of 330 ft² and a volume of 335 ft³.

differences in the rate of formation of HNO_3 , largely because of the strong tendency of N_2O_5 to hydrolyze at the water concentrations used during these experiments. Similarly, whether HNO_3 is formed in the gas phase, subsequently migrating to the wall, or whether it is formed directly on the wall, it is unlikely that the site of hydrolysis will have much of an effect on the observed chemistry. While nitric acid is commonly used as an oxidant when concentrated (60%) in the liquid phase (Godt and Quinn, 1956), it is ineffective as an oxidant at low concentrations. The highest attainable concentration of HNO_3 during the chamber runs is a value that is numerically equal to the initial NO_x concentration, which never exceeded 1.5 ppm.

We conclude, based on the preceding discussion, that no significant amounts of NO and NO_2 are lost directly to the walls and that the loss of N_2O_5 and HNO_3 to the walls should not alter the observed photochemistry. However, it is not possible at this time to ascertain the degree to which the walls might accelerate the oxidation of NO. Wall effects, then, probably do not have to be taken into account in our validation efforts.

5. Estimates of Experimental Error

Before comparing model predictions with experimental observations, it is desirable to establish both the accuracy and the precision of the measurements. Accuracy refers to the extent to which a given measurement agrees with the true but unknown value of the parameter being measured. Precision refers to the extent to which a given set of measurements agrees with the mean of the observations. Inaccuracies in determination of concentrations are largely attributable to lack of specificity or accuracy in analytical procedures, particularly in the instrumentation used to monitor concentrations during the course of an experiment. Imprecision is detected through the poor repeatability of an experiment, the results of which may or may not be accurately determined. There may be a wide variety of causes of imprecision, some of which are also attributable to instrumentation problems.

a. The Accuracy of the Analytical Instruments

The four pollutant species of primary importance in our modeling efforts, NO_2 , NO, O_3 , and hydrocarbons, were all measured using standard instrumentation and techniques.

- (i) Hydrocarbons were determined individually by gas chromatography; the accuracy of these measurements is estimated to be $\pm 10\%$ at a concentration level of 1 ppm.
- (ii) Oxidants were measured using two independent techniques: the Mast Ozone Meter and neutral KI analysis. Corrections to KI readings were required to account for interferences due to PAN and NO₂. Despite the corrections the KI measurements exceeded the Mast readings by an average of 50%. As Dr. S. L. Kopczynski (1972) of the Division of Chemistry and Physics who was in charge of executing the smog chamber experiments used in this validation study is

of the opinion that the KI technique is the more accurate of the two procedures, we have validated our model using the results of the KI analyses.

 (iii) Oxides of nitrogen were sampled manually into fritted bubblers containing Saltzman reagent. Nitric oxide was oxidized to form NO₂ by reaction with sodium dichromate. Dr. Kopczynski has estimated that this conversion is almost 100% efficient. Absorbance was read on a Beckman DU spectrometer reading 2 ppm at full scale.

In general, the accuracy of these various measurements is a function of the concentration level of the pollutant being measured. Accuracy is poorest over the low concentration range. As most pollutants are present at low concentrations at some time during the course of a reaction, questions of accuracy will inevitably arise with regard to chamber studies. For example, at concentrations of NO_2 below 0.15 ppm, concentrations can be determined no more accurately than $\pm 50\%$. At the higher concentrations encountered as the reaction proceeds, the accuracy of the readings improves substantially. Unfortunately, no recalibration of the oxidant or the nitrogen oxide analyzers was performed during the eleven-month study.

b. The Repeatability of Experimental Runs

Because replicate runs were made for only four of the experiments used for our validation studies, we have been unable to calculate a meaningfully statistical measure of the reproducibility of the experiments. But in those few instances for which a replicate run was

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available, the agreement between the two sets of data was quite good. Our impression of the chamber data is that, in spite of the lack of recalibration of the light intensity and chemical analyzers, the data are in general reproducible, were carefully taken, and are as suitable as any currently available for validation purposes. Although the data were taken in 1967 and 1968, at a time prior to the development of photochemical kinetic mechanisms for atmospheric reactions, the investigators did exercise sufficient care in quantifying those parameters important in validation of these models. For example, dilution rates and the rate of conversion of N0 to NO_2 in the absence of hydrocarbons were measured for all reactant systems. Probably the greatest weakness in the chamber data with regard to their use in validation is the lack of precise knowledge of the light intensity. As will be shown in Section ID1 the magnitude of light intensity has a substantial effect upon the time to the NO_2 peak predicted by the model.

D. Validation of the 39-Step Lumped Mechanism

Validation of the lumped kinetic mechanism in Table 4 consists in

- (i) obtaining estimates of the various input parameters to the mechanism--the reaction rate constants, parameterized stoichiometric coefficients α and β , initial concentrations of reactants, and average dilution rate constants.
- (ii) carrying out sensitivity studies for these parameters;i.e., establishing the effect of controlled variations in the magnitude of the various parameters on the

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concentration-time profiles for NO, NO_2 , O_3 , and hydrocarbon, and

(iii) generating concentration-time profiles for the various reactant mixtures using the specified initial conditions. These predictions are then compared with experimental results to assess the "goodness of fit".

In the first part of this section we discuss the basis for selection of the input parameters. In the second portion of the section, we present the validation results for each of the three hydrocarbon systems studied. Results are summarized as a series of plots displaying both predicted and measured concentrations.

1. Estimation of Parameters

Prior to obtaining kinetic information from the lumped mechanism all known parameters must be specified and uncertain parameters estimated. The input parameters to this mechanism include the rate constants, parameterized stoichiometric coefficients, initial reactant concentrations, and average loss rates of the reactants and products due to sampling.

a. The Rate Constants

While the kinetic mechanism is written in a general fashion, we have striven to formulate it in such a way that all important features of the detailed chemistry remain. Thus, our goal has been to include each elementary reaction thought to contribute to the overall smog kinetics. A reaction has been judged unimportant only if its inclusion in the mechanism results in no changes in the predictions of the

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decision variables, namely, the rate of oxidation of NO, the time to the NO_2 peak, and the rate of accumulation and maximum levels of O_3 . By virtue of the mechanism's detail we are able to use directly as input experimental determinations of the rate constants for the individual reactions in every case for which measurements have been made. (One problem with the simplified mechanism (e.g., HS and EM mechanisms) was that their highly compact nature precluded strict adherence to experimental values of certain rate constants.)

Several papers have been published in the past three years which review the vast literature of kinetic studies relevant to the reactions now thought to be important in smog formation. These include the detailed modeling study of Demerjian et al. (1973), the atmospheric chemistry and physics assessment in Project Clean Air (Johnston et al., 1970), and the detailed modeling study of propylene conducted by Niki et al. (1972). Their recommended values for the rate constants of the individual reactions incorporated in the lumped mechanism, as well as more recent or different determinations, are presented in Table 6 along with the values which we used in our validation studies. Note that for each reaction the validation value of the rate constant is within the range of values recommended by these three groups or other individuals. For some reactions a considerable span exists between the lowest and highest "best" estimate of the rate constants (e.g., the formation of PAN by reaction 33). This generally indicates that the rate constant has not yet been precisely determined experimentally; the estimated values in those instances have usually been reached by analogy to similar reactions with known rate constants. In Chapter II we discuss

TABLE 6

Validation Values of the Rate Constants and Their Comparison with the Recommended Values of Other Investigations

Reaction	Validation* Value	Demerjian et al. (1973)	Johnston et al. (1970)	Niki et al. (1972)	Others
1	.266 min ⁻¹	DEPENDS ON	EXPERIMENTAL SYST	EM	
2	2.0×10 ⁻⁵ ppm ⁻² min ⁻¹	2.0×10 ⁻⁵	2.3×10 ⁻⁵	2.2×10 ⁻⁵	
3	2.3×10 ¹	2.3×10 ¹	2.9×10 ¹	2.9×10 ¹	
4	3.5×10 ⁻³ ppm ⁻² min ⁻¹	3.4×10 ⁻³	2.5×10 ⁻³		
5	1.38×10 ⁴	8.1×10 ³	8.1×10 ³		1.38×10 ⁴ †
6	2.2×10 ⁻³ ppm ⁻² min ⁻¹	2.2×10 ⁻³			
7	1.1×10 ⁻¹	0.48-1.1×10 ⁻¹	1.1×10 ⁻¹	1.1×10 ⁻¹	
8	1.5×10^4	0.66-1.47×10 ⁴	1.5×10 ⁴	1.5×10^{4}	
9	4.5×10 ³	6.8×10 ³	4.5×10^{3}	4.4×10 ³	
10	1.5×10 ¹ min ⁻¹	1.5×10 ¹	1.4×10 ¹	1.4×10 ¹	
11	1.0×10 ⁻⁵	2.5×10 ⁻³	3.0×10 ⁻³	1.5×10 ⁻⁶	
12	1.0×10				
13	5.0				
14	4.3×10 ⁻⁶ ppm ⁻² min ⁻¹	<u><</u> 4.3×10 ⁻⁶	6.9×10 ⁻⁶	3.6×10 ⁻⁸	
15	4.5	<u><</u> 4.5		2.8×10 ⁻²	
16	1/10 k _l min ⁻¹	1/4×k1	1/10×k ₁	1/2000 k ₁	
17	1.5×10 ⁴	<u>></u> 1.5×10 ⁴	1.5×10 ³	6.0×10 ³ ′	
18	1.2×10 ⁴ **	0.8 k14		2.1×10 ³	

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Validation* Demerjian Niki Johnston Reaction Value et al.(1972) et al. (1973) **Others** et al. (1970) 2.2×10² 2.5×10² 2.6×10² 2.5×10² 19 7.0×10² ++ 2.9×10² 7.0×10² 2.0×10² 20 1/250 k₁^{†††} 1/250 k₁min⁻¹ 21 1/160 k₁ 6.8×10³¹ 6.8×10³ 4.4×10³ 3.7-4.4×10³ 22 1.6×10⁻² 1.5×10⁻² 0.9-1.6×10⁻² 1.7×10⁻² 23 9.4×10³ 2.5×10⁴ 2.5×10⁴ 24 1.07×10² 1.07×10^{2} 25 5×10³ 26 6.5×10¹ 3.2×10¹ 0.16-6.5×10¹ 27 6.0×10^{3 ++++} 5.7×10³ 3.8×10³ 3.8×10³ 28 $2 \times 10^{-3} \text{min}^{-1}$ 0.4-2.5×10⁻³ 29 1/1000 k₁ 2.2×10⁴ 2.3×10⁴ 2.3×10⁴ 30 9.1×10² 9.1×10² 2.9×10² 31 4.7×10^{2} 9.1×10² 1.5×10^{3} 32 4.9×10² 1.0×10^{2} 2.2×10 33 4.4×10⁻³ 2.4×10⁻² 2.4-5.6×10⁻² 34 3.0-4.9×10² 2.9×10³ 4.9×10² 35 2.5×10² 2.0-2.5×10² 9.9×10² 36

TABLE 6 (Continued)

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		TABLE 6 (Continue	TABLE 6 (Continued)			
Reaction	Validation* Value	Demerjian et al. (1973)	Johnston et al. (1970)	Niki et al.(1972)		
37	5.3×10 ³	5.3×10 ³	5.3×10 ³	5.3×10 ³		
38	1.0×10^{2}	1.0×10^2		5.3×10 ³		
39	1.0×10 ²	1.0×10^{2}		4.4×10 ³		

*Units of ppm⁻¹min⁻¹ unless indicated to the contrary; **Pseudo second order value * Schuck et al., 1966 **Davis, et al., 1972 ***Dodge, 1973 ****Morris and Niki, 1971

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in detail the reactions for which considerable uncertainty in either the value of the rate constant or nature of the elementary mechanism still remains and make recommendations for further important experimental investigations.

b. Parameterized Stoichiometric Coefficients

As we noted in Section IB3, two parameterized stoichiometric coefficients must be specified. Since the only olefin which we are considering in this validation study is propylene, a terminal olefin, α is always equal to 1/2. The value of β depends upon the fraction of total aldehydes formed during an irradiation which is not formaldehyde. The approximate values of β for the three systems validated are

System	_β_
n-Butane-NO _x	.75
Propylene-NO _x	.50
n-Butane-Propylene-NO _x	.63

The accuracy of these values is probably no better than ±20% because

- (i) the ratio of formaldehyde to higher aldehydes fluctuates somewhat during an irradiation,
- (ii) all the higher aldehydes may not have been detected with the analytical instruments, and
- (iii) the accuracy of the analytical techniques used to determine aldehydes in this study is poor. (See Chapter III for a discussion of aldehyde measurement methods.)

This uncertainty, however, introduces no substantial impediment to the validation effort since variations in β over the extremes of the uncertainty bounds have little effect on the predictions of the decision variables by the kinetic mechanism.

c. Initial Concentrations of Reactants

The initial concentrations of the reactants were not always determined at T = 0.0, that is, the instant at which the lights were turned on. In those cases we have estimated the initial concentrations by interpolating between the last measurement before and the first measurement after the irradiation was begun.

d. Average Dilution Rate

The analytical techniques used to follow the course of the reaction during an experiment required large volumes of gas from the chamber. Because a volume of clean air was added to the chamber equal to the volume of gas removed for sampling to maintain the total chamber pressure at 1 atmosphere, dilution generally amounted to 20-25% of the initial concentrations of reactants during a 6-hour irradiation. Ethane, a hydrocarbon which is virtually unreactive in photochemical smog, was added to the reactant mix as a tracer gas for dilution. If ethane is assumed to be unreactive, its loss from the chamber can be attributed entirely to sampling and dilution at an average rate constant of k :

$$\frac{-dc}{dt} = kc$$

or

$$k = \frac{2.3 \log(c_0/c_f)}{t_f^{-} t_0}$$

where o and f are the beginning and ending times of the irradiation. The average dilution rate constants for the experiments used for validation were:

EPA Run	$k \times 10^4 (min^{-1})$	EPA Run	$k \times 10^4 (min^{-1})$
306	7.5	307	9.5
314	8.5	333	10.0
345	7.5	348	7.9
318	8.2	349	9.3
325	8.5	352	9.5
329	8.9	457	6.9
459	4.8		

e. <u>Sensitivity of Kinetic Mechanisms to Variations in the Magnitudes</u> of Parameters

We have carried out a large number of validation runs during this study, many of which involved the investigation of the effect of varying the magnitude of a parameter on the predicted concentrationtime profiles. These efforts can thus be viewed, in part, as an informal sensitivity study of the lumped kinetic mechanism. On the other hand, we have completed a detailed formal sensitivity analysis of the simple HS mechanism (Section IA3). In comparing the HS mechanism with the new lumped kinetic mechanism (Section IA4) we found the most striking difference to be that a large number of stoichiometric coefficients having a poor correspondence to actual stoichiometries had to be specified in the simple mechanism. Otherwise, and excepting the obvious difference in detail, the two mechanisms present the same basic features of the smog formation process. A sensitivity analysis of the HS mechanism is then a good indication of the sensitivity of parameters in the lumped mechanism.

Among those parameters that are imprecisely known, the predictions of the HS mechanism are most sensitive to variations in the rate of photolysis of NO₂, k_1 , the initial concentration of NO₂, and the stoichiometries of the OH-HC, and RO₂-NO (which involves regenerating OH) reactions. Variations of ±50% in the water concentration, however, have virtually no effect on the predictions. In one sensitivity study using a set of data from the toluene-NO_x system in which the NO₂ peak recurred at 162 minutes, ±50% changes from the base values of (NO₂)₀, k_1 , β , and ε caused the following changes in the time to the peak T.

Parameter Change	Change in	T (minutes)
β - 50%	+	198
ε - 50%	+	174
. k ₁ - 50%	+	116
(NO ₂) ₀ - 50%	+	24
β + 50%	-	114
ε + 50%	-	106
k ₁ + 50%	-	43
(NO ₂) ₀ + 50%	-	20

 β and ϵ both govern the rate of NO oxidation due to the OH-hydrocarbon oxidation reaction. As we indicated earlier, the OH-

hydrocarbon oxidation reaction is primarily responsible for the hydrocarbon loss rate observed in smog, and the rate constant of that reaction correlates most closely with the photochemical reactivity of hydrocarbons in smog chambers. Thus, one would expect changes in the stoichiometries of reactions involved in the production or loss of OH to have an impact on the predictions of kinetic mechanisms. In terms of the lumped mechanism, we would expect changes in the stoichiometries of the reactions of OH with the four classes of hydrocarbons and in the termination rate of OH through reaction with NO₂ and NO (reactions 17 and 18) to affect the predictions materially. We would also expect variations in the two experimental parameters, k_1 (light intensity) and the initial NO₂ concentration to perturb the predictions of the lumped mechanism. During validation of the mechanism we have qualitatively observed these conclusions to hold true.

2. The Validation Results

In this section we present validation results for the lumped mechanism (Table 4) for the following reactant systems:

Reactant System	Number	of	Sets	of	Experimental	Data
n-Butane-NO _x				3		
Propylene-NO _x				4		
n-Butane-Propylene-NO _x				6		

The input parameters to the mechanism are those presented in Section ID1. The results are depicted as a series of figures. Figure numbers, EPA experiment identification number, and initial concentrations of reactants are given in the List of Figures, Table 7. Predictions of the mechanism are represented by solid lines, and the experimental data points are coded according to

□ N0
△ N0₂
◇ 0₃
○ Propylene
∞ n-Butane
∞ Peroxyacyl nitrates

a. n-Butane-NO_X

Plots of the predicted and experimental values of concentrations with time are shown in Figures 2 through 4. The $(n-butane)_0/(NO_x)_0$ ratios span a range from 2.4 to 10.4

b. Propylene-NO_X

The propylene-NO_x validation results are presented in Figures 5 through 8. For this system the $(propylene)_0/(NO_x)_0$ ratios for the four experiments are between 0.4 and 1.3.

c. $n-Butane-Propylene-NO_X$

The validation results for this binary hydrocarbon system are displayed in Figures 9 through 14. The hydrocarbon/ NO_{χ} ratios for the experiments considered here span approximately the same range as those used for the validations of the single hydrocarbon system. The

TABLE 7

Li	st	of	Figures
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Figure ^{**}	EPA Run	(N0 ₂) [*]	(NO) [*]	(n-Butane) <mark>*</mark>	$(Propylene)_0^*$
2a,b,c	306 [†]	0.03	0.30	1.60	
3a,b,c	314	0.02	0.29	3.17	
4a,b,c	345	0.12	1.28	3.40	
5a,b,c	318	0.06	1.12		0.51
6a,b	325	0.04	0.32		0.45
7a	329	0.06	0.26		0.24
8a,b	459	0.06	1.14		0.78
9a,b,c	307	0.05	1.23	3.06	0.36
10a,b,c	333	0.08	1.25	3.41	0.23
11a,b,c	348	0.08	1.23	3.39	0.50
12a,b,c	349	0.03	0.31	3.25	0.44
13a,b,c	352	0.07	0.27	3.29	0.26
14a,b	457	0.05	1.11	3.29	0.81

*Initial concentrations in units of parts per million (ppm)

[†]0.12 ppm of aldehyde also present initially

** Figure 1, presented in Section IA1, depicts a typical smog profile. The data are from EPA run 329.




































































 $(n-butane)_0/(NO_x)_0$ ratio extends from 2.4 to 9.7 and the $(propylene)_0/(NO_x)_0$ from 0.2 to 1.3.

E. Concluding Comments

The data base provided for the validation studies fulfills many of the important requirements that one would wish to place on it. The concentration levels of the hydrocarbons, nitrogen oxides, and oxidants are representative of those observed during smoggy days in Los Angeles. An important aspect of the data base is the variety of hydrocarbon systems included. High and low reactivity hydrocarbons were represented, as were single reactants (n-butane and propylene) and a binary mixture. Initial conditions for the runs cover a broad range of hydrocarbon to nitrogen oxide ratios. This is a particularly important property of the data base if the validated mechanism is to be part of an airshed model which will be used to evaluate proposed alternative control strategies. On the whole, the accuracy and precision of the measurements is adequate, although there are a number of important exceptions, which we will mention shortly.

While the data base possesses many desirable attributes, its shortcomings must be noted as well, for these determine the limits within which the model may be tested. Consider, for example, a data base for which concentrations have been determined with only passable accuracy. Wide ranging sets of parameters could easily produce predictions all of which fall within the broad limits of experimental uncertainty. Under such circumstances, it is not possible to satisfactorily test the adequacy of the mechanism to represent the data.

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We have mentioned the most notable deficiencies of the data base at one point or another in earlier sections. We summarize them here, with some comments.

- (i) Inaccuracy in measurement and in analytical procedures. As noted earlier, Mast and KI readings were badly discrepant, initial NO₂ was imprecisely determined, and light intensity was not known with sufficient accuracy. Also NO and NO₂ determinations were inaccurate at low concentrations.
- (ii) Lack of measurement of certain species, both in the gas phase and on the wall. It would be of value to monitor nitric and nitrous acid concentrations in future studies. Determination of wall concentrations of these species is also desirable.

Turning now to the results of the validation efforts, we make a number of observations. First, we have been able to demonstrate that, in general, there is good agreement between predicted and measured concentrations. In making this statement, we must emphasize that substantial uncertainties exist in the magnitude of light intensity and initial NO_2 concentration, as well as in the values of measured concentrations of HC, NO, NO_2 and O_3 , thus limiting the possibilities for critically testing the adequacy of the model. More specifically, the mechanism has shown good qualitative and quantitative agreement with observed values of the time to the NO_2 peak and final ozone levels reached for three different hydrocarbon- NO_x systems and for a wide

range of hydrocarbon to NO_{χ} ratios.

The predictions of the lumped mechanism agree most closely with the experimental data when the initial NO_x is less than about 0.5 ppm-a condition typical of polluted atmospheres. At initial concentrations of NO $_{\rm x}$ greater than 1 ppm, the rates of oxidation of NO and accumulation of NO2 predicted by the mechanism continue to agree well with the data; however, the rates of 0_3 accumulation and NO_2 oxidation after the peak are more rapid than those observed experimentally. In many of the experiments the high initial concentration of NO sufficiently delayed the attainment of the NO2 peak that a maximum level of ozone was not achieved before the end of the irradiation (usually 375 minutes). So, while it is apparent under those conditions that the onset of 03 accumulation predicted is somewhat premature, it is not possible to evaluate the accuracy of the simulated 0_3 maximum. In those experiments during which ozone reached a maximum asymptotic level (e.g., runs 306, 325, and 349) the agreement between the data and the predicted ozone maxima are good. The rates of oxidation of propylene and n-butane predicted by the mechanism match the data uniformly well regardless of either the initial concentrations or the hydrocarbon/NO, ratios. PAN validation data were available for only three sets of experiments, runs 325, 329, and 459. For the first two of these runs the predicted PAN concentrations are in good agreement with the data; for run 459, however, the predicted onset of PAN formation is too soon and the levels reached are too high compared to the data.

Earlier (Section IC) we noted that two of the experiments being used in our validation program were performed ten months after all the other data were obtained. In our attempts to validate the lumped mechanism against each of these experiments, runs 457 and 459, we have found that the predictions for each of the concentration-time traces is too rapid by about 80 minutes. Because in at least one of these cases (run 459) the hydrocarbon/NO_X ratio is not appreciably different from that of another system successfully validated (run 329), the possibility that chamber conditions might have changed significantly in the 10 month interim is raised. In particular, the radiation intensity might have decreased substantially in that period. While there is no way of checking a posteriori what changes, if any, occurred in the operating conditions of the smog chamber, this experience demonstrates the importance of continuously and accurately monitoring all the operating parameters of smog chambers.

The data and predictions are not always in perfect agreement for all species for the entire period of the irradiation. These discrepancies can be attributed to at least four possible sources of uncertainty:

> (i) The mechanism may be incomplete. It has been our intent to include every reaction presently thought to be important to explaining smog formation in the lumped mechanism. In the future, new reactions may be discovered and/or products of elementary reactions may be found to be different from what they are presently thought to be.

- (ii) The lumping process may introduce error. For example we have assumed the $CH_3CHCH_2O_2$ radical (product of the OH-OH propylene reaction) to react in the same fashion as the $CH_3CH_2CH_2O_2$ radical. To the extent that their reactivities are different error will be introduced into the predictions.
- (iii) There are uncertainties in the experimental data used for validation. None of the analytical measurements is entirely free of error; in addition, any chamber effects (such as surface effects) not accounted for in the model are potential sources of uncertainty.
- (iv) Not all of the rate constants are known with a high degree of certainty. Indeed, for a few of the reactions no experimental determination has yet been made of the rate constant. Even in cases of those reactions for which several determinations of the rate constants exist, there is often poor agreement between the various values.

Given these uncertainties, we believe that the validation results reported here indicate that the lumped mechanism provides a good description of smog chamber kinetics. In particular, the mechanism appears capable of predicting the concentration-time behavior of a variety of reactant systems over a wide range of initial conditions. However, a considerably more accurate and complete data base is required if the adequacy of the lumped mechanism is to be critically evaluated. We recommend that a carefully conceived experimental program be undertaken for the sole purpose of providing the data needed to carry out such an evaluation. Up to this point we have confined our attention to the development and validation of a kinetic mechanism capable of simulating smog chamber reaction processes. The ultimate objective of developing such a mechanism is its use in atmospheric simulation studies. Therefore, once a mechanism capable of describing smog chamber experiments becomes available, we must consider its adaptation for use in the prediction of atmospheric reaction phenomena. Here we shall briefly outline those elements of atmospheric processes which may not receive recognition in a mechanism based solely on laboratory studies.

> (i) Kinetic mechanisms for photochemical smog previously formulated have not included SO_2 as a primary reactant. Both the lack of high SO_2 concentrations in the Los Angeles basin and a lack of understanding of the processes responsible for SO_2 oxidation in a photochemical oxidizing environment are responsible for its omission. However, there is clear evidence in Los Angeles, for example, that areas of the basin with the highest SO_2 concentrations frequently experience heavy haze formation. In addition, laboratory smog chamber experiments in which SO_2 is present in many cases have exhibited exceptionally high rates of aerosol formation. Clearly, there is a great need to include SO_2 as a primary reactant in photochemical kinetic mechanisms.

- (iii) Many of the reported rate constants for atmospheric reactions have only been measured at 298^oK. In many cases, such as for hydrocarbon oxidation reactions, there is little information on activation energies, and thus on the temperature dependence of the rate constants. Obviously, application of a kinetic mechanism to atmospheric reactions requires knowledge of the temperature dependence of rate constants. Such dependence can easily be included in kinetic mechanisms; the difficulties lie, however, in the experimental measurement of values at different temperatures.
- (iv) Most smog chamber experiments are conducted with a constant value of the radiation intensity. Hence, constant values for the first-order photodissociation rate constants, such as for NO_2 , HNO_2 , H_2O_2 etc., prevail. In the atmosphere, however, the radiation intensity changes naturally throughout the course of a day as well as when clouds appear and hazes are present. As with the temperature dependence of rate constants, changes in radiation intensity can be easily accounted for in a mechanism as long as the effect of the intensity changes on the dissociation rate constants is known. The difficulty arises in relating the actual radiation intensity at any time to the values of these dissociation rate constants. In an actual atmosphere,

radiation intensity will vary with height above the ground due to the presence of aerosols which may scatter and absorb solar radiation. Ultimately, there must be included in full scale urban models a submodel which computes radiation intensity as a function of location and time in the presence of cloud cover and atmospheric aerosols.

(v)Smog chamber experiments are generally carried out with well-defined initial hydrocarbon concentrations and compositions (except in auto exhaust irradiation experiments). In the atmosphere, however, the hydrocarbon composition is a function of time and location. Lumped reaction mechanisms, as we have seen, require classification of hydrocarbons into groups depending either on the hydrocarbon class or reactivity. Thus, the application of these mechanisms to the atmosphere will require knowledge of the spatial and temporal distribution of hydrocarbons, at least by class. The mechanisms, of course, must have the ability to treat. such inhomogeneities. However, the key problem is that source inventories for hydrocarbon emissions and monitoring data generally report total hydrocarbons rather than a breakdown by class. The current lack of specific knowledge of atmospheric hydrocarbon distributions will hinder the application of lumped mechanisms to the atmosphere. In view of this lack of

knowledge, the lumping employed in atmospheric studies may very well be different than that used for smog chamber studies.

There are two other phenomena which may be important in the atmosphere and not in a smog chamber. First, there may exist sinks for gas phase species. Potential sinks include aerosol particles, vegetation and soil. Such sinks, while not altering the fundamental kinetics of the system, will have to be accounted for in an overall model. Second, the presence of turbulent concentration fluctuations will tend in some cases to cause the actual reaction rate to be different from the rate predicted on the basis of the mean concentrations. In order to account for the effect of turbulence on the observed reaction rates, it may be necessary to modify the kinetic equations so as to include the effect of turbulence within them.

Based upon our results (Figures 2-14) and the principles of formulation (Section IB), this kinetic mechanism appears to hold substantial promise for incorporation in airshed models. The mechanism describes the important inorganic chemistry in detail, yet minimizes the overall number of reactions by taking advantage of the general behavior of specific groupings of similar hydrocarbons and free radicals. Further, the mechanism is free of arbitrarily assignable stoichiometric coefficients. Thus, the new lumped mechanism represents a reasonably rigorous, yet manageable, description of the photochemistry of air pollution.

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II. INVESTIGATION OF SPECIFIC ELEMENTARY REACTIONS AND PARTICLE GROWTH PROCESSES AFFECTING THE COURSE OF SMOG FORMATION

As we have noted in Chapter I, atmospheric contaminants participate in a large number of elementary reactions. At this time it appears that most of the important reactions that contribute to the pollutant formation in the atmosphere have been identified. Yet, our complete understanding of the mechanism of smog formation depends upon our ability to measure rate constants and to determine the mechanisms and products of several elementary reactions presently thought to be significant. In this chapter we have attempted to gather and discuss what we feel are the most important problems remaining to be solved that involve fundamental chemical kinetics.

Although our primary objective in this discussion is to identify those areas of pursuit that are most important to achieving an understanding of the pollutant-generating gas phase reactions in the atmosphere, we also examine briefly the phenomenology of gas to particle conversion, that is, the mechanism of aerosol growth. As this is a large and complex topic, one which is not well understood, we have limited the discussion to a coverage of only the key issues that require further study. We have included this cursory examination primarily to emphasize that gas phase reactions of pollutants and the formation of light-scattering aerosols are coupled processes, and thus should be investigated in a related fashion.

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A. Rate Constants and Elementary Reaction Mechanisms Requiring Further Study

The formulation of a descriptive and predictive chemical mechanism of smog formation requires identification of all the important reactions contributing to the chemical dynamics. Similarly, thorough investigation of a specific reaction is achieved only when the reaction rate constant has been carefully determined and the reaction mechanism properly specified. Due to the large number of important reactions that take place in the atmosphere, the rapid rates of many of them, and the low concentrations of most reactants (e.g., free radicals), the experimental investigation of photochemical smog formation is an enormously large and difficult task. Much has been accomplished, however, in recent years. Excellent compilations and discussions of kinetic and mechanistic studies which have been carried out can be found in Leighton (1961), Johnston et al. (1970), Altshuller and Bufalini (1971), and Demerjian et al. (1973). In this section we limit ourselves to a consideration only of those inorganic and organic reactions whose rate constants or mechanisms require further investigation in order to assess their importance with regard to the dynamics of pollutant transformations.

As will be seen in the following section the important inorganic reactions that occur in the atmosphere are reasonably well known. Approximately 15 species, mostly nitrogen-containing, participate in about 20 elementary reactions. Most of the reaction mechanisms are well understood, and the remaining problems of interest concern mainly the determination of the reaction rate constants. The set of reactions

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involving organic constituents, on the other hand, is extremely complex, involving hundreds of reactants. Simplified descriptions of these processes can be achieved only in that the organics can be divided into five general classes, the constituents of each class having a tendency to react similarly with a particular reactant (such as 0, 0H, and 0_3 . See Chapter I). Also of interest is the identification and determination of products of hydrocarbon-oxidant reactions and the measurement of rates of free radical reactions.

1. Inorganic Reactions

In this section we focus our attention on both the direct photolysis and thermal reactions of importance that occur in the atmosphere and that involve inorganic species. [Included among the inorganics are free radical species (e.g., 0, 0H, HO₂, NO, NO₂, NO₃), inorganic acids and acid anhydrides (e.g., HNO_2 , HNO_3 , N_2O_5), peroxides (e.g., H_2O_2), and other simple oxides (e.g., CO, SO_2).] Photodissociation reactions result in the generation of free radical species which initiate the photochemical smog process. The thermal reactions important in smog, on the other hand, are mainly chain continuing or chain terminating processes which result in the oxidation of NO, the accumulation of O_3 , and the formation of stable products such as HNO_3 and CO_2 .

a. <u>Direct Photolysis Reactions</u>

The rate constant for photodissociation of a species is normally expressed as the product of the specific absorption rate, k_a , and the quantum yield, ϕ . The specific absorption rate is a function of the intensity and spectral distribution of the incident radiation. Rates of photodissociation reactions are usually known only with uncertainty because of the difficulty in measuring the spectral distribution of sunlight and artificial radiation sources. We defer the discussion of light intensity measurements until Chapter III.

At least three inorganic species, NO_2 , HNO_2 , and H_2O_2 , will photolyze when exposed to incoming solar radiation of spectral composition typically observed at the earth's surface. Of these NO_2 dissociation is clearly the most important. At this point the significance of HNO_2 decomposition and the effect of this reaction on smog dynamics has not been clearly established, largely because HNO_2 is rarely, if ever, measured either in the atmosphere or in smog chambers. Probably the least important contributor to smog formation of the three reactions mentioned above is the photolysis of H_2O_2 . H_2O_2 does not photolyze readily and, because it is produced late in the smog formation cycle, has little effect on the overall chemical dynamics. (Ozone will also photolyze slowly. Because O_3 does not accumulate until the NO_2 maximum has been reached, this reaction would not be important until late afternoon, if at all.)

 $(1) NO_2$

 NO_2 is the primary energy absorber of those pollutants present in the atmosphere. The photodissociation of NO_2 ,

$$NO_2 + hv \rightarrow NO + O$$

has long been recognized as the most important chain initiation reaction in smog formation. We shall discuss the experimental

measurement of the photolysis rate constant for this reaction in Chapter III.

(2) HNO₂

A second energy-absorbing species thought to be present in polluted air and in smog chambers is nitrous acid. (We discuss the chemistry of nitrous acid formation subsequently.) At wavelengths greater than 3000Å two primary photodissociation reactions are possible (Leighton, 1961):

HONO +
$$h\nu \rightarrow OH$$
 + NO - ($\sim 60 \text{ kcal}$)
HONO + $h\nu \rightarrow H$ + NO₂ - ($\sim 80 \text{ kcal}$)

The rate of photolysis of HNO_2 is about 1/10 that of NO_2 (Johnston et al., 1970). The importance of HNO_2 in initiating smog formation is a consequence of the high reactivity of the OH radical with hydrocarbons^{*}. In the case of the second reaction the H atom combines rapidly with O_2 to form an HO_2 radical. The HO_2 radicals may then react with NO or another HO_2 radical, thereby initiating reactions which ultimately lead to the formation of OH radicals.

$$HO_{2} + NO \rightarrow OH + NO_{2}$$
$$HO_{2} + HO_{2} \rightarrow H_{2}O_{2} + O_{2}$$
$$H_{2}O_{2} + h\nu \rightarrow 2OH$$

Hydroxyl radicals react about fifty times more rapidly with alkanes, and about ten times more rapidly with olefins, than do oxygen atoms.

Although measurements of atmospheric HNO_2 concentrations have not been reported, we can estimate roughly the equilibrium concentration of HNO_2 that would be established under typical atmospheric conditions. Using equilibrium constants determined by Wayne and Yost (1951) and concentrations of NO (0.2 ppm), NO_2 (0.1 ppm), and humidity (63% at 25^oC) which are typically observed in Los Angeles just before sunrise, we estimate the equilibrium concentration of HNO_2 to be about 0.026 ppm or about 1/4 of the NO_2 concentration. At these low concentrations HNO_2 will form at a rate of about 0.10 ppm/hour. (If the concentration of NO were 0.40 ppm and NO_2 were 0.20 ppm, the rate of nitrous acid production would rise to about 0.40 ppm/hour, and the equilibrium concentration would be about 0.05 ppm). Thus, nitrous acid may well be an important source of free radicals early in the morning in a polluted atmosphere.

(3) H₂O₂

Recent evidence suggests that hydrogen peroxide may exist in significant concentrations in polluted air. Bufalini et al. (1972) measured 0.18 ppm of H_2O_2 under severe smog conditions in Riverside, California and they suggested that H_2O_2 forms primarily as a result of HO_2-HO_2 recombination. However, hydrogen peroxide is probably not a major factor in hydrocarbon oxidation (by production of OH radicals) for the following reasons:

(i) Under equivalent irradiation conditions, its

photodissociation rate is only 1/250 that of NO_2 (Leighton,

1961).

- (ii) Maximum concentrations of H_2O_2 observed in the laboratory and the atmosphere are much less than the corresponding maximum concentrations of NO₂ (Bufalini et al., 1972).
- (iii) H₂O₂ forms at the fastest rate after the NO₂ peak, coincident with the onset of oxidant formation and after much of the hydrocarbon has been oxidized.
- (iv) H_2O_2 actually serves as a sink for HO_2 radicals, since the subsequent production of OH radicals from photolysis is slow.

For these reasons it is probably important to measure the concentration of H_2O_2 only for the purposes of modeling the post- NO_2 -peak smog formation behavior.

b. Thermal Reactions

When a mixture of NO_2 , NO_2 , O_2 , and H_2O is irradiated in air, a large number of "secondary" reactions can occur subsequent to NO_2 photolysis. These "secondary" reactions are thermal rather than photolytic in nature, since the energy contained in the reactants and that produced by their collision, rather than light energy, drives the reaction. In this section we discuss the important inorganic reactions that occur in the atmosphere, examining in particular the formation of the inorganic acids, HNO_3 and HNO_2 , and the oxidation of NO, CO, and SO_2 . Before doing this, however, we briefly discuss the effect of temperature on the rate of the homogeneous reactions contributing to smog formation.

It has been observed by several investigators that increasing the operating temperature of a smog chamber results in an increase in the photooxidation rates of hydrocarbons and in the ozone levels attained. (Early literature on this subject has been reviewed by Altshuller and Bufalini (1965).) This is the effect one would expect of reactions having substantial activation energies. However, most of the inorganic and organic reactions contributing to smog formation for which activation energies (E_{Δ}) have been determined have values of E_{Δ} less than 5 kcal (see Johnston et al., 1970). For instance, the NO-0, reaction (Section II.A.1.b.(1)), which contributes substantially to NO and O_3 loss rates and the NO $_2$ formation rate, has an activation energy of 2.5 kcal. Increasing the temperature from $77^{\circ}F$ to $95^{\circ}F$ $(25^{\circ}C \text{ to } 35^{\circ}C)$ increases the rate constant from 29.4 ppm⁻¹min⁻¹ to 33.8 ppm⁻¹min⁻¹, (a 15% change, which by itself should have little effect on the time to the NO2 peak or the ozone level attained). The activation energy of the NO_2-O_3 reaction (Section II.A.1.b.(1)), on the other hand, is 7.0 kcal, and a 10°C increase in temperature results in a 46% increase in the rate constant. The only reaction of those listed in Johnson et al. (1970) having a high activation energy is the reaction

$$N_20_5 \rightarrow N0_2 + N0_3$$

which has an activation energy of 21 kcal.

To determine the effect of temperature on the rate of smog formation it will be necessary to incorporate the thermal dependence of the Various rate constants into kinetic mechanisms. However, activation energies have not yet been determined for all the reactions thought to be important in smog formation (for example, the HNO_2 formation and HO_2 -NO reactions). Thus, we recommend that an effort be made to obtain the data needed to establish k versus T relationships.

(1) Reactions of 0_3 with NO and NO_2

Ozone, which forms as a product of NO_2 photolysis by the reactions,

$$NO_{2} + hv \xrightarrow{k_{1}} NO + O$$

$$NO_{2} + hv \xrightarrow{k_{2}} O_{3} + M \qquad M = \text{third body}$$

is destroyed rapidly in the presence of NO by the reaction

$$0_3 + N0 \xrightarrow{k_3} N0_2 + 0_2$$

As the overall smog formation process proceeds, NO is depleted and NO₂ and O₃ accumulate. When NO₂ and O₃ reach sufficiently high concentration levels, the reaction

$$0_3 + N0_2 \xrightarrow{k_4} N0_3 + 0_2$$

becomes more important than the 0_3 -NO reaction.

Two determinations have been made of the rate constant for the 0_3 -NO₂ reaction, k_4 : 0.106 ppm⁻¹min⁻¹ by Johnston and Yost (1949) and 0.0485 ppm⁻¹min⁻¹ by Ford et al. (1957). The earlier measurement was made at partial pressures of NO₂ between 0.001 and 0.01 atmospheres--pressures that are much higher than those typically observed. The latter determination was made at concentrations of NO₂ and O₃ below 1 ppm. In that study O₃ and NO₂ entered a flow reactor at known concentrations. The effluent stream was analyzed continuously for NO_2 using a wet method similar to the Saltzman method (see Chapter III), while ozone was determined in situ by ultraviolet photometry. The accuracy of the rate constant determined by Ford et al. is affected by several factors, including the constancy of the inlet reactant concentrations, the completeness of mixing, and the accuracy of the NO_2 and O_3 measurements. Because of the possible sources of error and the lack of agreement between the two experimental determinations of k_4 , it would be worthwhile to reevaluate this rate constant^{*}.

(2) The Chemistry of NO₃, N₂O₅, and HNO₃

Any NO_3 formed by reaction 4 before the NO_2 peak will react rapidly with NO to regenerate NO_2 by the reaction,

$$NO_3 + NO \rightarrow 2NO_2$$

After the NO_2 peak, a time after which NO has reached low levels, NO_3 will react primarily with NO_2 , presumably leading to an

Eschenroeder (1972) found it necessary, in validating a photochemical mechanism proposed by him, to use a value of $k_4 = 0.005 \text{ ppm}^{-1}\text{min}^{-1}$, while Hecht and Seinfeld (1972) used a value of $0.006 \text{ ppm}^{-1}\text{min}^{-1}$. Employing values closer to the lowest experimental value of k_4 resulted in a reduced maximum NO₂ concentration, in much more rapid disappearance of NO₂, and in greatly (60%) reduced ozone levels. Because both mechanisms are subject to a large amount of uncertainty, there is no assurance that values of k_4 necessary to simulate smog chamber data are, indeed, closer to reality. Nonetheless, the modeling results serve to raise questions about the validity of k_4 determinations carried out to date.

equilibrium concentration of N_20_5 .

$$NO_3 + NO_2 \stackrel{k_6}{\neq} N_2O_5$$

In the presence of water, however, $N_2^{0}0_5$ can hydrolyze to form nitric acid.

$$N_20_5 + H_20 \xrightarrow{k_8} 2HN0_3$$

Smith (1947) has observed HNO_3 to oxidize NO by a process with the following overall stoichiometry:

$$2HNO_3 + NO \rightarrow 3NO_2 + H_2O$$

A possible reaction sequence to account for this (Johnston et al., 1955; Gray et al., 1972) is

$$HNO_3 + NO \rightarrow HNO_2 + NO_2$$
$$HNO_3 + HNO_2 \rightarrow 2NO_2 + H_2O$$

The magnitudes of the rate constants and the effect of surfaces on the rates of these two elementary reactions have not yet been established quantitatively. But, in view of the large amount of HNO_3 which forms in smog, such an investigation would be valuable.

Beyond those two reactions, HNO₃ is not thought to enter into any significant reactions with the other pollutants present in a smog chamber. And while the acid will photodissociate at shorter wavelengths, the photolysis does not proceed at wavelengths present in smog chambers (Bérces and Förgeteg, 1970a,1970b). (In the atmosphere, however, HNO_3 can react rapidly with NH_3 to form NH_4NO_3 , a constituent of atmospheric aerosols.)

Although nitric acid has been found on the walls of smog chambers (Gay and Bufalini, 1971), the rate of hydrolysis of N_2O_5 has not been established, and it is not yet certain that reaction 8 is the primary source of HNO_3 . (An alternate source of HNO_3 is the reaction of OH and NO_2 .) Wilson (1972) has charged a humidified reactor with N_2O_5 and observed that the oxide disappears very slowly. This behavior suggests that gas phase hydrolysis of N_2O_5 is very slow. Thus, the presence of a third body covered with at least a monolayer of water may be required to promote the hydrolysis reaction.

If the hydrolysis of N_2O_5 is slow, one could reasonably expect a large steady state concentration of N_2O_5 to be present in smog chambers. Wilson (1972) carried out an experiment in which he irradiated a hydrocarbon-NO_x mixture until the NO had been oxidized and the O_3 maximum reached. He then extinguished the lights and injected NO into the system in an amount in excess of that needed to destroy all ozone present. Subsequently, he observed that the remaining NO was slowly oxidized to NO₂. A possible explanation for this observed behavior is that N_2O_5 had accumulated during the HC-NO_x irradiation and then reacted with the excess NO via reactions 5 and 7. Were this the case, one would expect to observe three parts of NO₂ formed for each part of NO consumed. Note that this is the same stoichiometry as that observed for the HNO₃-NO oxidation process just discussed.

In summary, the atmospheric chemistry of N_2O_5 requires further investigation. In particular, it will be important to measure the gas phase rate constant for the N_2O_5 - H_2O reaction, the rate of the HNO₃-NO reaction, and the steady state concentration of N_2O_5 in a dry system.

(3) The Chemistry of HNO₂

The photolysis and estimated equilibrium concentration of nitrous acid in the atmosphere have been discussed earlier in this chapter. We briefly examine here the reactions which produce HNO₂. Nitrous acid is known to form in aqueous solution by the reactions

$$N0 + N0_{2} \stackrel{k_{9}}{\stackrel{\neq}{_{10}}} N_{2}^{0_{3}}$$

$$N_{2}^{0_{3}} + H_{2}^{0} \stackrel{k_{11}}{\stackrel{\rightarrow}{_{2}}} 2HN0_{2}$$

Gratzel et al. (1970) have studied this system and have determined the pseudo-first order rate constant for the hydrolysis of N_2O_3 to be $3.18 \times 10^4 \text{min}^{-1}$. Nitrous acid is presumed to form in the atmosphere by the same mechanism, although the homogeneous gas phase hydrolysis of N_2O_3 may be very slow, as is the case for N_2O_5 . Wayne and Yost (1951) studied the third order gas phase reaction,

$$NO + NO_2 + H_2O \rightarrow 2HNO_2$$

obtaining a rate constant of 4.3×10^{-6} ppm⁻²min⁻¹ for the reaction. Westberg (1972) has questioned the accuracy of this determination, based on thermodynamic considerations.

In the ambient system nitrous acid can form at night through the hydrolysis of N_2O_3 , so that an equilibrium concentration of HNO_2 may be reached by sunrise. Hydrolysis of N_2O_3 is probably also a favored reaction on wet surfaces, such as on particles or walls. As such, it very likely occurs on surfaces in smog chambers. Because of the potentially important role of HNO_2 in atmospheric photooxidation reactions, we recommend that the rate of formation of this species in the gas phase be carefully assessed.

(4) Reactions of OH with NO and NO_2

From our discussion in Chapter I, it should be clear that OH is the most important oxidizer of hydrocarbons in smog. Thus, any reactions which affect the concentration of OH can result in a pronounced change in the rate at which smog is observed to form. Two such reactions are the terminations of OH with NO₂ and NO.

$$0H + NO_2 \xrightarrow{k_{12}} HNO_3$$

$$K_{13}$$

$$0H + NO + M \xrightarrow{k_{13}} HNO_2 + M$$

Morley and Smith (1972) have determined k_{12} between 20 and 300 torr, a region which they have shown to be a transition

between third and second order kinetics. Based on their data they have estimated 15,000 ppm⁻¹min⁻¹ to be the lower limit of the rate constant at 300° K and atmospheric pressure. By a separate technique Simonaitis and Heicklen (1972) have determined k_{12} to be 13,000 ppm⁻¹min⁻¹ at 300° K and atmospheric pressure. There have been no determinations of k_{13} at pressures greater than 30 torr (Morley and Smith, 1972). However, Demerjian et al. (1973) have estimated $k_{13} = 0.8 k_{12}$ at atmospheric pressure. Because of the importance of OH in the smog formation process, an effort should be made to confirm this estimate experimentally.

(5) Oxidation of NO by HO_2

Until recently there has been little direct evidence to substantiate the hypothesis that HO_2 is an important oxidizer of NO in the smog formation process. Wilson and Ward (1970) have observed that irradiation of NO (\sim 1 ppm) in the presence of large amounts of CO (\sim 500 ppm) in air results in the complete oxidation of NO to NO₂ and the formation of O₃. The mechanism generally assumed to explain this observation is as follows. Water in the air reacts with NO and traces of NO₂ to form nitrous acid, which subsequently photolyzes to form OH radicals. The following reactions then occur:

OH + CO
$$\stackrel{k_14}{\rightarrow}$$
 CO₂ + H
H + O₂ + M $\stackrel{k_{15}}{\rightarrow}$ HO₂ + M
HO₂ + NO $\stackrel{k_{16}}{\rightarrow}$ OH + NO₂

The rate constant for reaction 14 is now well established (see the next section), and the combination of H with O_2 is very fast. Apparently the first reported value for k_{16} was that determined by Johnston et al. (1970), 3 ppm⁻¹min⁻¹. Recently, however, Davis et al. (1972) have experimentally established k_{14} as being 700 ppm⁻¹min⁻¹. The earlier low value is probably incorrect, since with such a value, the oxidation of NO in the presence of CO and light cannot be satisfactorily explained. We recommend that the value determined by Davis be used in subsequent calculations.

(6) Oxidation of CO

Carbon monoxide has been shown to accelerate the oxidation of NO to NO₂ when present in concentrations of 100 ppm or more (Westberg et al., 1971). The effect of CO is explained by reactions 14-16; accordingly, the oxidation of CO by OH (reaction 14) the first step in the chain, has received a great deal of attention. Demerjian et al. (1973) have averaged the experimental determinations of k_{14} of several investigators and obtained an average value of 250 ppm⁻¹min⁻¹. Because ambient concentrations of CO are well below 100 ppm, often on the order of 5-30 ppm, CO probably has little effect on smog formation (Dodge and Bufalini, 1972).

A simplified example demonstrates the acceleration in the rate of oxidation of NO in the presence of CO due to an increase in the ratio of the rate of radical formation to the rate of radical termination. The four most important reactions in smog involving OH are

	k = 15,000 ppm ⁻¹ min ⁻¹	HN03	\rightarrow	^{N0} 2	0H +	
	k = 12,000 ppm ⁻¹ min ⁻¹	HN02	<i>→</i>	NO	OH +	
for propylene	k = 25,000 ppm ⁻¹ min ⁻¹	1R0 ₂	0 ₂ →	HC	OH +	
	$k = 250 \text{ ppm}^{-1} \text{min}^{-1}$	1H02	0 ₂	CO	0H +	

If propylene, NO, and NO_2 are all present at a concentration of 1 ppm,

 $R = \frac{\text{Rate of radical formation}}{\text{Rate of radical termination}} = \frac{25,000}{15,000+12,000+25,000} \approx .48$

With 100 ppm CO added to the system,

 $R = \frac{25,000+25,000}{15,000+12,000+25,000} \simeq .65$

Thus, the addition of 100 ppm of CO to this system results in a 35% increase in the ratio of the rate of radical formation to the rate of radical termination. The effect of CO is even more striking in a system containing a hydrocarbon of lower reactivity such as n-butane for which the OH-n-butane rate constant is $3800 \text{ ppm}^{-1}\text{min}^{-1}$. In that case, if (n-butane) = (NO) = (NO₂) = 1 ppm

$$R = \frac{3,800}{15,000+12,000+3,800} \simeq .12$$

Upon addition of 100 ppm CO, R increases to

$$R = \frac{3,800+25,000}{15,000+12,000+3,800+25,000} \simeq .52$$

The ratio of the rate of radical formation to the rate of termination has, therefore, increased 4-fold upon addition of the CO. Thus, the effect of high concentrations of CO on the rate of smog formation would be expected to be proportionately greater for systems containing hydrocarbons of low reactivity than those containing very reactive hydrocarbons.

Recently, there has been some interest in the possible oxidation of CO by HO_2

$$HO_2 + CO \rightarrow OH + CO_2$$

Westenberg (1972) has determined experimentally the ratio of the rate of this reaction to that of HO_2 and H. In particular, he estimated that the HO_2 -CO reaction was probably very fast, with a rate constant on the order of $8.8 \times 10^4 \text{ppm}^{-1}\text{min}^{-1}$. If this is the case, the HO_2 -CO reaction,

 $HO_2 + CO \xrightarrow{k_{17}} OH + CO_2$

would have the effect of raising the OH concentration predicted by kinetic mechanisms. Consequently, the rate of loss of hydrocarbon through reaction with OH and the rate of generation of NO-oxidizing free radicals would increase. The value Westenberg obtained for the HO₂-CO rate constant, however, depends crucially on the kinetic mechanism upon which the data analysis was based. In his analysis, he omitted from the mechanism the reaction between OH and HO2,

$$OH + HO_2 \rightarrow H_2O + O_2$$

a reaction which must be of some importance. This omission resulted in an overestimation of the HO₂-CO rate constant (Dodge, 1973). Davis et al. (1972), too, have recently completed a study of the HO₂-CO reaction and have obtained a value for the rate constant of less than 8×10^{-5} ppm⁻¹min⁻¹. Thus, it now appears that reaction 17 is too slow to be of importance in smog.

(7) Oxidation of SO₂

The oxidation of SO₂ in an atmosphere containing oxides of nitrogen and hydrocarbons and in the presence of sunlight is an extremely complicated process, one which is not fully understood. The following reactions have been studied thus far:

(i) the direct photolysis and quenching of SO_2 ,

(ii) the reaction of SO_2 in its excited states with O_2 , and

(iii) the oxidation of SO_2 by 0 and O_3 .

If these were the only SO_2 oxidation reactions occurring, we would expect a maximum rate of disappearance of SO_2 in the atmosphere of about 2% per hour, a value which is considerably lower than that observed in an atmosphere containing NO_x and hydrocarbons. We shall not endeavor to examine photochemical

oxidation reactions involving SO₂ in detail here, as a thorough review of these reactions has recently been presented by Bufalini (1971). Rather, we will restrict ourselves to a discussion of reactions which have recently been postulated to explain the atmospheric photochemistry of SO₂.

Cox and Penkett (1971) have reported that SO_2 is oxidized by a product of the O_3 -olefin reaction, presumably the so-called "zwitterion".

$$e^{\Theta}$$

RCHOO ^{Θ} + SO₂ \rightarrow SO₃ + RCHO

Since the disappearance rate of SO_2 in a smog chamber experiment increases during the period of ozone accumulation (Wilson and Levy, 1970), this reaction is plausible. The zwitterion, a peroxide characterized by strong charge separation, should be an effective oxidizing agent. Wilson et al. (1972) have suggested that SO_2 may be oxidized by either NO_3 or N_2O_5 , or both:

 $NO_3 + SO_2 \rightarrow SO_3 + NO_2$ $N_2O_5 + SO_2 \rightarrow SO_3 + 2NO_2$

This hypothesis is of interest in that it implies that only 0_3 and $N0_2$, the precursors of $N0_3$ and N_20_5 , are needed to oxidize S0_2. While Wilson et al. (1972) made their observations for a system also containing hydrocarbons, it would be interesting to perform a "dark" reaction for a system of $N0_2$, 0_3 , and $S0_2$ in air. Carrying out the reaction in the dark would prevent the
formation of 0 atoms, which are known to oxidize SO_2 .

 $0 + SO_2 + M \rightarrow SO_3 + M$

It has long been speculated that peroxy radicals (HO₂, RO₂, etc.) might be important in the photochemical oxidation of SO₂. However, this now seems to be unlikely. Recent preliminary results obtained by Davis et al. (1972) indicate that the HO₂-SO₂ reaction is very slow, having a rate constant of only about 0.8 ppm⁻¹min⁻¹.

c. Summary

In the foregoing presentation we have discussed several inorganic reactions of importance, or possible importance, in smog formation which require further investigations and understanding. Many of these reactions have already been studied in detail; however, some may require a careful re-determination of the rate constants. Specifically, we recommend that:

- (i) The rates of photodissociation of NO_2 , HNO_2 , and H_2O_2 be measured carefully in both smog chambers and the atmosphere. Additionally, the concentrations of HNO_2 and H_2O_2 should be monitored continuously, as is now done for NO_2 , so that their importance as free radical initiators in the smog system can be evaluated.
- (ii) The 0₃-NO₂ rate constant be re-determined. The magnitude of this rate constant strongly affects the NO₂ disappearance rate and peak ozone levels predicted by smog mechanisms.

- (iii) The rate of reaction of N_2O_5 and H_2O in the gas phase be measured. Nitrogen balances in smog chambers have been notoriously poor, a difficulty that is attributable to the formation of HNO_3 . A point of interest in the development and validation of kinetic mechanisms is to establish whether HNO_3 forms in the gas phase and is transported to surfaces, or whether the hydrolysis takes place predominantly on walls and particles.
- (iv) The rate of formation of HNO_2 by the hydrolysis of N_2O_3 be re-determined in the gas phase. Again, HNO_2 should be measured routinely in smog chambers and the atmosphere if its formation rate is significant.
- (v) The rate of reaction of OH and NO be determined. Such knowledge is needed if we are to explain the rate of hydrocarbon oxidation by OH up to the NO₂ peak accurately.
- (vi) The rates at which NO_3 , N_2O_5 , zwitterions, and free radicals react with SO_2 be determined. This information will aid in explaining the observed rates of SO_2 oxidation in photochemical smog formation.
- 2. Organic Reactions

Although the irradiation of a system containing NO, CO, H₂O, and air will result in the oxidation of NO and production of ozone, the addition of any of several organic species to the system substantially accelerates the photo-oxidation process. Organics that will enhance the oxidation rate include olefins, aldehydes, ketones, most paraffins and aromatics, and the longer chain acetylenes. These species enter the atmosphere in several ways.

- (i) Auto exhaust contains large amounts of unburned and partially burned gasoline.
- (ii) The filling of gas tanks displaces air saturated with gasoline into the atmosphere.
- (iii) Organic solvents used in metal working plants, dry cleaning, and as carriers for paints evaporate into the air.
- (iv) Organic products escape to the atmosphere from chemical manufacturing plants such as petroleum refineries.

The contribution from motor vehicles is the highest, however, being about 66% of the total organics and 86% of the reactive organics found in the Los Angeles atmosphere.

In a study of the effect of varying engine operating conditions on exhaust composition, Jackson (1966) found that ethylene, propylene, and butenes constituted approximately 34% of the hydrocarbons found in exhaust, toluene and xylenes about 10%, and unreactive hydrocarbons (methane, ethane, propane, acetylene, and benzene) about 24%. Eccleston and Hurn (1970) have measured the composition of exhaust emissions from eight automobiles in an effort to determine the effect of switching from leaded to unleaded gasolines. The average emissions from cars using regular leaded gasoline were:

38.34%	paraffins
36.45%	olefins
13.34%	aromatics
1.41%	oxygenates
10.61%	acetylenes

Running the cars on a regular, low olefin fuel resulted in a large increase in the aromatic content and a moderate decrease in the olefinic content:

paraffins
olefins
aromatics
oxygenates
acetylenes

Exhaust analysis of the cars run on an unleaded, high olefin fuel showed a moderate increase in aromatic emissions and an almost equal decrease in olefinic emissions, when compared with emissions measured using regular leaded fuel:

35.92%	paraffins
31.34%	olefins
21.06%	aromatics
1.86%	oxygenates
10.13%	acetylenes

Thus, switching from leaded to unleaded gasoline resulted in an increase in combined olefinic and aromatic emissions and reduced paraffinic emissions. Because olefins and aromatics are, as a class, more reactive than are paraffins with respect to the oxidation of NO, removal of lead from gasoline will probably result in an atmospheric hydrocarbon mix of increased photochemical reactivity.

In 1967 Altshuller et al. (1971) measured the hydrocarbon composition of the atmosphere at two locations in the Los Angeles basin. They found that atmospheric organics consist of about:

				1 ×	
53%	paraff	ins	(excluding	methane)	
16%	olefin	S			č
20%	alkyl	benz	enes		
11%	acetyl	ene			

Considerable effort has been expended in the past to study the reactions of paraffins and olefins with oxidants. Yet, Altshuller's study shows that aromatics constitute a significant percentage of the total hydrocarbon in the Los Angeles basin. Altshuller et al. (1971) found that toluene and m-xylene are two of the ten individual hydrocarbons present in the greatest concentrations and that these two hydrocarbons constitute about half of the alkylbenzene fraction. As will become apparent in the discussion that follows, the elementary reaction mechanism for the oxidation of aromatics in the atmosphere is poorly understood. In view of the high aromatic content of the atmosphere and of auto exhaust, this lack of understanding stands as an impediment to progress in the kinetic modeling of photochemical smog.

In this section we begin by examining the mechanism and products of the oxidation of each class of hydrocarbons (paraffins, olefins, aromatics, and acetylenes) by 0, 0H, 0_3 , and 10_2 . We then discuss the reactions of aldehydes and ketones that can occur in the atmosphere. Finally, we describe the reactions of free radicals, the products of hydrocarbon oxidation reactions. Some of this material to be presented has been discussed previously (in Chapter I) in explicating the development of generalized kinetic mechanisms. However, particular attention will be given here to those elementary reactions whose mechanisms require further investigation.

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a. The Mechanisms of Oxidation of Hydrocarbons in Smog

Elucidation of the mechanisms of hydrocarbon-oxidant reactions that contribute to smog formation has proven to be an arduous task. The low concentrations of the reactants, the typically rapid rates of reaction, and the short lifetimes and low concentrations of the products of the primary oxidation have, in general, precluded definitive experimental investigations. In this section we discuss the reactions of the four most common classes of hydrocarbons (paraffins, olefins, aromatics, and acetylenes) with 0, 0H, and 0_3 , the oxidants thought to be the most important in smog formation. We also briefly examine the role of singlet oxygen in hydrocarbon oxidations. We will not tabulate the rate constants of the hydrocarbon-oxidant reactions here, since this has been done recently by Johnston et al. (1970) and Demerjian et al. (1973). However, where omissions have been made in their tabulations, or where new data have become available, we will so note.

(1) <u>O Atom Oxidation Reactions</u>

Oxygen atoms form as a result of NO₂ photolysis and are generally thought to be the species that initiates the reactions leading to smog formation in smog chambers. However, while O atoms react rapidly with olefins, reactions of aromatics and acetylenes with O atoms proceed slowly, at rates about one to two orders of magnitude slower than for olefins.

(a) Reactions with Paraffins

The reaction of 0 with paraffins probably results in the abstraction of a H atom (Leighton, 1961).

 $RH + 0 \rightarrow R \cdot + OH$

The result of the reaction then is free radical branching to an alkyl radical and an OH radical.

(b) Reactions with Olefins

Oxygen atoms generally add to olefins forming an excited epoxide, which then decomposes to an alkyl and an acyl radical (Leighton, 1961)



or

$$R_{1}C + R_{2} - C + R_{4}$$
, etc.

This reaction thus results in the formation of two free radicals.

(c) Reactions with Aromatics

The mechanism for 0 atom attack on aromatics is not yet known. Among the products that have been observed from the reaction chain initiated by 0 attack on aromatics are peroxides, acids, and alcohols (Eventova and Pryktova, 1960). The reaction of 0 with benzene is very slow. With monosubstituted aromatics 0 might attack either the alkyl side chain (as it would a paraffin) or the ring. There is little evidence to indicate which of the two mechanisms predominates, but studies of toluene and NO_x in smog chanbers have led to the observation of benzaldehyde and peroxybenzoylnitrate as products (Heuss and Glasson, 1968). The fact that these products are formed indicates that at least some toluene-oxidant reaction does not result directly in chain opening. Since 0 attack on an alkyl side chain of a substituted aromatic is such a reaction, we speculate about the reaction in some detail.

In the case of a mono-substituted aromatic, 0 attack on the side chain would probably occur at the carbon atom in the alpha position relative to the ring location. The carbonhydrogen bond at that position has an unusually low bond dissociation energy, as the aromatic ring stabilizes alpha free radicals. Four canonical structures can be drawn to demonstrate the delocalization of the free electron over the aromatic ring.

 $CH_2 - CH_3 + 0 \rightarrow \bigcirc -CH - CH_3 \equiv \bigcirc -CHCH_3$ $\leftrightarrow \textcircled{CH-CH}_{3} \leftrightarrow \swarrow^{CH-CH}_{3}$ $\leftrightarrow \swarrow^{CH-CH}_{3}$

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Among the dialkyl substituted aromatics one might expect the meta-substituted isomers to be the most reactive with respect to smog formation. Consider the reactions of ortho, meta, and para xylene. The initial hydrogen abstraction is identical in each case, a radical forming for which four delocalization structures can be written:



Thus, the initial product is a very stable free radical. The addition of molecular oxygen to the ortho or para free radicals at any of the four positions, or to the meta free radical in positions M_1 or M_2 , results in a loss of free radical delocalization; that is, only one canonical structure can be written. Thus, the peroxyl radical is less stable than the alkyl radical, and there is a tendency for the radical to split off the O_2 again. Positions M_3 and M_4 of the meta free radical are special cases, however, with the addition of molecular oxygen favored at these sites. Upon addition of oxygen the radical takes the form,





with the free electron localizing on the outer oxygen. Note that in each case the two oxygens, two carbons on the ring, and the carbon and a hydrogen of the methyl group form a sixmembered ring. Given the proximity of these various groups and atoms to each other, transfer of an H atom from the methyl group to the peroxy radical is highly likely. Thus we would expect the following reaction to occur:



In each case radicals form ($M_3^{"}$ and $M_4^{"}$) which create the opportunity for an additional degree of delocalization to occur. Thus, reactions involving the meta radical differ from these involving the ortho and para radicals in that oxidation is energetically favorable at more than one position on the ring. In the presence of sunlight and photochemical oxidants the oxidation will probably result in complete fragmentation of the radicals $M_3^{"}$ and $M_4^{"}$. However, it is not possible at this time to specify the mode or degree of branching.

From the foregoing discussion it is apparent that little is known about the mechanism of 0 atom oxidation of aromatics. In addition, we should note that rate constants for O attack on aromatics in the gas phase have been measured only for benzene and toluene. Thus, as a serious gap exists in our understanding and knowledge of the O aromatic reaction system, we strongly recommend that

- (i) rate constants for 0 attack on important aromatics other than benzene and toluene (such as o, m, and p xylene, ethylbenzene, 1,2,4-trimethylbenzene) be measured and
- (ii) the mechanism of the O-aromatic reaction and the radicals formed either directly as products or as the result of fragmentation of the initial products in the reaction be determined.

(d) Reactions with Acetylene

The reactions of 0 with acetylene have been studied in flames (Fenimore and Jones, 1963) over a temperature range of 970⁰ to 1660⁰K and in shock tubes (Glass et al, 1965), also at very high temperatures. Possible products of the reaction suggested by these investigators include

H + HC₂O Fenimore and Jones
O + C₂H₂
$$\stackrel{?}{\leftarrow}$$
 CH₂ + CO Fenimore and Jones
C₂H + OH Glass et al.

Fenimore and Jones have determined the rate constant to be between 2.45×10^4 and $4.90 \times 10^4 \text{ppm}^{-1} \text{min}^{-1}$, with little temperature dependence over the range 970-1660^oK. At room temperature the rate constant may be slower than that for the O-olefin reactions and faster than that for the O-paraffin reactions (Leighton, 1961), but apparently it has not been conclusively measured. It is desirable that the mechanism and rate of O attack on acetylene be determined, since acetylenes constitute a significant portion of atmospheric hydrocarbons.

(2) OH Radical Oxidation Reactions

Hydroxyl radicals enter the photochemical smog system as a result of HNO₂ photolysis and as products of the degradation reactions of free radicals such as those that follow the O-hydrocarbon reactions.

$$HNO_{2} + hv \rightarrow OH + NO$$

$$CH_{3} + O_{2} \rightarrow CH_{3}OO \xrightarrow{NO} CH_{3}O + NO_{2}$$

$$O_{2}$$

$$HO_{2} + HCHO$$

$$NO$$

$$OH + NO_{2}$$

Reactions of OH with hydrocarbons are very similar to those of O, with two exceptions:

- (i) the reactions of OH with a given hydrocarbon are generally very much faster than those of 0 and
- (ii) hydrogen abstraction reactions do not result in chain branching since the \cdot OH becomes H₂O, whereas \cdot O

becomes •OH.

(a) Reactions with Paraffins

The paraffin-OH reaction results in hydrogen abstraction, an alkyl radical and water being formed.

$$RH + OH \rightarrow R \cdot + H_2O$$

Note that this is a chain transfer rather than a chain branching reaction. The rate of reaction of an individual hydrocarbon with OH generally increases with the number of H atoms on the molecule, especially secondary and tertiary hydrogens. Rate constants for these reactions are compiled in Johnston et al. (1970).

(b) Reaction with Olefins

Hydroxyl radicals react with olefins by addition at the double bond. Morris et al. (1971) have observed OH adducts directly in the reactions of OH with C_2H_4 and C_3H_6 .

$$OH + CH_3CH = CH_2 \rightarrow CH_3CHCH_2OH \text{ or } CH_3CHCH_2$$

Recently, the rate constants for OH attack on several olefins have been measured by Morris and Niki (1971). Their results indicate that, for a given olefin, the rate constant for the OH-olefin reaction is about ten times greater than for the corresponding O-olefin reaction. Less is known about the reactions of the OH adduct radical that take place subsequent to the initial addition, although possible reaction mechanisms have been proposed by Westberg and Cohen (1969), Niki et al. (1972) and Hecht and Seinfeld (1972). As such, it is important to establish the reactivity of this adduct with respect to NO oxidation and to identify its decomposition products. With this information the role of the OH-olefin reaction in smog formation can be firmly established.

(c) Reactions with Aromatics

It is current speculation that hydroxyl radicals abstract alpha hydrogen atoms from branched aromatics in the same manner as we have assumed for 0.

$$\bigcirc -CH_2CH_3 + OH \rightarrow \bigcirc -CHCH_3 + H_2O$$

If the reaction does, indeed, proceed as indicated, it would once again be a chain transfer rather than a branching step. The arguments presented earlier concerning the delocalization stabilization of free radicals formed by H abstraction from alkyl and dialkyl aromatics also hold in this case. It is also possible that OH adds to the ring. But, at this time, the experimental evidence is insufficient to allow specifying the exact mechanism of the reaction.

(d) <u>Reactions with Acetylene</u>

The OH radical is generally thought to react with acetylene by abstracting a hydrogen atom.

$$OH + HC \equiv CH \rightarrow HC \equiv C \cdot + H_2O$$

The acetyl radical thus formed may react in air as follows (Stevenson and Tipper, 1967)



The overall result of the indicated reaction sequence, then, is a chain transfer, with HO₂ replacing OH as the active species. Semi-quantitative measurements of the OH-acetylene reaction reported in Johnston et al. (1970) indicate that at ambient temperatures the reaction is quite slow, being about as fast as the OH-ethane reaction. We recommend that a quantitative value of OH-acetylene rate constant be obtained. If, indeed, it is a slow reaction, then the photochemical oxidation of acetylene will not contribute appreciably to smog formation.

(3) 0₃ Oxidation Reactions

Ozone begins to form in significant amounts when the NO_2 concentration reaches a level about twenty-five times that of

the NO concentration. Ozone is not nearly as strong an oxidizing agent as O or OH. However, concentrations of ozone of about .25 ppm or greater are not uncommon in polluted atmospheres; at these concentrations ozone and olefins will react at appreciable rates.

(a) Reactions with Paraffins and Aromatics

Ozone does not react at a significant rate with either paraffins or aromatics. Several paraffin-ozone rate constants have been determined, and these have been summarized by Peters and Wingard (1970).

(b) Reactions with Olefins

The reactions of ozone with olefins in the gas phase have been studied extensively during the past two decades, and rate constants for the ozonolysis reaction are available for a large number of olefins (see Johnston et al., 1970). However, the mechanism of the olefin-ozone reaction in the gas phase has not yet been established, and the initial decomposition products have not yet been conclusively identified. Although the exact mechanism is still unresolved, ozone is thought to add to the olefin double bond in the liquid phase to form a molozonide intermediate, the molozonide then decomposing into an aldehyde and a diradical (or "zwitterion").

$$C_{3}H_{6} + O_{3} \rightarrow CH_{3}CH - CH_{2} \rightarrow HCHO + CH_{3}CH - CH_{2} \rightarrow HCHO + CH_{3}CH - CH_{2} \rightarrow HCHO + CH_{3}CH - CH_{3}CHO + H_{2}COO + CH_{3}CHO + CH_{3}CH$$

Ozonolysis in the gas phase may proceed by this same mechanism or by allylic oxidation, which would lead to the same decomposition products.

We recommend that the mechanism of the reaction in the gas phase be firmly established. In particular, it will be important to identify the transient intermediates such as diradicals, and to establish subsequent reactions of these species in polluted air.

(c) <u>Reactions with Acetylenes</u>

Rate constants for reactions of ozone with acetylene and higher alkynes have been determined by DeMore (1971). The low values for the rate constants indicate that these reactions have little, if any, influence on the smog formation process. (Typically the rate constants for ozonolysis of acetylenes are about 10^{-4} ppm⁻¹min⁻¹.)

(4) Singlet Oxygen

There have been numerous recent publications concerning the possible role of singlet molecular oxygen in smog formation. (For a review see Pitts et al., 1969 and Johnston et al., 1970.) Singlet oxygen can be produced in the air by such processes as the photolysis of ozone, the oxidation of NO by ozone, and energy transfer through collision with excited molecules. The concentration of singlet oxygen has not been determined in the atmosphere, but Frankiewicz and Berry (1972) have estimated that it is only about two orders of magnitude greater than that of 0. In view of those low concentrations and the low rate constants for ${}^{1}O_{2}$ -olefin reactions summarized by Herron and Huie (1970) we may assume that singlet oxygen is probably not a major hydrocarbon oxidant.

b. The Mechanisms of Oxidation of Oxygenated Hydrocarbons

Seizinger and Dimitriades (1972) have shown that aldehydes and ketones are present in the exhaust of automobile engines fueled by simple hydrocarbons. As indicated earlier, oxygenates constitute only about 1.5% of the hydrocarbons found in auto exhaust. Thus, the most important source of atmospheric oxygenates may be the oxidation of hydrocarbons and the decomposition of free radicals. Of the oxygenates produced in this manner, aldehydes seem to form more readily than ketones, for ketones are produced only when reaction occurs at a carbon atom bonded to at least two other carbon atoms in the molecule being oxidized, e.g.,



Leighton (1961) has supported this view, concluding that the atmospheric processes that result in the formation of aldehydes apparently do not generate ketones in comparable amounts. In this section, therefore, we focus our attention on the reactions of aldehydes.

Aldehydes will photodissociate in sunlight and react with O atoms, forming alkyl radicals (and, thus, peroxyalkyl radicals), formyl radicals (and, thus hydroperoxy radicals), and hydroxyl radicals. Therefore, the reactions of aldehydes can contribute significantly to the initial accumulation of RO_2 , HO_2 , and OH.

(1) Photolysis

Aldehydes photodissociate in sunlight at wavelengths greater than 3000\AA in chain initiating reactions.

RCHO + $hv \rightarrow R \cdot + \cdot CHO$

Leighton (1961) has estimated that the rate of this photolysis reaction is about one-hundredth the rate of NO₂ photodissociation. In the case of formaldehyde, a second primary photodissociation is possible (Calvert et al., 1972).

HCHO +
$$hv \rightarrow H_2$$
 + CO

This reaction pathway, which does not directly result in the formation of free radicals, has a probability of occurrence about equal to that for the chain initiating reaction.

(2) O Atom Oxidation Reactions

The typical rate constant for the O-aldehyde reactions falls between those of the O-olefin and O-paraffin reactions. The reaction is one of chain branching

 $\begin{array}{c} 0 + \text{RCHO} \rightarrow \text{RC} \bullet + \text{HO} \bullet \\ & & \\ 0 \\ \end{array}$

resulting in the formation of an acyl radical.

(3) OH Oxidation Reactions

Hydroxyl radicals abstract a hydrogen atom from aldehydes forming an acyl radical and water.

$$OH + RCHO \rightarrow RC \bullet + H_2O$$

The chain transfer reaction takes place about as rapidly as the reaction of OH with propylene. The rate constants for the reaction of OH with formaldehyde and acetaldehyde have been determined by Morris and Niki (1971). They are both about 22,000 ppm⁻¹min⁻¹ as compared with 25,000 ppm⁻¹min⁻¹ for the propylene-OH reactions. Thus, the reactions of OH radicals with aldehydes may serve as an important mechanism for removal of aldehydes from the atmosphere.

(4) 0_3 Oxidation Reactions

The kinetics of the ozone-aldehyde reactions apparently have not been studied in detail. Leighton (1961) has estimated that the reaction is probably slower than the ozone-olefin reaction by about two orders of magnitude. As a result, this reaction probably does not contribute significantly to the overall smog formation process. However, organic acids, constituents of atmospheric aerosols, might form as a result of the ozonolysis of aldehydes. Consequently, it would be worthwhile to determine the rate constant, mechanism, and products of the ozonolysis reaction for several different aldehydes.

c. Free Radical Reactions

The reaction between a single hydrocarbon species and a particular oxidant (say, 0, 0H, or ozone) often yields more than one set of products. For instance, in the case of the OH-propylene reaction, OH can add to either side of the double bond.

$$CH_3CH=CH_2 + OH \rightarrow CH_3CHCH_2OH \text{ or } CH_3CHCH_2$$

Adding to the difficulty of identifying or specifying the products of initial reaction steps involving free radicals is the fact that the fate of the radicals in subsequent reactions is often unknown. For example, it has not yet been determined if the products of the propylene-OH reaction are stable entities or if they decompose rapidly as a result of the excess heat supplied by the formation reaction. Because of uncertainties such as this, it is extremely difficult to estimate the overall chain length and number of NO molecules oxidized per OH-propylene reaction. Difficulties in specifying products and estimating chain lengths are, of course, enhanced as the complexity and size of the hydrocarbon species involved in the reaction increases.

In considering the reactions of highly substituted molecules, the number of NO molecules oxidized per hydrocarbon molecule consumed will depend strongly upon the degree of fragmentation (i.e., the degree of branching) taking place, as well as upon the rate of the initial hydrocarbon oxidation reaction. In particular, high molecular weight hydrocarbons are often considerably more reactive with respect to NO oxidation than are smaller, straight-chain hydrocarbons. For a classification of NO oxidation rates by hydrocarbon type the reader is referred to the summary in Johnston et al. (1970).

As noted in Chapter I, the oxidation of the various classes of hydrocarbons by 0, 0H, and ozone results in the formation of several different types of free radical products. Some of these radicals, notably alkyl and acyl, are extremely reactive, combining immediately with molecular oxygen to form peroxyradicals.^{*} In this discussion we give

^{*} If the alkyl radical is a product of highly exothermic reaction, it is possible that the 0_2 might abstract a hydrogen at a position alpha to the free radical, forming an olefin rather than adding at the site, e.g.,

 $\begin{array}{rl} \mbox{CH}_3\mbox{CH}_2\mbox{CH}_3\mbox{H}_2 & \rightarrow \mbox{CH}_3\mbox{CH}_2\mbox{CH}=\mbox{CH}_2\mbox{H}_2\mbox{H}_2\mbox{OH}_2\m$

This reaction is observed in high temperature flames (i.e., 425° C) (Benson, 1968). At ambient temperatures, however, probably no more than 1% of the R-O₂ reactions proceed in this manner, the remaining 99% resulting in the formation of the conventional peroxyalkyl radicals. Even so, this type of reaction may be a source of olefins in the oxidation of paraffinic systems and, as a consequence, merits further experimental investigation.

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our attention only to the more slowly reacting radicals,

R02	alkylperoxy
RCO3	acylperoxy
RO	alkoxy

those that substantively influence the photochemical reaction process. We note that the HO_2 radical, closely related to RO_2 , has been discussed earlier, in the section dealing with inorganic reactions.

Peroxyradicals enter into reactions of interest with three species: NO, NO₂, and ROO. Unfortunately, the rate constants for each class of reactions is presently unknown. The primary mechanism by which NO is thought to be oxidized to NO_2 without the consumption of ozone is through reaction with peroxy radicals.

 $RO_2 + NO \rightarrow NO_2 + RO$

The rate of this type of reaction probably decreases as the size of the R group increases, because large R groups have a greater number of vibrational degrees of freedom over which to distribute the energy of the free radical. Demerjian et al. (1973) have estimated that the rate constants for the $CH_3O_2 \cdot NO$ and $CH_3CO_2 \cdot NO$ reactions are 910 and 470 ppm⁻¹min⁻¹ respectively. Spicer et^Oal. (1971), however, have found the $CH_3O_2 \cdot NO$ reaction to be quite slow. As the time to the NO_2 peak predicted by kinetic mechanisms currently in use is quite sensitive to the magnitude of this rate constant, it is of interest to establish its Value for the reaction of NO with each of several different peroxy radicals.

As NO is oxidized and NO₂ accumulates during smog formation, the reaction of peroxy radicals with NO₂ becomes increasingly important. If the peroxy radical is an acyl peroxy radical, stable products, peroxyacylnitrates (PAN), will form

$$\begin{array}{c} \text{RCOO} + \text{NO}_2 \rightarrow \text{RCOONO}_2\\ 0 & 0 \end{array}$$

Formylperoxynitrates, however, are thought to be extremely unstable, if, indeed, they do form at all; they have never been observed in smog chamber studies. Similarly, alkylperoxynitrates and arylperoxynitrates have yet to be observed in smog chambers, and it is not known whether or not these species are stable. Rather, the reaction of peroxyalkyl radicals with NO₂ might go through a peroxynitrate transition state, resulting in the formation of NO₃.

 $ROO + NO_2 \rightarrow [ROONO_2] \rightarrow RO + NO_3$

This reaction is endothermic, however, and is thus of low probability. Given these gaps in knowledge, it is clearly of interest to determine the mechanism of the RO_2 - NO_2 reactions and to estimate the associated rate constants. This information will be particularly useful in the validation of kinetic mechanisms, as the magnitudes of the reaction parameters strongly affect the predicted asymptotic level of ozone, the height of the NO_2 peak, and the rate of decay of NO_2 after the peak.

The population of peroxy radicals in the smog system is limited by radical-radical recombination reactions. These reactions may be direct recombinations to form a peroxide and 0₂

$$RO_2 + RO_2 \rightarrow ROOR + O_2$$

or disproportionations to form an aldehyde (or ketone), an alcohol, and 0_2 .

$$RO_2 + RO_2 \rightarrow R'CH + R'CH_2OH + O_2$$

Because the rate of radical-radical recombination influences the radical population and the time scale of NO oxidation, the rate constants for this class of reactions must also be determined.

It had been thought that, because of the high rates of the OHolefin reaction, peroxyradicals might also react rapidly with hydrocarbons. However, Hendry (1973) recently studied the reaction of HO_2 with olefins and of CH_3O_2 with tetramethylethylene and butadiene in the liquid phase and reached a different conclusion. He found that the rate constants for the reactions are quite small, on the order of 10^{-4} ppm⁻¹min⁻¹. It is likely that this reaction is also slow in the gas phase and can be ignored in accounting for the consumption of hydrocarbons.

Alkoxy radicals are formed as a product of the RO_2 -NO reaction and some RO_2 -NO₂ reactions

$$RO_2 + NO \rightarrow RO + NO_2$$

(Peroxyacyl radicals react with NO to form acylate radicals and NO₂; the acylate radical, however, is very unstable and loses CO₂, forming an aklyl radical.)

$$\begin{array}{c} \text{RC00} + \text{N0} \rightarrow \text{RC0} + \text{N0}_2 \\ 0 & 0 \\ \downarrow \rightarrow \text{R} + \text{C0}_2 \end{array}$$

Alkoxy radicals react predominantly with 0_2 to form an aldehyde and $H0_2$;

$$R0 + 0_2 \rightarrow RCH0 + H0_2$$

the rate constant for the pseudo-first order reaction has been determined by Heicklen (1968) to be about $4.4 \times 10^3 \text{ppm}^{-1}\text{min}^{-1}$, when R is CH₃ or C₂H₅. The only competing reactions might be those of RO with NO and NO₂ to form nitrites and nitrates,

$$RO + NO \rightarrow RONO$$

 $RO + NO_2 \rightarrow RONO_2$

However, the low concentrations of nitrites and nitrates observed in smog chamber product analyses suggest that these reactions are not sufficiently rapid to be important.

We recommend that an effort be made to establish the mechanism and determine the rate constants for the reactions of several organic peroxy radicals with NO, NO₂, and RO₂. Also of interest, but of lesser importance at this time, is the study of rate constants for the reactions of oxy radicals with O₂, NO, and NO₂, and the investigation of alternative mechanisms for the R·-O₂ reactions.

d. Summary

In this section we have examined the reactions of paraffins, olefins, aromatics, acetylenes, and aldehydes with the most important oxidants found in the atmosphere. We have also discussed the possible subsequent reactions of the free radical products of these oxidation reactions. During the course of the discussion we have identified a number of reactions that require investigation. In summarizing our findings, we recommend that the following studies merit immediate attention.

- (i) Branched aromatics constitute approximately 20% of the hydrocarbon mix in polluted atmospheres such as that of Los Angeles. Thus, the rate of reaction of branched aromatics with both 0 and 0H should be measured. The products of these oxidation reactions should also be determined.
- (ii) The rate of oxidation of NO predicted by kinetic mechanisms depends strongly upon the products assumed to form in the OH-olefin reactions. Thus, subsequent decomposition reactions of the OH-olefin adducts should be identified.
- (iii) Although the 0_3 -olefin reaction does not appear to consume a significant portion of the total olefin, the suggested intermediates of the reaction, so-called zwitterions, may be powerful oxidants. Thus, the mechanism and products of the 0_3 -olefin reaction require further study. It is also of interest to investigate the reactions of zwitterions with atmospheric pollutants.

- (iv) Peroxy radicals are thought to be important oxidizers of NO. It is believed that they also react with NO₂ to form stable products. The importance of these processes cannot be fully assessed, however, until the rate constants for these reactions have been determined.
- (v) The population of free radicals in photochemical smog may possibly be limited by the rates of radical-radical recombinations. Thus, the rates of these termination reactions should be measured.
- B. Investigation of Particle Growth Processes and the Effect of Particles on Smog Formation Kinetics

It has long been recognized that atmospheric photooxidation processes are frequently accompanied by aerosol* formation. Despite this early recognition, the available smog chamber data and the existing atmospheric data have been neither sufficient nor adequate to characterize fully either the physical or chemical mechanisms which govern photochemical aerosol formation in the atmosphere or the interaction of aerosols with the homogeneous gas-phase formation of photochemical smog. This deficiency in understanding is due to the experimental difficulties associated with (i) measuring the distributional properties of aerosols, and (ii) generating a representative aerosol distribution.

Suspended liquid droplets and solid particles

Ultimately, it will be useful to formulate a model for the combined gaseous and particulate components of an urban atmosphere. The success of such an endeavor depends upon our degree of understanding of aerosol

- (i) sources
- (ii) growth kinetics, and
- (iii) interactions with the gas phase constituents.

The first of these topics must necessarily be investigated primarily in the atmosphere and is beyond the scope of this discussion. The second and third topics, however, can be investigated meaningfully in the laboratory and will be discussed here.

1. Particle Formation and Growth

Aerosols can be classified into two distinct groupings--the larger, so-called "primary" aerosols which consist of particulates introduced into the atmosphere from sources (e.g., dust, smoke) and the smaller, sub-micron size, "secondary" aerosols which are produced in the atmosphere by condensation and chemical reaction. We consider the secondary aerosols here specifically because they are

- (i) responsible for the reduction in visibility associated with smog
- (ii) implicated in aggravating respiratory ailments, and
- (iii) products of photochemical smog.

Both chemical and physical mechanisms play important roles in aerosol formation and growth. Chemical reactions provide species Convertible from the gas to the particulate (liquid or solid) phase and may take place in the particles themselves. Physical processes such as nucleation, condensation, absorption, adsorption, and coagulation are primarily responsible for determining physical properties; i.e., number concentration, size distribution, optical properties, settling properties, etc. of the formed aerosols. Based on the results of the 1969 Pasadena Smog Experiment, Husar and Whitby (1973) have proposed the following mechanism for photochemical aerosol formation:

"The driving force for the gas-particle conversion is provided by a gaseous photochemical reaction or chain of reactions. The gaseous reaction(s) produces a supply of molecular species (or radicals) which, upon collision with each other, agglomerate and form molecular clusters; i.e., homogeneously nucleate. If suitable aerosol particles or ions are present, the monomers or radicals deposit preferentially on the existing surfaces and thus the nucleation is heterogeneous. The growth rate of the newly formed particles is controlled by the diffusion rate, i.e., the collision rate of the condensable species. The condensation^{*} itself may be physical (governed by supersaturation) or chemical (if the condensable species react with each other upon collision). If the concentration of the droplets is sufficiently high, they may interact by coagulation."

In an initially particle-free chamber, Husar and Whitby found that the chronological evolution of a photochemical aerosol may be characterized by:

In this context, the term "condensation" is used to designate a diffusion controlled growth process, regardless of the nature of the accommodation process; i.e., physical or chemical.

- (i) Initial rapid increase in total number concentration by nucleation.
- (ii) Coagulation when the aerosol concentration reaches a sufficiently high level (maximum concentration when production rate equals coagulation rate).
- (iii) The attainment of a steady-state surface area sufficient to accommodate all the vapor (the nucleation rate then diminishes). Decay of number concentration by coagulation. Gas-particle conversion rate associated with the steady-state surface areas.

Although particle-free systems have been the subject of most smog chamber studies, it is well-recognized that the study of the growth of atmospheric aerosols must include consideration of the presence of foreign nuclei and therefore of heterogeneous nucleation. Heterogeneous nucleation is extremely complex, depending on the size distribution and surface properties of the foreign nuclei, as well as on the concentration and chemical composition of the vapor. There is considerable evidence that in Los Angeles the mode of nucleation of photochemical aerosols is primarily heterogeneous. Thus, the total nuclei count is governed by ground sources and not by self-nucleation (Husar and Whitby, 1973).

In order to investigate the physical and chemical behavior constituents of photochemical smog in the formation and growth mechanisms of aerosols, we recommend that the following studies be undertaken:

- (i) A complete chemical identification of the individual constituents of secondary aerosols should be made. Combined gas chromatography-mass spectrometry systems offer promise in this regard. Organic species represent a significant portion of the atmospheric photochemical aerosol on a weight basis (Friedlander, 1973). Only after the relative abundance of individual species (e.g., organic acids and diacids, aldehydes, paraffins, polynuclear aromatics, organic and inorganic nitrates, sulfates, H₂O, etc.) in the aerosol is assessed will it be possible to postulate a chemical mechanism for the growth of particles. With such information, however, it will also be possible to assess the importance of aerosols as a sink for gas-phase pollutants.
- (ii) The threshold levels of specific hydrocarbons and SO₂ should be established for a polluted atmosphere in which aerosol is formed. Hydrocarbons selected for investigation should be those which participate in reactions leading to the formation of oxidation products observed in the atmospheric aerosol (Task i). For instance, if adipic acid (C₆ diacid) were observed during the first task, it would be necessary to determine threshold levels of cyclohexene and 1,7octadiene necessary for the formation of aerosol. Further, threshold levels of hydrocarbon mixtures must be established. In so doing, it will be possible to judge the importance of preferentially controlling the emissions of individual

hydrocarbons in an effort to meet a given visibility standard.

- (iii) The rate of chemical oxidation of SO_2 and NO_2 at the surfaces of aerosols should be determined. Although sulfates in particles can result from the photochemical oxidation of SO_2 in the gas phase, followed by condensation, it is also possible that (1) SO_2 is oxidized in liquid droplets through reaction with O_3 or metal ions, or (2) SO_2 is catalytically oxidized on the surfaces of solid particles. Similarly, nitrate formation results from the reaction of NO_2 with NaCl, a pathway for nitrate production additional to that provided by the gas phase NO_3 reaction.
- (iv) The effects of changes in factors such as temperature, humidity, stirring intensity, and turbulence level, all of which are known to affect the growth rates and size distributions of particles, must be quantitatively assessed.

2. The Effect of Particles on Smog Formation Kinetics

We have thus far examined the ways in which photochemical smog can contribute to aerosol formation and growth. Because of the high surface area that aerosols present to the gas phase, it is also possible that their presence affects the rate of formation of smog. Before meaningful studies can be carried out, however, we must be able to reconstruct experimentally the measured atmospheric spectrum of aerosol Properties, notably with respect to size and chemical composition. If this effort is successful, it will then be possible to determine if the kinetics of the overall formation process of smog is affected by the presence of particles. For example, particles may quench free radical chains or adsorb free radical initiators such as NO₂ or HNO₂, thereby slowing the oxidation of NO, or they may oxidize NO at the surfaces if they are catalytically active or if they contain strong oxidants, thereby accelerating smog formation. If aerosols are shown to affect the rate of smog formation, it would then be useful to alter the characteristics of the simulated aerosol in the chamber to investigate the effects of changes in (i) chemical composition and (ii) number and size distribution on the resultant smog kinetics. Only upon completion of such studies can validation of kinetic mechanisms be meaningfully undertaken using data collected in smog chambers in which particles were present initially. III. CONTROLLED EXPERIMENTAL STUDIES IN SMOG CHAMBERS

The formation of photochemical smog occurs in an extremely complicated system, one in which meteorology, continuous emissions of pollutants, and photochemistry all play important roles. In order to isolate the effects of photochemistry from other variables present in an atmospheric environment, investigators have simulated the chemical reaction process by irradiating the primary pollutants in static reactors, so-called smog chambers, some of the results of which are described briefly in this chapter. The observed results must be interpreted with great care, however, for even in a smog chamber factors other than the photochemistry can still influence the course of the overall smog formation process. We therefore devote much of this chapter to procedural considerations such as wall effects, radiation simulation, analytical procedures, and reproducibility of experiments. In short, we point out the necessity of completely characterizing the smog chamber before experimental studies are conducted. Finally, we discuss ways in which an operating system can be used to generate data for the validation of kinetic mechanisms, to demonstrate interactions between specific pollutants and typical urban air pollution samples, and to investigate scavenging processes that occur in the natural environment.

A. Chamber Effects

A very important question to examine at the outset of experimental smog chamber studies is how and to what degree the design, construction,

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and operation of the chamber affect the observed results. Similar smog chamber experiments performed in different chambers, but with the same hydrocarbons, have not all exhibited the same concentration-time behavior. Because initial concentrations are similar, it appears that effects characteristic of the chambers themselves are influencing the courses of the experiments. Possible explanations for the disparate behavior include differing degrees of mixedness, surface effects, and irradiation intensity between chambers. Indeed, experiments performed in a single chamber are not always reproducible in the same chamber a month later (Westberg, 1972). The problem of non-reproducibility is quite possibly serious enough to render much of the existing smog chamber data unsuitable for the purposes of model validation. If smog chamber experiments are to be used as a tool for broadening our understanding of smog formation, individual chamber effects must be minimized or eliminated. At the very least they must be understood quantitatively. In this section, therefore, we undertake to point out what we consider to be the most critical of chamber effects. So that the examination of chamber effects can be comprehended in the perspective of current experimental methods, however, we begin our discussion by surveying the various types of smog chambers in common use.

Smog chambers can be classified into three general categories. The earliest and most popular were the large environmental chambers having volumes from fifty to five hundred cubic feet. The large volume is appealing because of the "wall-less" nature of the atmosphere being simulated. Due to their size, these chambers have traditionally been constructed of the most convenient materials, e.g., plate glass, aluminum, or Teflon-lined materials. Although the size has as an

advantage reduced surface to volume ratios, there are several inherent shortcomings in this type of chamber:

- (i) Due to the large surface areas involved, cleaning of surfaces can be a long and tedious task, one which is often neglected.
- (ii) Direct measurement of light intensity in these chambers by the conventional procedure (see Section IIIA3) requires that all of the 0_2 in the chamber be displaced by an inert gas such as nitrogen. This is both difficult and expensive. (Alternately, k_1 , the photolysis rate of NO_2 , can be determined in a smaller bag inside the chamber, but this procedure requires proper and accurate compensation for the absorption of light by the bag.)
- (iii) Unless the chamber is carefully designed and stirred, a significant percentage of the chamber contents may not be well mixed.
- (iv) A large bank of analytical instruments must be available to monitor the chemistry, and each of these instruments must be recalibrated regularly to insure its accuracy. (A notable exception to the former problem is use of long path infrared systems (to be discussed shortly), in that the single spectrometer is capable of monitoring all of the major contaminants.)

A second type of smog chamber is simply a plastic or Teflon bag. Because of their reduced volume, bags are convenient to work with and have the advantage of allowing easier measurement of the light intensity. Bags, however, suffer the disadvantages cited above, as well as having

- (i) a high surface to volume ratio,
- (ii) no facilities for mechanical stirring, and
- (iii) pollutant adsorption on, or reaction with, the surface material.

The third popular type of smog chamber is the long path infrared spectrometer (LPIR) with a small (\sim 100 liters) reactor enclosing the optics. LPIR's have as an advantage the fact that all the pollutants are monitored using a single instrument, the spectrometer, so that only the optics require adjustment to assure accurate monitoring. The reactors, however, have less favorable surface to volume ratios than do environmental chambers, and they are very difficult to clean by wet methods. Removal of the reactor for cleaning is a delicate and time consuming task, and care must be taken not to misalign the optics. Finally, mechanical stirring devices cannot be introduced into such a system.

In the past considerable effort has been expended in simply identifying the precursors of atmospheric reaction products and in obtaining general information about the importance of such factors as the influence of hydrocarbon to NO_x ratios on the level of oxidant formed. Each of the three systems described above can be used in performing this task. However, the general aspects of smog formation are now understood reasonably well. Thus, future scientific inquiry must necessarily be conducted in a detailed, quantitative manner, if it is to be justified. This means that, beyond monitoring the concentrationtime behavior accurately in new smog chamber runs, the effect of each operating parameter of the system on the overall smog process must be carefully assessed. Until this is the case, it will not be possible to establish a correspondence between smog chamber experiments carried out under identical initial conditions, but performed in different chambers. In short, it will not be possible to distinguish between the two categories of factors contributing to the observed (apparent) photochemistry:

- (i) those associated with the gas phase chemistry (Chapter II) and
- (ii) those associated with the interactions of the operating chamber with the chemistry.

It is for this reason that we begin our discussion of controlled experimental studies in smog chambers by considering effects associated with the experimental system which can alter the course of the reaction and thus reduce accuracy and quality of the reported data.

In our estimation, those factors causing similar smog simulation experiments to differ from chamber to chamber (and, for that matter, from chamber to atmosphere) fall into three broad classes:

- (i) degree of stirring and mixedness in the chamber,
 - (ii) surface effects, and
- (iii) radiation simulation.

The first of these, the effect of gas-phase heterogeneities on the rate of the overall photochemical reactions, has been alluded to in the context of atmospheric turbulence in Chapter I. It is a problem that, once recognized, can be solved in controlled experimental studies by careful chamber design. The key point is that the experimenter must insure that the contents of his chamber are well mixed so that the chamber is in practice an ideally-mixed vessel. Only then can the concentration changes be represented by the usual ordinary differential reaction rate equations.

The complete elimination of surface effects is probably an impossible goal. Rather, we must be satisfied with controlling and, at the very least, understanding the influence of the surfaces on the photochemistry. The extent of surface-gas phase interactions can be determined by measuring the rates at which known concentrations of pollutants adsorb or decompose on the walls, and those values should complement the gas phase material balance to account for the entire initial reactant charge (less that lost by sampling and dilution).

The problems associated with radiation simulation are two-fold:

- (i) the achievement of a uniform light intensity distribution throughout the chamber and
- (ii) the careful measurement of light intensity.

Solution to the former problem can be achieved by careful placement of the lamps. Light intensity measurement techniques are presently available; however, they are cumbersome, particularly those which require the complete displacement of 0_2 from the reactor. Convenient methods must be developed to encourage the routine monitoring of light intensity. These three factors, then, represent the most serious influences of smog chambers on the homogeneous gas phase chemistry. Given a quanititative assessment of each of these operating parameters, however, it will become possible to extract meaningful kinetic data from smog chamber experiments.

1. Stirring and Mixedness in the Chamber

Although smog chambers are often thought of as atmospheric or environmental simulation chambers, one of their primary functions is to permit the study of the macroscopic smog kinetics in an uncomplicated and controlled system. Variables that the experimenter may wish to control are the concentrations of the reactants, the temperature and humidity of the chamber, and the radiation intensity. Another variable of interest, one that is more difficult to define precisely, is the degree of mixing in the chamber. We have noted in Chapter I that heterogeneities in the reactant-gas mixture will lead to the observation of "apparent" kinetics, that is, reaction rates that differ from those occurring in a well-mixed, homogeneous system. Certainly, the atmosphere is not a homogeneous reactor; however, if smog chambers are to be used as a tool for studying chemistry solely, they must, ideally, be well mixed. The achievement of a homogeneous system is primarily a matter of careful design.

The flow patterns observed in a smog chamber depend critically on two factors, the geometry of the chamber and the stirring apparatus employed. In some conventional smog chambers equipped with mixing devices, it has been estimated that a poorly mixed region characterized by laminar (versus turbulent) flow develops at the walls or boundary of the chambers and can encompass upwards of 25% of the total volume of the chamber (Liu, 1973). The judicious placement of mechanical stirrers can reduce that problem substantially.

2. Surface Effects

Ideally, the presence of surfaces in the reactor should not affect the results of a smog chamber experiment. In practice, however, there is little reason to believe that is the case. Carbon and nitrogen material balances for the gas phase materials over the course of an irradiation have often been poor. For example, Altshuller et al. (1970) reported that they were able to account for only 3% of the initial carbon and 10-20% of the initial nitrogen after a 6 hour irradiation of toluene in NO_v. Part of the difficulty may be explained by the failure of many investigators to measure all of the products of the photochemical reactions. In the irradiation of ethylene-NO, mixtures, CO and CO₂ are important carbon-containing products which are not always monitored (Gay and Bufalini, 1971). The irradiation of aromatic-NO, mixtures results in the formation of acetylene as a major carbon-containing product; failure to measure that species probably accounts for the poor carbon balance reported by Altshuller et al. (1970) for toluene and m-xylene. Another reason for poor carbon balances is that free radicals and polar species such as aldehydes and organic acids are adsorbed on the walls. The relative contributions of these two effects in accounting for the initial carbon charge has yet to be assessed in quantitative terms."

^{*}Other possible reasons for poor material balances are (i) that strongly polar products such as organic acids may be lost to the sides of sampling tubes leading to the monitoring instrument and (ii) that the analytical instruments may be improperly calibrated.

The major reason for poor nitrogen balances is definitely attributable to surface effects^{*}. The work of Gay and Bufalini (1971) supports this hypothesis, in that they were able to obtain a consistent nitrogen balance when they included the nitrate and nitrite washed from the walls of their irradiation vessel. Their results suggest that the presence of surfaces may affect both the observed rates and the product distributions.

The necessity of achieving and maintaining a mass balance for carbon and nitrogen over the entire course of a photochemical smog experiment cannot be overemphasized. Without a mass balance there is no assurance that all the important products in the system are being detected. Nor can one be sure that the products have been measured accurately. Certainly, the problems associated with achieving a consistent material balance are great, but a 100% balance should be the goal.

While it seems unlikely that surface effects can ever be completely eliminated, it is possible to identify, quantify, and minimize the various types of surface-gas interactions. Topics to be discussed in this regard include studies of the rates at which various chamber surface materials adsorb constituents of smog, the effect of surface to volume ratios on the rate of wall adsorption, the cleaning and preparation of the surfaces, and the effects of wall temperature and the amount of water adsorbed on the walls on the rates of wall reactions.

It had been thought that molecular nitrogen might be a product of the ethylene-NO_x reactant system (Bufalini and Purcell, 1965), but Gay and Bufalini (1971) have since disproved this hypothesis.

a. <u>Surface Materials and Wall Adsorption Studies</u>

Recently, several groups have begun to explore the influence of various surface materials on the loss rate of pollutants in chambers. At Lockheed Missiles and Space Company, Jaffe (1972) is investigating the effect of four surface materials on the results observed in his chamber during hydrocarbon-NO $_{\rm x}$ irradiations. They include Pyrex, stainless steel, aluminum, and Teflon. In work recently completed, Sabersky et al. (1973) have determined the loss rate of ozone in a small chamber containing large sheets of several different materials. They found that the decomposition rate of ozone was the least for aluminum and plate glass, was 6 times greater for Lucite, 24 times greater for polyethylene, and almost 100 times greater for neoprene. In their experiments the temperature of the system was maintained at $72^{\circ}F \pm 1^{\circ}F$ and the relative humidity at 50% ±5%. Mixing was accomplished through the use of several large fans. These investigators are presently carrying out a similar set of experiments using nitric oxide.

Tentative results for the effects of Teflon on reaction dynamics are available from two sources. Holmes (1973) of the California Air Resources Board has postulated that ozone is absorbed by the Teflon surface of the ARB chamber during cleaning operations, at which time the walls are exposed to 20 to 40 ppm of ozone for 24 hours. His conjecture is based upon the fact that ozone continues to appear in his nitrogen-filled chamber for several days after the original ozone has been flushed from the system, the ozone presumably being re-emitted by

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the Teflon. It is important to investigate this phenomenon in some depth, since Teflon FEP bags are widely used as reactors, and the uptake of 0_3 by the bag could alter the course of the reaction. Also, several experimenters have reported the use of Teflon sampling tubes (Gay and Bufalini, 1971). Gay and Bufalini (1971), however, have found 93% of the initial nitrogen charge present (in the form of nitrogen-containing compounds) in the gas phase in a trans-2-butene-NO_X experiment carried out in a Teflon FEP reactor. They suspect that Teflon might have a lower adsorption rate for oxides of nitrogen than does glass, but this observation is based on a single run.

Clearly, an optimal surface material must be identified before further expensive smog chamber studies are carried out. The best material will be the one showing the lowest loss rate for each pollutant individually (i.e., NO, NO₂, O₃, various hydrocarbons, aldehydes) and collectively (i.e., under irradiated smog chamber conditions). Furthermore, it will be recessary to determine quantitatively the loss rate for each pollutant once a material has been selected.

b. Surface to Volume Ratios

The effect of surface to volume ratio on smog chamber experiments has been largely ignored in the past. In a recent study, however, Sabersky et al. (1973) found that the ozone decay rate in their chamber was directly related to the surface to volume (S/V) ratio. Certainly, increasing the S/V will in turn increase the probability of a given molecule striking the surfaces. Thus, other factors being equal (e.g., concentrations, wall conditions, mixing rate, etc.), a reduction in the ratio will lessen surface effects.

Ideally, the S/V ratio should be as close to zero as possible. Unfortunately, problems other than those associated with surface effects arise in using large chambers. Thus, we must set as a goal the understanding of the effects of S/V ratio on smog chamber experiments, so that we can correct or otherwise compensate for them (rather than eliminate them). In his current study, Jaffe (1972) plans to compare chamber results using two different S/V ratios for the same initial conditions. In principle, identical chamber runs should be performed at four or five S/V ratios. Also, baffling or other packing (e.g., turnings) of the same composition as the walls can be added to the chamber to evaluate the effect of increased surface area.

c. Cleaning and Preparation of the Surfaces

In order to obtain reproducible results from a chamber, the chamber surfaces must, among other things, be brought to a known initial condition. Several techniques have been used with varying degrees of success. The most common technique of cleaning a chamber between runs, especially a large environmental chamber, is simply to force filtered laboratory air through the chamber with lights on and fans running either overnight or until no more pollutants are detected by the monitoring equipment. Unfortunately, this technique does little to remove the adsorbed materials from the walls of the chamber.

A second technique is to evacuate the chamber using a vacuum system. This is an efficient way of removing the bulk gas, especially for small chambers. Removal of material from the walls would require

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several days of pumping unless the walls were heated to drive off the water and other species. Under these conditions, pumping would only require several hours. The cleaning efficiency of this technique, however, remains to be assessed.

A method used by some experimenters for cleaning the surfaces involves allowing high levels of ozone, for example, 20 to 40 ppm, to react with materials on the walls of the chamber for several hours. This procedure results in complete oxidation of all substances which will react readily with ozone, but it does not remove any of the oxidation products from the walls.

A technique reported by Gay and Bufalini (1971) for cleaning of the walls of a small (72 liter) boro-silicate glass reactor involves washing the surfaces before each irradiation with aqueous cleaning solution, acetone, and finally with distilled water (the latter, several times). This is the surest way of removing material from the surfaces, but it is a time-consuming, manual task that is unsuitable for larger environmental chambers. Whatever surface material is chosen for future chambers, it will be necessary to evaluate the various methods of cleaning the surfaces. At this time it appears that the three-stage washing technique of Gay and Bufalini is preferable to other suggested procedures.

Independent of the relative degree of success or failure of each of these cleansing techniques, there remains some question as to whether "the cleanest surface is the best". Sabersky et al. (1973) found that the decomposition rate constant of ozone on Lucite decreased by 50% over the first eight hours of the material's exposure and then continued to

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decrease slowly as the chamber "aged". The same general trend was observed for neoprene (70% decrease in the rate constant in the first 100 minutes of exposure). These results suggest that clean walls can be partially deactivated by intentionally exposing them to ozone. Surfaces of metal-walled chambers become deactivated as an oxide layer forms at the air-wall interface. If the oxide layer remains intact after cleansing, the cleansing procedure might well result in a stable and reproducible surface condition.

d. Effect of Adsorbed Water on Wall Reactions

Even in so-called dry systems it is reasonable to assume that an adsorbed layer of water will be found on the walls of the chamber. This would certainly be the case in experiments run under ambient conditions with 25-75% relative humidity. Although little attention has apparently been paid in the past to carefully controlling the relative humidity in smog chambers, there is reason to believe that the amount of water in a chamber markedly affects the rate of loss of pollutants to the surfaces.

In one set of experiments Cox and Penkett (1972) found that a three-fold increase in the relative humidity (from 30% to 86%) resulted in a 35-fold increase in the first order decomposition rate constant (from 0.00425 min^{-1} to 0.139 min^{-1}) of SO₂ on a gloss paint surface. In examining the decomposition of ozone on aluminum surfaces they found that increasing the relative humidity from 32% to 83% resulted in a three-fold increase in the first order loss constant, from 0.0038 to 0.0112 min⁻¹. They accounted for the degree of mixed-ness of the system in their calculations, but because of their

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experimental method, they were forced to add NO to the ozone system prior to the experiment to prevent aerosol formation from occurring. Since NO reacts rapidly with ozone and since experimental data collected are based upon a single determination, the 0_3 loss data should be scrutinized carefully. Nevertheless, the substantive effect of variations in relative humidity on the loss rate of SO₂ and 0_3 seems to be clearly established in this work. In related work Mueller et al. (1973) have found that the decomposition rate constant of ozone on aluminum is greatly influenced by the relative humidity. Sabersky et al. (1973), however, found the rate constant for ozone loss on Lucite to be little affected by humidity over a range of 15-90% RH. This effect is, as yet, unexplained, although it may be a function of surface material, the temperature of the surface, and, consequently, the amount of water on the surface.

The most direct way in which water can serve as a scavenging agent for the chamber pollutants is through the dissolution of the gases in the adsorbed water layer on the walls. In examining vegetation as a sink for atmospheric pollutants, Hill (1971) demonstrated a relationship between the absorption rate and the solubility in water of each pollutant he studied. In particular, SO_2 is very soluble in water (39.4 cc/cc H₂O at 20^OC), O_3 is slightly soluble (0.26 cc/cc H₂O), and NO (.05 cc/cc H₂O) and CO(.02 cc/cc H₂O) are much less soluble. The loss rate data for SO_2 and O_3 collected by Cox and Penkett (1972) confirm this general trend. Although Gay and Bufalini (1971) did not investigate the problem of NO₂ adsorption in detail, they found that when they irradiated 6 ppm of NO₂ for four hours in air about 10% of the initial NO_2 was adsorbed on the walls, hydrolyzing to equal amounts of nitrate and nitrite,

$$6NO_2 + 3H_2O \rightleftharpoons 3HNO_3 + 3HNO_2$$

 $3HNO_2 \ddagger HNO_3 + 2NO + H_2O$

We have not found chamber adsorption data for NO or CO.

One pollutant not included in the solubility table found in Hill (1971), but which forms in significant quantities after the NO_2 peak, is N_2O_5 , the acid anhydride of nitric acid.

This species hydrolyzes readily by the reaction

$$N_20_5 + H_20 \rightarrow 2HNO_3$$

Gay and Bufalini (1971) have suggested that this is the major source of nitrate on the walls. To test the hypothesis they performed two experiments. Knowing that N_2O_5 forms by the reactions:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

 $NO_3 + NO_2 \stackrel{>}{\neq} N_2O_5$

they first introduced 6 ppm of NO_2 and 1.6 ppm of O_3 into a 72 liter glass reactor and allowed them to react for four to six hours. Gas phase analysis did not indicate the formation of nitrate, but washing the walls with a basic solution yielded 3.1 ppm of nitrate and 0.1 ppm of nitrite. (The stoichiometry of the above reactions suggests that a maximum of 3.2 ppm of nitrate would form if all the O_3 reacted with NO_2 .) In the second experiment they introduced vaporized nitric acid into their reactor. After three hours nearly all of the nitric acid was still confined to the gas phase. These experiments strongly suggest that N_2O_5 is adsorbed and hydrolyzed on the walls of the reactor rather than hydrolyzing in the gas phase and then diffusing to the surfaces as nitric acid.

The literature concerning the effect of water on the photo-oxidation rate of hydrocarbons has been reviewed recently by Altshuller and Bufalini (1971). Although various investigators have seen some increase in reactivity when water was added to an experimental system, Altshuller and Bufalini attributed these observations to changes in the reactivity of walls. Presumably, water can deactivate surface sites on a wall with the consequence that free radicals are longer lived. This hypothesis is worthy of further inquiry.

In the future, investigators should attempt to estimate the amount of water on the surfaces of smog chambers. One should expect that the quantity of water will depend both upon the relative humidity in the system and the temperature of the walls. Wall uptake studies should also be performed for individual gaseous pollutants to assess the rate of loss of these species to the walls under various typical experimental conditions. It now appears that N_2O_5 and SO_2 are strongly affected by the amount of water on the walls, O_3 and NO_2 are affected to a moderate degree, and based solely on solubility data NO and CO may be affected the least. Data for the interaction of aldehydes and the various classes of hydrocarbons with water-covered surfaces remain to be determined. -189-

e. Effect of Temperature

In Chapter II we noted that several investigators have observed the rate of smog formation to accelerate when the operating temperature of a chamber is raised. We presented as one possible explanation the fact that the majority of reactions contributing to smog are thermal, and for the most part will proceed somewhat faster at higher temperatures. It is not presently known, however, if this effect is sufficient to explain completely the effect of changes in temperature on the rate of smog formation. Dimitriades (1967) has suggested that surface effects might change with the temperature of the walls. For example, water evaporates from the surfaces as their temperature increases, potentially exposing more reactive sites and decreasing the probability of pollutant loss by dissolution in the water layer and by heterogeneous hydrolysis. The effect of temperature on surface effects might be determined by repeating an identical smog chamber experiment at a constant air temperature but with heated and/or cooled walls. If no change in the rate of smog formation were observed, the effect of temperature could be attributed entirely to changes in the rates of the thermally-induced elementary reactions. Otherwise, surface effects must be determined as a function of temperature, so that proper compensation can be made when interpreting the data.

3. Radiation Simulation

The principal driving force in the smog reaction system is the photolysis of NO₂:

$$NO_{2} + hv \rightarrow NO + 0$$

Although there are other absorbing species present in the atmosphere (e.g., peroxides, aldehydes), these can, in general, be neglected as either they are found at low concentrations relative to NO_2 or their photolysis rates are low. As a result, the rate of photolysis of NO_2 , k_1 , can serve as a useful measurement of the ultraviolet light intensity. Because of the importance of this photo-initiation reaction to the overall smog kinetics^{*}, the measurement of the spectral distribution, spatial intensity distribution, and absolute intensity of the radiation are extremely important. If they are not determined with care, one can neither meaningfully compare experiments performed in different chambers, nor extract quantitative information from an individual experiment.

a. Artificial Irradiation

Tuesday (1961) has shown that the spectral distribution of fluorescent lamps centered at 3550Å is somewhat different than that of the ultraviolet spectrum of the sun. A question then arises as to whether these differences significantly affect the course of photochemical smog formation. Laity (1971) studied this problem by comparing product concentrations observed after irradiation of several synthetic smog mixtures by blacklight fluorescent lamps with concentrations observed when identical mixtures were irradiated using natural sunlight. (In this study it was not necessary for the output of the lamps to remain constant in intensity, for the results were compared

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An example of the sensitivity of predicted smog profiles to variations in k_1 has been presented in Section IDle.

with those obtained for irradiation by sunlight, which varied in intensity over the course of the experiment. In chamber kinetic studies, however, it is important that the intensity be constant, or at least well defined.) He found no significant discrepancies between comparable mixtures over the period of the irradiations, thereby justifying the use of blacklight fluorescent lighting in smog chamber studies.

While the output of lamps undergoes a natural deterioration with age, a process accelerated by operating the lamps at an overvoltage, a critical factor in stabilizing the UV output of the blacklight fluorescent lamps is that the operating temperature of the lamps be kept constant (Dimitriades, 1972). Holmes et al. (1973)^{*} report that a rise of 30⁰F in the temperature of the air surrounding the lamps results in a 40% decrease in the UV output. Because temperature increases of this magnitude are not uncommon in smog chambers, these results highlight the importance of placing the lamps outside the chamber where they can be maintained at a constant temperature by forced air cooling. Outside installation of the lamps, however, introduces the additional constraint that at least portions of the chamber walls be transparent to UV radiation, thereby restricting the choice of surface materials.

b. Distribution of Light Intensity

Since variations in light intensity at various locations within the chamber result in differing rates of NO_2 photolysis, hence of smog formation, it is vital that the radiation be uniform throughout the

A preprint of this paper can be found in Appendix B.

chamber. Often, lamps are located on one or two sides of cylindrical or box-shaped chambers. Because intensity is inversely proportional to the distance from long cylindrical lamps, such a configuration can lead to intensity gradients in the chamber. It should be noted that Niki (1973) has built a cylindrical chamber of glass with lamps placed in a geometric configuration about the reactor such that the maximum variation in intensity in the chamber is no more than 5-10%. Thus, the existence of intensity gradients in chambers need not be accepted as an inevitable consequence of a particular geometric configuration.

c. Measurement of Light Intensity

Although it would be desirable to determine the radiation within a chamber by measuring the intensity as a function of wavelength, such an approach requires equipment which is both complex and expensive. Thus, it has become customary in photochemical smog studies to calibrate UV sources by measuring a manifestation characteristic of the light source, namely, the photolysis rate of NO_2 . The rationale for this method is that the fundamental photochemical process in smog formation is the photolysis of NO_2

$$N0_2 + hv \rightarrow N0 + 0$$

and that the rate of this reaction determines, to a large extent, the rate of the overall process. The method, first suggested by Tuesday (1961), consists of photolyzing an initial charge of NO_2 in an inert atmosphere (e.g., N_2) and in some manner determining the first order rate constant for NO_2 decay, k_1 , from the NO_2 -time data.

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Originally, a pseudo first-order decay parameter, k_d , was taken as a measure of the light intensity. But because the decay of NO₂ in N₂ is not a first-order process, k_d reflects the combined result of a large number of reactions (see Table 1) rather than the result of just the single reaction 1. Therefore, k_d is not a fundamental rate constant of the system. When smog chamber data are used for the purpose of validating chemical mechanisms, k_1 , not k_d , must be specified.

Holmes et al. (1973) have shown that k_1 can be determined directly from the NO₂-time data obtained by irradiating NO₂ in dry, oxygen-free nitrogen. One simply notes the initial ([NO₂]₀) and final ([NO₂]) concentrations of NO₂ and the length of photolysis (Δ t) ; k_1 is then determined from the following equation:

$$k_{1} = \frac{1}{2\Delta t} \left\{ (1 + R_{1} - R_{2}) \ln \frac{[NO_{2}]_{o}}{[NO_{2}]} + R_{2} \left[\frac{[NO_{2}]_{o}}{[NO_{2}]} - 1 \right] \right\}$$
(1)
$$R_{1} = 0.27$$
$$R_{2} = 0.16$$

The validity of this equation was established both through experiments in a long path infrared spectrometer cell and through computer simulation of the "Ford-Endow" mechanism (Ford and Endow, 1957) for the reactions taking place in the NO_2-N_2 -light system (see Table 1). Since one can obtain k_1 directly via this procedure, we suggest that future investigators use k_1 rather than the pseudo-first order decay constant for NO_2 , k_d , to characterize UV intensity in photochemical TABLE 1. Reactions and Rate Constants for the Photolysis of Nitrogen Dioxide in $\rm N_2$ and $\rm O_2$

No.	Reaction
1.	$NO_2 + hv \rightarrow NO + O$
2.	$0 + 0_2 + M \rightarrow 0_3 + M$
3.	$0_3 + NO \rightarrow NO_2 + O_2$
4.	$0 \div NO_2 \Rightarrow NO \div O_2$
5.	$0 + NO_2 + M \rightarrow NO_3 + M$
6.	$NO_3 + NO \rightarrow 2 NO_2$
7.	$0. + NO + M \rightarrow NO_2 + M$
8.	$2 \text{ NO} + \text{O}_2 \rightarrow 2 \text{ NO}_2$
9.	$NO_3 + NO_2 \rightarrow N_2O_5$
10.	$N_2O_5 \rightarrow NO_3 + NO_2$
11.	$NO_2 + O_3 \rightarrow NO_3 + O_2$

Rate Constant

To be Estimated 2.33 x 10^{-5} ppm⁻² min⁻¹ 2.95 x 10^{1} ppm⁻¹ min⁻¹ 1.38 x 10^{4} ppm⁻¹ min⁻¹ 4.50 x 10^{-3} ppm⁻² min⁻¹ 1.48 x 10^{4} ppm⁻¹ min⁻¹ 2.34 x 10^{-3} ppm⁻² min⁻¹ 7.62 x 10^{-10} ppm⁻² min⁻¹ 4.43 x 10^{3} ppm⁻¹ min⁻¹ 1.38 x 10^{1} min⁻¹ 1.06 x 10^{-1} ppm⁻¹ min⁻¹

Reference

Johnston (1968) Johnston and Crosby (1954) Schuck et al. (1966) Schuck et al. (1966) Schott and Davidson (1958) Kaufman (1958) Glasson and Tuesday (1963) Schott and Davidson (1958) Mills and Johnston (1951) Johnston and Yost (1949) -194-

smog experiments. Further, the technique is simple enough to encourage frequent calibration of the lamps.

It is impractical or impossible to purge and fill large environmental chambers with a NO_2/N_2 mixture. Rather, one can formulate the NO_2/N_2 mixture in a semi-transparent Tedlar bag and irradiate it for a short period, determining both the initial and final NO_2 concentrations. Equation (1) can then be used to calculate k_1 , although a correction must be made for transmission by the Tedlar. Such a technique is used by California Air Resources Board investigators in establishing k_1 for experiments carried out in their 1100 ft³ chamber (Holmes et al., 1973).

Determination of the light intensity in an outdoor chamber is a more difficult problem, as it is impossible to control the intensity of the sunlight. (In his study Laity (1971) found that " k_d " outdoors varied between 0.15-0.30 min⁻¹ depending on the day and time.) Consequently, it is necessary to determine k_1 several times during the course of a run, and, particularly, to note any abrupt changes in the light intensity. In view of Laity's results showing that fluorescent lamps produce the same results as sunlight for comparable experiments and the fact that it is impossible to control the intensity of natural sunlight, there does not appear to be any advantage in performing outdoor smog chamber studies if kinetic information is being sought.

Because it is difficult to remove all the 0_2 from the system, as is required in determining k_1 by the procedure just described, it would be useful to develop a means for determining k_1 in air. We devote Appendix C to a discussion of a general method by which k_1 can, in principle, be determined directly and accurately from the NO₂ concentration-time data observed when an arbitrary mixture of NO₂ and NO (if any) is photolyzed in air. The essential feature of the method is that a computer estimation algorithm (presented in Appendix C), rather than a simple expression such as (1), is required to determine the value of k_1 .

4. Summary

While it would be desirable to develop and design an entirely new smog chamber after techniques have been developed for reducing chamber effects, consideration of such an approach must be tempered by an evaluation of costs and development time involved. Failing the development of a new chamber, it is necessary to establish quantitatively in an existing chamber:

- (i) the completeness of mixing,
- (ii) the interactions between the surfaces and the gas phase chemistry, and
- (iii) the uniformity and intensity of the artificial irradiation.

Furthermore, particular effort must be made to establish material balances during smog chamber irradiations. If smog chamber data are to be used for validating kinetic mechanisms, no variable associated with the smog chamber system that can potentially affect the outcome of the photochemical process should be ignored or overlooked. All such variations must be monitored and reported.

B. Analytical Procedures

The usefulness of reproducible smog chamber data ultimately depends to a large degree on the reliability and completeness of the chemical measurements. Five species, namely NO_2 , NO, O_3 , hydrocarbons, and aldehydes, are the most important reactants in smog and, with the exception of aldehydes, have generally been measured in chamber experiments. In this section we examine alternative analytical techniques that may be used in determining the concentrations of these five species. There are, however, many other species present in smog (such as peroxides and nitric acid) which one might wish to monitor, both to elucidate the mechanism of smog formation and to validate kinetic mechanisms. These species are discussed in Section IIIClc.

Analytical instruments fall into two classes. The first class includes instruments which may be used to make a direct measurement of some physical property of the species under observation. An example of such an instrument is the infrared spectrometer, which detects the amount of infrared radiation absorbed by specific pollutants. The second class of instruments, and by far the most common, is the chemicophysical. In this case the pollutant being measured first undergoes chemical transformation; the product of the reaction is then measured using an appropriate analytical technique. As an example, the classical "wet" chemical techniques are all chemicophysical. In these, a sample of the pollutant is collected for a period of time in a liquid absorber. The sample is then reacted with another reagent, resulting in a change in color or in the formation of another product. The

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intensity of the color or the concentration of the products are related to the concentration of the original pollutant. Many newer types of instrumentation, such as chemiluminescent devices (which are based on measuring the light emitted when the pollutant being monitored reacts with another reagent), are also chemicophysical.

A number of criteria may be specified for evaluating the appropriateness and utility of an analytical technique for a particular application. These include:

- (i) the accuracy, specificity, and ease of calibration of the instrument,
- (ii) the precision or reproducibility of the measurements,
- (iii) the volume of gas required to make a determination, and
- (iv) the response time of the instrument.

In the discussion that follows, we first examine these criteria individually. We then use them in evaluating the quality of measurements to be expected from analytical instruments which either have been employed extensively in the past, or have recently been developed, to measure NO_2 , NO, O_3 , hydrocarbons, and aldehydes.

1. Accuracy and Primary Standards

The accuracy of a method, that is, the extent to which the observed or measured value and the "true" value agree, depends on both the specificity of the technique and the accuracy of calibration. Lack of specificity, or the presence of interferences due to species other than the one desired, is the greatest shortcoming of all wet methods. For example, in the measurement of ozone by the potassium iodide (KI) method (see Section IIIB5c), peroxides, NO_2 , and peroxyacylnitrates, in addition to ozone, will all give a positive response, while SO_2 and dust give a negative response relative to the value observed without the interference. Thus, the accuracy of the indicated O_3 concentration is, at best, questionable when these other species are present.

The accuracy of calibration procedures depends upon the availability of primary standards. The well-established wet chemical techniques fare very well in this regard (Katz, 1968), while suitable primary standards are still being sought for many of the gas phase monitoring techniques. For instance, as yet, no primary standard for 0_3 has been developed, and ozone sources such as air ozonizers must be calibrated by potassium iodide titration or other techniques before each use as an ozone source. Nitric oxide and many hydrocarbons, on the other hand, can be obtained in prepurified gas cylinders and can thus serve as precision gas standards for those species.

Recently, O'Keefe and Ortman (1966) developed permeation tubes as calibration standards. They found that liquified gases, such as SO_2 , NO_2 , and hydrocarbons, sealed in Teflon tubing, would permeate through the walls of the tubing at a constant rate which is dependent upon the surface area of the tubing and the temperature of the surroundings. The success of this technique depends on the fact that the equilibrium vapor pressure of a liquid is a constant when temperature is held constant. Under these conditions, the permeation rate of the gas through the tube is constant, and the absolute amount of gas released by the tube over a period of time can be calculated from the change in weight

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of the tube. Permeation tubes have been used successfully for SO_2 , H_2S , many hydrocarbons, anhydrous NH₃, anhydrous HF, $COCl_2$ (phosgene), and organic mercury compounds (c.f., Saltzman et al., 1971). Unfortunately, it has been found that NO₂ permeation tubes are seriously affected by relative humidity and the past history of exposure (Saltzman et al., 1971). Thus permeation tubes for NO₂ are not suitable as a primary standard unless they have been recently calibrated.

The frequency of recalibration must be established for each instrument in the laboratory. Loss of calibration can occur as a result of aging and decomposition of chemical reagents or because of changes in ambient operating conditions (i.e., temperature, relative humidity, pressure). The need for recalibration will also depend on the sensitivity of the plumbing, the stability of the electronic components, and the conditions under which the instrument is used. Recalibration should be performed sufficiently often to assure the accuracy of the results. Any observed drift between calibrations should, of course, be noted. Finally, the calibration experiments should be performed over the full concentration ranges of the species observed during an experiment (e.g., for NO₂ concentrations vary from 0.005 ppm to 2 ppm).

2. Precision

Precision refers to the extent to which a given set of measurements agrees with the mean of the observations. Although the precision of each instrument must be determined individually, it has been found, in general, that both wet chemical techniques and instrument-based techniques such as chemiluminescence produce highly reproducible

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results (Maugh, 1972). It is, of course, important that the precision of the measurements be reported with the results. Care should be taken to establish the precision as a function of concentration. We have found that the predicted time to the NO_2 peak can be shifted by 15 minutes or more because of uncertainties of $\pm .02$ ppm in an initial NO_2 concentration of .04 ppm in photochemical simulation studies. Thus, it is particularly important to know precision bounds at low NO_2 concentrations if the predictions of kinetic mechanisms are to be correctly evaluated.

3. Sampling Procedures

The reliability of a measurement depends to a large degree on the technique used to sample the bulk gas. Presumably, a representative sample can be drawn from any location within a well-mixed reactor. The sampling tube material should be selected to minimize the heterogeneous loss of pollutants during sampling. Further, the residence time in the sampling line should be as short as possible to minimize the possibility of chemical reaction along the path. The overall accuracy of a measurement will depend upon careful calibration of the air flow rate into the monitoring equipment, for the signal output of the instrument must be corrected for the total volume of gas being determined. Calibrated low capacity rotameters can be used to measure low air sampling rates, while very high volumetric flow rates can be calibrated more accurately with such devices as Venturi meters or Pitot-static tubes.

One final consideration related to sampling is that it is desirable to minimize the total volume of air required for the

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analytical instruments so as to minimize the loss of reactants from the smog chamber. It is not uncommon for up to 25% of the initial reactants to be removed from a moderate sized chamber (10,000 liters) through sampling over a six hour irradiation. Such removal can be reduced substantially by using newer measurement techniques, such as chemiluminescence, which requires samples no larger than a few cubic centimeters. (Older wet methods often require that many liters of gas be bubbled through a concentrating solution before a reading can be made). In any case it is important to report the dilution rate in the experiments so that corrections for losses can be made.

4. Response Time

In smog chambers in which the concentrations of pollutants are changing continuously, knowledge of the response time of the measuring systems is necessary for interpreting the data relative to real time. Response time is the time from the moment the pollutant enters the sampling instrument to the moment that the measured value is obtained. The measured value, in turn, is taken to be a specified percentage of the final or true value, such as 90%. Thus, if it requires two minutes to achieve 90% of full response, two minutes is the response time. For systems in which the sample lag time is great Mage and Noghrey (1972) and Schnelle and Neely (1972) have shown that the transient and frequency response of the instruments can be accounted for by use of a transfer function.

Measurements carried out using instrumentation employed in chamber work are generally made either on a continuous, discrete, or

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averaged time basis. The first and most desirable type of measurement is continuous and is carried out using instruments with very fast response times, such as infrared spectrometers. A second class of measurements, discrete, includes those analyses in which a sample is injected into the instrument. Gas chromatographic analysis is an example of a discrete procedure. The sensitivity of discrete measuring instruments to short-term fluctuations and sharp peak concentrations will depend upon the rapidity with which determinations can be made. In the limit, as the time between measurements goes to zero, discrete measurements, of course, become the same as continuous measurements. Monitoring devices which require a pollutant to be collected over a finite period of time in order to obtain measurable concentrations yield integrated or averaged results. Most wet techniques operate on this principle. Such methods, of course, suffer from the obvious disadyantage that they are insensitive to short-term variations in concentration. Thus, wet chemical techniques, which require a tenminute or longer sampling time, will represent a sharp NO_2 peak as a lower and broadened peak because of their slow response times (and, thus, low time resolution).

5. Analytical Techniques Available for Measuring the Pollutants

Because of the wide variety of analytical instruments presently available for monitoring the constituents of smog, there is often uncertainty concerning which procedures are "best". Although recommended procedures are published regularly by the U.S. government in <u>The</u> Federal Register, review articles on current trends in instrumentation suggest that techniques now in use will soon be replaced by more rapid, more reliable, more efficient and certainly more expensive techniques (Maugh, 1972). A logical goal in upgrading analytical devices would be to develop a single instrument capable of measuring many or all of the pollutants simultaneously. Microwave spectrometers, which measure the rotational energy of polar molecules at discrete frequencies, appear promising in this regard, but commercial availability is at least two years away (Maugh, 1972). Because of the uncertainties concerning analytical procedures, it is worthwhile to examine briefly the techniques most often used to measure the standard pollutants (NO₂, NO, O₃, HC's, aldehydes) and to discuss the advantages and disadvantages of techniques now becoming available.

a. NO₂

Nitrogen dioxide has generally been determined by the Saltzman method (Saltzman, 1954). In this technique the sample is bubbled through an absorbing reagent at a rate of about 0.4 liter/minute for 10 minutes in order to concentrate the NO_2 . Reaction of NO_2 with the absorbing solution results in a color change which can be related to the NO_2 concentration. The technique is quite reproducible but suffers interferences from ozone and PAN (Leithe, 1970). The primary sources of error in this method are chemical interferences, inefficiency of collection, and the aging of reagents.

No substantial improvement over the Saltzman method has, as yet, been made for determining NO_2 . Hodgeson et al. (1972) have suggested reducing the NO_2 to NO using a gold catalyst and measuring the resulting NO by chemiluminescence (see Section IIIB5b). The problem with this approach is that the gold will reduce all the higher oxides of nitrogen (i.e., nitrates, PAN, nitrite, NO_2) to NO, so the technique lacks specificity. One promising approach for measuring NO_2 which is currently being developed involves exciting NO_2 to a higher energy state with a tunable dye laser. The NO_2 concentration can then be determined by measuring the fluorescence of the excited molecules (Nader, 1972).

b. <u>NO</u>

Until recently, there was no available technique for determining nitric oxide concentrations directly. The pollutant gas was passed over an oxidizing agent such as dichromate which oxidizes NO to NO_2 . Total oxides of nitrogen are then determined as NO_2 by the Saltzman method, and NO is calculated by subtracting the NO_2 reading made at the same time from total NO_x . In addition to all the difficulties involved with the Saltzman method, the technique depends on the efficiency of oxidation of NO. Efficiencies of only 70-85% are not uncommon, and thus measurements of NO made by this method are unreliable (Tokiwa and Mueller, 1971).

Recently Stedman et al. (1972) and Hodgeson et al. (1972) have shown that NO can be determined very accurately by chemiluminescence. In this technique the pollutant sample is exposed to a large excess of ozone. The ozone reacts rapidly with the NO to form NO₂ in an excited state.

$$NO + O_3 \rightarrow NO_2^* + O_2$$

Collapse of the excited NO₂ to the ground state is accompanied by the emission of light, which is then measured and related to the initial NO.

$$NO_2^* \rightarrow NO_2 + light$$

This technique is sensitive to 10^{-3} ppm of NO, has an overall response time of ten seconds, and requires a flow rate from the chamber of only 20 cc/minute. Interferences can be caused by collisional deactivation of the excited NO₂ (this problem is reduced by operating the system at low pressures) and by the reaction of other species present with O₃, the products of which may also chemiluminesce. Stedman et al. investigated the possibility of interferences from SO₂, NO₂, Cl₂, H₂O, CH₄, C₂H₂, C₂H₄, and C₃H₆ at a concentration of 100 ppm in air, but found that these species did not emit a detectable amount of light in the region of the NO^{*}₂ luminescence. An interesting feature of this instrument is that it can be used as an ozone detector as well by subjecting an air sample to an excess of NO. In view of its accuracy, response time, sensitivity, stability, and versatility, this instrument shows great promise for the future.

c. 03

Traditionally, ozone determination has been based on reaction of the species with potassium iodide (KI)

 $2KI + 0_3 + H_20 \rightarrow I_2 + 0_2 + 2KOH$

and measurement of the amount of iodine which is liberated by the reaction. Under well controlled laboratory conditions, this method can be quite accurate, and the technique remains as one important method for calibrating ozone sources. However, automatic monitors for ozone based on the KI reaction suffer from numerous difficulties. Several species, including NO_2 , peroxides, and PAN, give a positive response for O_3 in varying degrees, while the presence of SO_2 and reducing dusts result in a serious negative interference (Katz, 1968). Although some of the interfering species such as SO_2 can be removed by chemical scrubbing before the pollutant gases reach the ozone monitor and others can be corrected for mathematically (e.g., NO_2), the KI method must be regarded, at best, as a method for determining the total oxidant concentration in a smog chamber. An additional difficulty with the method is that the oxidant must be collected in a concentrating solution by bubbling gas from the chamber at the rate of 1-2 liters per minute for 15 minutes; full development of the color requires an additional 30-60 minutes. Thus, in summary, the KI method provides a non-specific, averaged oxidant concentration with poor response time.

Two techniques have recently been developed as commercial products for determining ozone. The first method is based on the chemiluminescence of the ozone-ethylene reaction (Warren and Babcock, 1970). An air sample containing ozone is exposed to a large excess of ethylene in a reaction vessel. The light released during the reaction is then measured using a photomultiplier tube and related to the ozone concentration.

Ozone can be determined by its chemiluminescent reaction with many species besides ethylene. We have already mentioned that the reaction of 0_3 with NO has been used successfully by Stedman et al. (1972). Recently, Kummer et al. (1971) have pointed out that ozone

will undergo chemiluminescent reactions with many olefins and sulfides including tetramethylethylene and dimethylsulfide, and that these reactions result in a much greater intensity of emitted light than does the ozone-ethylene reaction.

Chemiluminescent methods for ozone appear to be free of interferences from other species present in smog, and they are sensitive and fast. However, they suffer the disadvantage of having to be operated at very low pressures in the reaction vessel (0.5-5 Torr). Tanks of gaseous reagents must also be used in operating the equipment.

The second technique marketed recently measures the ultraviolet absorption of ozone in a sample of polluted air (Bowman and Horak, 1972). The air is divided into two portions in the instrument. One portion passes over a catalyst which converts the ozone to oxygen and becomes the reference gas, while the other portion is untreated. Ozone concentration is then calculated from the difference in UV absorption of the two samples. The referencing technique has the advantage of minimizing interference from moisture and other pollutants, since they are present in equal amounts in each sample, and the differencing method ideally produces a net signal of zero. Because the source of the UV light is a mercury vapor lamp, mercury contamination in the air can provide a serious interference. The mercury can be eliminated, however, with a gold surface absorber placed at the sample inlet. Another potential source of interference is the presence of any molecules which absorb ultraviolet radiation, such as SO₂ and aromatics. However, tests conducted at concentration levels of 0.2 ppm of SO2 and

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1.00 ppm of benzene showed no detectable response. The instrument is sensitive to 0.001 ppm, has an accuracy of $\pm 3\%$, precision of $\pm 1\%$, and has a response time of 30 seconds (90%). One negative feature of the instrument, when it is to be used for chamber studies, is that it requires a flow rate of 3 liters/minute; thus, it is not suitable for continuous monitoring in small chambers.

d. Hydrocarbons

Measurement of the concentrations of individual hydrocarbons cannot be made until the hydrocarbons are separated from the other pollutant gases and from each other. This is in contrast to the requirements placed on analytical procedures employed in the measurement of NO_2 , NO_3 , and O_3 , which involve the use of an unrefined sample of bulk gas. Gas chromatography has been applied very successfully for separating hydrocarbons. With appropriate choice of columns (see Altshuller, 1968) and a flame ionization detector, paraffins having carbon content of up to at least C_6 , olefins up to at least C_6 , aromatics in the C_6-C_{11} range, and acetylenes can be resolved and measured accurately. The principal drawbacks of GC analyses are the time required to separate a sample and the complexity and maintenance requirements of the measurement. Although discrete samples are analyzed, the cycling time is much too large to approximate continuous monitoring. Unfortunately, no significantly better techniques for measuring individual hydrocarbons than gas chromatography have yet

been suggested.

e. Aldehydes

No satisfactory method exists at this time for measuring individual aldehydes. Total aldehydes have been determined in chambers using both infrared spectrometry and wet chemical techniques. Wet chemical techniques based on the use of chromotropic acid or other reagents have been employed to measure formaldehyde, but these methods suffer from several types of interferences (e.g., olefins and aromatics) (Altshuller, 1968). Some progress has been made by Seizinger and Dimitriades (1972) in separating and identifying aldehydes by gas chromatography, but the technique is still cumbersome and time consuming. Again, we are not aware of any current improvements being made for the rapid measurement of individual aldehydes.

6. Summary

The shortcomings of analytical techniques based on wet chemical methods are very serious, notably a general lack of specificity and poor response time. Newer techniques, based upon chemiluminescence and determination of the spectral properties of various molecules, have

Total hydrocarbon analyses of samples from the bulk gas can be made directly using a flame ionization detector; total non-methane hydrocarbons can also be determined by difference if the methane is separated from the gas with an activated charcoal column and determined individually. Because of the complexity of the hydrocarbon mixture and the fact that all carbon-containing molecules give a response, these measurements contribute little to elucidating the state of the system.

already been shown to provide rapid, accurate, and continuous measurements of NO and O_3 at low concentrations. In the future these techniques should be used for monitoring smog chamber experiments. There is still a need, however, to develop rapid and accurate analyzers for NO₂, hydrocarbons, and aldehydes.

Even with the appearance of the newer instruments, the quality of the data will depend upon the extent to which the instrumentation is properly calibrated and maintained. The experimenter must recalibrate each instrument sufficiently often to guarantee the accuracy of the observed data; the degree of maintenance required will depend on the stability of the components of each instrument and the conditions of use.

Permeation tubes and standard precision gases can be used as primary standards for many gases, but a primary standard for ozone is still not available.

C. Recommended Smog Chamber Studies

Our discussion thus far has been limited to an examination of the operational aspects of a smog chamber. Once a system is operating reliably and reproducibly, it is possible to perform a large number of simple experiments useful in model verification and mechanism elucidation. In this section we discuss some chemical systems, including both artificial smog mixtures and polluted urban air samples that might be examined profitably, as well as ways in which smog chambers can be used to assess various atmospheric scavenging processes.

1. Simple Hydrocarbon-NO_x Systems

Although hundreds of individual hydrocarbons are present in polluted atmospheres, the majority of the reactive hydrocarbons can be classified as paraffins, olefins, and aromatics. Because each member of a class (e.g., paraffins) tends to react with a given oxidant in a manner and at a rate similar to that of other members of the class, it is possible to approximate crudely the atmospheric hydrocarbon mixture using a simple mixture of a single paraffin, olefin, and aromatic. By further implementing the principles of design in the choice of the initial reactant concentrations for a program of experiments and by measuring the concentration of some of the secondary products with time, it is possible to obtain data that should prove to be very valuable for validating chemical mechanisms.

a. <u>Hydrocarbons to be Studied</u>

As a prelude to atmospheric validation, it is desirable to demonstrate the validity of a chemical mechanism using smog chamber data based on the reactions of relatively simple hydrocarbon mixtures. Such mixtures, if properly formulated, will simulate actual atmospheric mixtures in terms of the range in reactivity of the individual components and the composition by hydrocarbon grouping. For example, an appropriately chosen mixture of n-butane, propylene, and toluene, which are assumed to typify paraffins, olefins, and aromatics, respectively, may well be a suitable surrogate. Note that each individual species

> (i) constitutes a significant percentage of its class of compounds in polluted atmospheres,

- (ii) reacts with 0, OH, and 0_3 at rates typical of its respective class, and
- (iii) has been thoroughly studied, both with respect to its elementary reactions with oxidants^{*} of interest and in the more complex reaction environment of the smog chamber.

Any chemical mechanism valid for atmospheric reaction systems must certainly be capable of describing the dynamics of systems composed of the species mentioned, individually and in combination. Thus, we recommend a three-stage experimental program. In the first phase each individual hydrocarbon would be studied in a smog chamber over a wide range of $HC/NO_{\rm X}$ ratios; in the next stage the hydrocarbons would be investigated in pairs; finally, the full three hydrocarbon system would be examined.

b. Statistical Considerations in Formulating the Initial Conditions

Selection of the initial conditions should be based upon levels of hydrocarbons and NO_X presently observed in the atmosphere and those expected as a consequence of current and future emission abatement programs. Statistical planning of experiments should prove of value in selecting sets of initial conditions that provide the most useful data base, in terms of both information content and ease of analysis. Randomization, factorial and fractional factorial designs, replication of runs, and augmentation of designs should all be considered at the planning stage. See Hunter (1960) and Davies (1960) for further information regarding the statistical design of experiments.

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An exception is the OH-toluene reaction, for which neither the rate constant nor the mechanism of reaction have yet been determined.

c. <u>Additional Species Identification and Measurement in the Smog</u> <u>Chamber Useful for Model Validation</u>

As model validation is essentially the process of comparing concentration-time profiles for primary and secondary products predicted by the chemical mechanism with those observed experimentally, the "quality" of a validation effort increases with the number of species monitored. Usually, concentration-time profiles are reported only for hydrocarbon, NO, NO₂, and O₃. Other species have generally not been followed because specific and accurate analytical methods have not been available for them. While we are aware of the experimental difficulties that such measurements involve, we still believe it is of importance to enumerate species that must eventually be measured if real progress is to be made in model validation. We recommend that the following species be monitored in future chamber studies:

> (i) <u>Aldehydes</u> Aldehydes are formed as direct products of some hydrocarbon oxidation reactions and also as products of alkoxy radical decomposition. They begin to appear as soon as the hydrocarbon is oxidized and can accumulate to significant (ppm) levels during smog chamber experiments. Because aldehydes are one of the most important classes of secondary products in smog, the confirmation of kinetics mechanisms' predictions for this species provides an excellent additional check on the accuracy of the mechanisms. For generalized models, the measurement of total aldehydes would be sufficient; for more detailed mechanisms it would be desirable to have separate

measurements of at least formaldehyde and acetaldehyde.

 (ii) <u>Hydrogen Peroxide</u> Hydrogen peroxide has been observed in smog chamber studies and in the atmosphere by Bufalini et al. (1972). It is formed by the recombination of hydroperoxyl radicals,

 $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

and knowledge of its concentration, along with the rate constant for the recombination reaction (about $5300 \text{ ppm}^{-1}\text{min}^{-1}$ (Johnston et al., 1970), provides one gauge for estimating the concentration of HO₂ radicals. H₂O₂ can, of course, photodissociate to form OH radicals, but this reaction is slow, being less than 0.5% of the rate of photolysis of NO₂ (Leighton, 1961).

- (iii) <u>Pernitrates</u> Nitrogen containing species such as PAN represent an important class of secondary products. Measurements of PAN are presently carried out on occasion. We recommend that pernitrates be measured routinely in future chamber experiments.
 - (iv) <u>Nitric Acid</u> Nitric acid currently appears to be the principal sink for nitrogen in the smog system. Little of the HNO_3 seems to be present in the gas phase; it forms mainly on the walls and on particles. Thus, continuous measurement of HNO_3 is very difficult. These difficulties not withstanding, accurate, continuous analysis of HNO_3 would be most valuable.

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(v) <u>Nitrous Acid</u> As indicated in Chapter II, nitrous acid may be present in significant quantities in the atmosphere at sunrise, and also in smog chambers prior to irradiation. Thus, the photolysis of HNO_2 may strongly affect the early oxidation rate of hydrocarbons and NO. We recommend that HNO_2 be monitored in order to establish the possible importance of this effect as well as to confirm the levels of HNO_2 predicted by kinetic mechanisms.

2. Controlled Irradiation of Polluted Air Samples from Urban Areas

Because of the number, diversity and complexity of species present in urban atmospheres, the irradiation of simple mixtures may not always be sufficiently representative of pollutant chemistry. It is thus of interest to examine the chemistry of more complex contaminant mixtures. One means for doing this is to charge or "dope" a sample of urban air with a known amount of pollutant and irradiate the mixture in a controlled system. During the 1975 RAPS program in St. Louis some studies of this type are apparently being planned. We recommend that at least four specific doping studies be carried out. For each study an "undoped" or control sample must also be irradiated simultaneously. The experiments recommended are:

- (i) Raise the CO level in one bag to 25 ppm and irradiate for 8 hours or until sundown, if outdoors. The goal is to assess the effect of low levels of CO on the rate of oxidation of NO and O_3 formation in the atmosphere.
- (ii) Add .25 ppm of toluene to one bag. Increased usage of unleaded gasolines in the future will result in greater

emissions of aromatics. This experiment is designed to examine that effect.

- (iii) Add .25 ppm of SO_2 to one bag. Measurement of the effect of SO_2 on O_3 levels and on the time to the NO_2 peak, as compared with the magnitude of these quantities measured for an undoped sample, is the primary objective.
- (iv) Dilute one bag 25% with clean air. This experiment is designed to study the effect on smog levels of a uniform reduction in all pollutants.

These are a few examples of the kinds of doping experiments that can be performed. Others may also be of interest, such as adding water vapor to one bag, irradiating bags of varying surface roughness, and adding various types of particulates to the bags. The intent of each experiment is to reveal the effect of varying a single parameter on the observed concentration dynamics.

3. Controlled Assessment of Natural Scavenging Processes

Surface sinks are one of two broad categories of "ultimate pollutant receptors", aerosols being the other. A number of recent studies indicate that both soils and vegetation take up several of the major pollutants at significant rates. Levy (1970) and Inman et al. (1971) have observed in laboratory studies that nonsterile soils take up carbon monoxide at very rapid rates. Fungi appear to be the organisms involved in the biochemical reactions. Abeles et al. (1971) have reported that hydrocarbons, sulfur dioxide, and nitrogen dioxide react with soil through microbial or chemical means. Vegetation has also been

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observed to react with atmospheric pollutants. Katz and Ledingham (1939) measured absorption rates of SO_2 by alfalfa, and Tingey (1968) has estimated rates of uptake of NO_2 by alfalfa and oats. Hill (1971), in a rather extensive study, has rank-ordered major pollutants according to the rate at which they absorb into alfalfa. He observed that SO_2 , NO_2 , and ozone were absorbed most rapidly, NO quite slowly, and CO not at all. Finally, the more reactive pollutants undergo transformation in contact with materials. Sabersby et al. (1973), for example, have measured relatively rapid ozone decomposition rates on surfaces such as rubber, fabrics, and plastic. The importance of determining rates of losses of pollutants to atmospheric sinks is twofold:

- (i) it is essential to establishing quantitative methods for estimating losses as a function of a number of variables that influence loss rates;
- (ii) it is essential to completion of material balances over a control volume in the atmosphere.

In general, loss rate for a particular pollutant is related to specific rate of absorption by soil, vegetation, or material, the surface properties of the absorbing substance, concentration of the pollutant in the gas phase, humidity, surface area, surface roughness, and turbulent eddy diffusivity. Also, radiation intensity can influence the rate of absorption by vegetation. To our knowledge, there has been only one attempt to correlate loss rates with these variables through atmospheric observation. Hill (1971) has observed that light intensity, wind speed, height of the vegetative canopy (surface roughness), and pollutant concentration all affect pollutant uptake rates. He has estimated the degree to which changes in a variable influence uptake for a particular species--increase in wind speed from one to two mph increases 0_3 uptake by 50%, increase in height of canopy increases uptake rates about linearly, and increase in S0₂ concentration results in a proportionate increase in uptake rates.

The effects of certain influencing variables are best determined in the chamber. For example, specific absorption rates as a function of concentration, temperature, relative humidity, light intensity, and wind speed have been studied under controlled conditions (see Hill, 1971). Effects of surface properties can also be examined in this way. Eventually, effects of levels of turbulence and degree of surface roughness must be simulated in the laboratory. Studies of this nature, however, are likely to be rather involved and complex.

To summarize, in order to better understand the nature of surface scavenging processes, we recommend that the effects of variables having a significant influence (as delineated in preceding paragraphs) on the specific absorption rates of the major individual constituents of smog by soil, vegetation, and materials (e.g., cement, asphalt, paint, etc.) be quantitatively determined.

D. Summary

Before smog chamber data can be used to validate photochemical simulation models, the reproducibility and reliability of the data must be established. Thus, successful validation will depend upon the quantitative assessment of all the heterogeneous effects in the

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chamber, careful measurement of the light intensity over the course of the irradiation, and knowledge of any shortcomings in the analytical measurements.

Reproducibility is a measure of the overall precision in smog chamber experiments. Given identical initial conditions (e.g., concentrations, temperatures, humidity, stirring rates, etc.) the concentration-time profiles of the individual pollutant species should be coincident for runs performed on different days or weeks. Lack of reproducibility may be due to one or more of several possible causes, as discussed earlier in this chapter. First, the activity of the walls may change with time, illustrating the necessity of insuring that the walls are at a known, standard, initial condition before each run. Second, the light sources in the chamber may deteriorate with time. The possibility of this occurring can be examined by measuring k_1 . Third, the analytical instruments may be out of calibration.

As a good test of repeatability, we suggest carrying out, as often as is necessary to guarantee the accuracy and stability of the experimental technique and the reproducibility of the results, a control experiment with initial conditions such as the following: 3 ppm toluene, 1.25 ppm NO, 0.05 ppm NO₂. Kopczynski (1972) has shown that about half of the hydrocarbon will be lost, the NO₂ peak will be reached in about two hours, and about 0.5 ppm of ozone will form. Tests such as these are admittedly time consuming, for they require an entire day, but they are absolutely necessary if the chamber data are to be used for mechanism validation purposes. It is also necessary for the investigator to characterize his chamber quantitatively. Some considerations include knowledge of the rate of loss of the individual pollutants to the walls under standard operating conditions, the effect of relative humidity and mixing on the observed photochemistry, the shortcomings, inaccuracies, and imprecisions of the analytical instruments, and the rate of dilution of the reactants due to sampling. The necessary procedures must, of course, be carefully defined and meticulously planned.

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Appendix A

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Development and Validation of a Generalized Mechanism for Photochemical Smog

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• A detailed 81-step mechanism for the photooxidation kinetics of the propylene- NO_x -air system, based on consideration of the possible important reactions which might be occurring, is presented. From the detailed mechanism is deduced a general 15-step mechanism for photochemical smog formation. The flexibility of this mechanism lies in adjustable rate constants and stoichiometric coefficients, which are chosen according to the particular hydrocarbon and initial reactant ratios. The general mechanism is validated with smog chamber data on propylene, isobutylene, *n*-butane, and a mixture of propylene and *n*-butane. The general mechanism is also shown to simulate accurately the effect of CO on smog chamber photooxidation kinetics as well as the inhibitory effect of high initial concentrations of nitric oxide on the maximum concentration of ozone attained.

The formation of photochemical smog occurs by a complex scries of reactions which is still not thoroughly understood. In recent years several reviews of atmospheric chemistry have appeared (Leighton, 1961; Wayne, 1962; Altshuller and Bufalini, 1965, 1971; Stephens, 1966; Haagen-Smit and Wayne, 1967; Johnston et al., 1970), and a number of kinetic mechanisms for photochemical smog have been proposed (Eschenroeder, 1969; Friedlander and Seinfeld, 1969; Westberg and Cohen, 1969; Behar, 1970; Wayne et al., 1970). In each case only limited success was achieved in matching predicted concentration-time behavior from the mechanism with experimental smog chamber data. It is clear, however, that a detailed understanding of the photochemical smog system will only be achieved by a combined study of smog chamber data and theoretical mechanisms.

In addition to elucidating the nature of the photochemical smog system, a kinetic mechanism will be a necessary component of an atmospheric simulation model, such as for the Los Angeles basin. Such urban atmospheric models, capable of simulating chemical reaction as well as convection and diffusion, will play an important role in assessing the effect of various emission control strategies on air quality. A kinetic mechanism for use in an atmospheric simulation model must obey some additional requirements. First, since a polluted urban atmosphere typically contains upward of 100 hydrocarbon species, the mechanism should be general enough to predict the behavior of a complex mixture of hydrocarbons. Second, since an atmospheric simulation model may consist of a set of partial differential equations, the kinetic mechanism must be as compact as possible to avoid excessive computing times in the numerical integration of the model.

Our objective in this paper is, thus, twofold. First, as a fundamental study of the photochemical smog reactions for a typical hydrocarbon species, we will formulate a detailed kinetic mechanism for the photooxidation of propylene in the presence of air, oxides of nitrogen, carbon monoxide, and water. Propylene was chosen because it has been widely studied in smog chambers and it exhibits behavior similar to the complex hydrocarbon mixture present in smog. The mechanism is deduced from a systematic analysis of the important possible reactions that could be occurring. Second, for use with an atmospheric simulation model, we will formulate a compact mechanism that has the flexibility of representing the behavior of a varied mixture of hydrocarbons. Both the detailed and the simplified mechanisms are integrated numeri-

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	Table 1. Reactions in the $NO_2-O_2-CO-H_2O$ System				
No.	Reaction	Rate constant	Ref.		
.1	$NO_2 + h\nu \longrightarrow NO + O$	$0.37 \min^{-1^{a,d}}$	к. н		
2	$O + O_2 + M \longrightarrow O_3 + M$	$2.2 \times 10^{-5} \text{ ppm}^{-2} \text{ min}^{-1}$ $2.0 \times 10^{6} \text{ min}^{-10}$	Kaufman and Kelso (1967)		
3	$O_3 + NO \longrightarrow NO_2 + O_2$	$22.5 \pm 2 \text{ ppm}^{-1} \text{ min}^{-1}$ 21.8	Clyne et al. (1964)		
4	$O_3 + NO_2 \longrightarrow NO_3 + O_2$	0.049 ppm ⁻¹ min ⁻¹	Ford et al. (1957)		
.5	$NO_3 + NO_2 \longrightarrow N_2O_5$	858 ppm ⁻¹ min ⁻¹	Altshuller and Bufalini (1965)		
6	$N_2O_6 \longrightarrow NO_3 + NO_2$	2.76 min ⁻¹	Altshuller and Bufalini (1965)		
7	$N_2O_5 + H_2O \longrightarrow 2 HNO_3$	0.75 min ⁻¹⁰	л — — — — — — — — — — — — — — — — — — —		
8	$NO_3 + NO_2 \longrightarrow NO + O_2 + NO_2$	0.49 ppm ⁻¹ min ⁻¹	Johnston et al. (1970)		
9	$O + NO_2 \longrightarrow O_2 + NO$	5150 ppm ⁻¹ min ⁻¹	Altshuller and Bufalini (1965)		
10	$NO_2 + NO \longrightarrow 2 NO_2$	1.40 × 10 ⁵ ppm ⁻¹ min ⁻¹	Johnston et al. (1970)		
11	$NO + NO_2 + H_2O \longrightarrow 2 HNO_2$	0.001 ppm ⁻¹ min ⁻¹⁶			
12	$HNO_2 + h\nu \longrightarrow NO + OH$	$0.01 \min^{-1^{a}}$			
13	$CO + OH \rightarrow CO_2 + H \rightarrow$	196 ppm ⁻¹ min ⁻¹	Baulch et al. (1968)		
14	$H \cdot + O_2 + M \longrightarrow HO_2 \cdot + M$	very fast			
15	$HO_2 \cdot + NO \longrightarrow NO_2 + OH \cdot$	30 ppm ⁻¹ min ⁻¹	Johnston et al. (1970)		
16	$HO_2 \cdot + NO_2 \longrightarrow HNO_2 + O_2$	0.001 ppm ⁻¹ min ⁻¹			
17	$OH \cdot + NO_2 + M \longrightarrow HNO_3 + M$	1470 ppm ⁻¹ min ⁻¹⁶	Johnston et al. (1970)		
18	$OH + NO \rightarrow HONO$	104 ppm-1 min-1			
19	$HO_2 \cdot + HO_2 \cdot \longrightarrow H_2O_2 + O_2$	70 ppm ⁻¹ min ⁻¹			
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validation studies. b Pseudo-first-order value. c Pseudo-second-order value. d If no light intensity alue shown is the reference is cited, the values in column 2 were estimated by the authors.

cally and their predictions compared to available smog chamber data.

Rate constants for each of the possible reactions in smog formation are, unfortunately, not available. In fact, only for some of the more widely studied reactions are there rate constant values which have been measured. The flexibility in a proposed kinetic mechanism lies, therefore, in the adjustment of rate constants which have not been measured experimentally. We use this procedure in attempting to match mechanism predictions and experimental data as closely as possible.

We will not consider the role of oxides of sulfur or the generation of photochemical aerosols in this work. These aspects remain as topics of current investigation.

Detailed Propylene Mechanism

We now present a detailed kineuc mecnanism for the photooxidation of propylene in the presence of air, NO, NO₂, CO, and H₂O. We have divided the reactions according to classes.

Reactions in the NO_z-O₂-CO-H₂O System. Table I presents the reactions in this class that are most important. Reactions 1-3 are the principal inorganic reactions in smog formation. However, the other reactions in Table I are important to describe some secondary effects. As the concentration of NO decreases, as a result of the overall oxidation of NO to NO2 in the smog system, Reaction 4, even though much slower than 3, will convert small quantities of NO2 to NO3 in the latter stages of the reaction. NO3 can then react with either NO2 or NO (Reactions 5, 8, and 10), with rates depending on the relative abundance of NO2 and NO, to form N2O5 or regenerate NO2 and small amounts of NO. N2O5 can decompose (Reaction 6) or hydrolyze to nitric acid (Reaction 7). Reaction 7 can account for the formation of HNO3 on the walls of smog chambers, often cited as the reason for the inability to obtain a nitrogen balance on the products in smog chambers, and also for formation of HNO₈ vapor in the

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atmosphere, which might eventually become incorporated in atmospheric aerosols in which high yields of nitrate products have been observed (Gay and Bufalini, 1969; Campion and Black, 1969; Hidy and Friedlander, 1970).

Recent smog chamber experiments have indicated that OH. radicals play a central role in photochemical smog. Reactions 11 and 12, although long recognized (Leighton, 1961), have only recently been suggested as a possible important source of OH · radicals in the smog system (Stedman et al., 1970). The OH · radical is a highly reactive species capable of reaction with hydrocarbons, CO, and aldehydes. CO, until recently, was ignored as a possible participant in the photochemical smog system because of its assumed low reactivity. However, a newly revised estimate of the activation energy of Reaction 13 indicates that the rate constant for this reaction is high enough to make it a possibly important reaction (Baulch et al., 1968; Dixon-Lewis et al., 1966). In addition, recent experiments reported by Holmes (1970), Westberg et al., (1971), and Stedman et al. (1970) have shown that CO accelerates the conversion of NO to NO2 over the rate in the absence of CO. Also, when H₂O and CO are both present, the rate of conversion of NO to NO2 is increased over that with only CO present. Although the experiments reported by Stedman et al. involved CO concentrations higher than those normally found in the atmosphere, recent unpublished work by Holmes (1971) has shown an accelerating effect of CO at concentrations as low as 10 ppm. Reaction 14 is very rapid so that 13 and 14 can be combined as

$CO + OH \cdot \xrightarrow{O_2} CO_2 + HO_2 \cdot$

The net effect of Reactions 13-15 is to convert NO to NO2 with no net loss of OH · radicals.

An extremely important conclusion arises from examination of Reactions 11--15, namely, that it is possible to convert NO to NO2 in significant quantities in the absence of hydrocarbons (Wilson, 1971). Both CO and H₂O are required for this con-

version in the absence of hydrocarbons. If H_2O is not present, HNO₂ cannot form, and the necessary OH \cdot radicals are not produced. Finally, HNO₂ and HNO₃ can be formed from OH \cdot and HO₂ \cdot reactions as in Reactions 16–18, and H₂O₂ from the HO₂-HO₂ recombination Reaction 19.

Oxidation of Propylene by O and O₃. The addition of a hydrocarbon such as propylene to the irradiated NO-NO₂-air system results in three well-known phenomena: the disappearance of hydrocarbon, a rapid and almost quantitative conversion of NO to NO₂, and the accumulation of a significant amount of O₃. Reactions 1-3 represent a cycle in which O₃ and NO are produced and consumed in equal quantities. If NO is converted to NO₂ by a path other than 3, for example, Reactions 13-15, then NO₂ and O₃ accumulate. In explaining the role of hydrocarbons in the conversion of NO to NO₂, we observed that a key step is the reaction between hydrocarbons and O and O₃. The reactions of C₃H₆ and O and O₃ and the subsequent reactions involving the free radicals formed are presented in Table II.

The elementary step of the olefin-atomic oxygen reaction is usually conceived as the addition of O to the double bond to form an activated complex,



Cvetanovic (1956) found that the major products of the $C_8H_{6^-}$ O reaction in the absence of O_2 were propylene oxide, propionaldehyde, acetone, and CO. In a study of the $C_3H_{6^-}NO_x$ system, however, Altshuller et al. (1967) found formaldehyde and acetaldehyde as major products. Thus, one expects fragmentation rather than stabilization of the activated complex, resulting in Reactions 20 and 21, with 20 being the more likely. Altshuller et al. (1967) have suggested a third possibility, Reaction 22, involving an epoxide intermediate,



which would then react with O_2 rapidly to form a molozonide intermediate,



The formation of such an intermediate is also a likely initial step in Reactions 23 and 24. In Reactions 22–24, either of the O—O bonds of the molozonide intermediate may cleave to form unstable biradicals,

$$\begin{array}{c} CH_{3}CHCH_{2}O \cdot \longrightarrow CH_{3}\dot{C}H + HCHO \\ | & | \\ OO \cdot & OO \cdot \\ CH_{3}CHCH_{3}O_{2} \cdot \longrightarrow H_{2}\dot{C}OO \cdot + CH_{3}CHO \\ | \\ O \end{array}$$

The biradical products can also be written as zwitterions,

CH₈CHOO⁻ and H₂COO⁻. The zwitterions can undergo a variety of decomposition reactions yielding methane, hydrogen, methanol, methyl formate, formic acid, and ketene (Leighton, 1961). Since each of these does not appear significantly as products in the C₃H₆-NO_x system, we have not included these reactions. The branching steps 25 and 28 have been included as representing a likely decomposition. Also the zwitterions can react with NO and NO₂ as in Reactions 26, 27, 29, and 30.

The CH₃ \cdot and C₂H₅ \cdot radicals formed in Reactions 20 and 21 readily add O₂ in Reactions 31 and 35 to form peroxymethyl and peroxyethyl radicals. The peroxyalkyl radicals then oxi-

	Table II. Oxidation of P	ropylene by O and O_3	
~ No.	Reaction	Rate constant	Ref.
20 21	$C_{3}H_{6} + O \longrightarrow CH_{3}CH_{2} + CHO \\ C_{3}H_{6} + O \longrightarrow CH_{3} + CH_{3}CO$	2925 ppm ⁻¹ min ⁻¹ 500 ppm ⁻¹ min ⁻¹	Range of values 3675-4410 ppm ⁻¹ min ⁻¹
22	$C_3H_6 + O \longrightarrow C_2H_4O_2 + HCHO$	250 ppm ⁻¹ min ⁻¹	Johnston et al. (1970)
23	$C_3H_6 + O_3 \longrightarrow C_2H_4O_2 + HCHO$	0.007 ppm ⁻¹ min ⁻¹	Range of values 0.0091-0.0165 ppm ⁻¹ min ⁻¹
24	$C_{3}H_{6} + O_{3} \longrightarrow CH_{3}CHO + CH_{2}O_{2}$	0.007 ppm ⁻¹ min ⁻¹	Johnston et al. (1970)
25	$C_2H_4O_2 \longrightarrow CH_3O_1 + CHO_1$	0.3 min ⁻¹	
26	$C_2H_4O_2 + NO \longrightarrow CH_3CHO + NO_2$	3.0 ppm ⁻¹ min ⁻¹	
27	$C_2H_4O_2 + NO_2 \longrightarrow CH_3CHO + NO_3$	0.1 ppm ⁻¹ min ⁻¹	
28	$CH_2O_2 \longrightarrow OH \cdot + CHO \cdot$	0.3 min ⁻¹	
29	$CH_2O_2 + NO \longrightarrow HCHO + NO_2$	3.0 ppm ⁻¹ min ⁻¹	
30	$CH_2O_2 + NO_2 \longrightarrow HCHO + NO_8$	0.1 ppm ⁻¹ min ⁻¹	
- 31	$CH_3 \cdot + O_2 \longrightarrow CH_3O_2 \cdot$	3 × 106 min ^{-1a}	
32	$CH_3O_2 + NO \longrightarrow CH_3O + NO_2$	6 ppm ⁻¹ min ⁻¹	
33	$CH_3O + O_2 \rightarrow HCHO + HO_2$	$5.15 \times 10^4 \text{min}^{-1^a}$	
34	$CH_{3}O_{2} + NO_{2} + M \longrightarrow CH_{3}NO_{3} + M$	16.2 ppm ⁻¹ min ⁻¹⁰	
35	$CH_3CH_2 + O_2 \longrightarrow CH_3CH_2O_2$	3 × 10 ⁶ min ^{-1a}	
36	$CH_3CH_2O_2 + NO \longrightarrow NO_2 + CH_3CH_2O$	6 ppm ⁻¹ min ⁻¹	
37	$CH_{3}CH_{2}O + O_{2} \longrightarrow CH_{3}CHO + HO_{2}.$	5.15 × 104 min ⁻¹⁰	
38	$CH_{3}CH_{2}O + NO_{2} + M \longrightarrow CH_{3}CH_{2}NO_{3} + M$	16.2 ppm ⁻¹ min ⁻¹⁰	
e Pseudo-fi	rst-order value. • Pseudo-second-order value.		

Alkoxyl radicals which result from the oxidation of NO to NO₂ by peroxyalkyl radicals (Reactions 32 and 36), undergo reactions with O₂ (Reactions 33 and 37) in which hydrogen is abstracted. Alkoxyl radicals will also react with NO₂ forming alkyl nitrates (Reactions 34 and 38) which are observed as minor products in smog chambers.

Reaction of Propylene and OH.. Hydroxyl radicals will react significantly with olefins, as well as with aromatic and saturated hydrocarbons, especially the larger and branched members of the series. Two possible mechanisms for the C_3H_6 -OH. reaction are presented in Table III. Because references are not generally available we have not included that column. The two mechanisms differ depending on the location of addition of OH. to the C_3H_6 molecule. The first mechanism (Reactions 39-45) is a result of addition of OH. to the number one carbon atom of C_3H_6 . The peroxy radical formed in Reaction 39 can decompose (Reaction 40) or oxidize NO to NO₂ (Reaction 41). Reaction 40 might proceed by formation of a

	Table III. Reaction of Propylene and OH-	1
No.	Reaction	Rate constant
	Mechanism 1	
39	$C_{3}H_{6} + OH \cdot \xrightarrow{O_{1}} CH_{3}CHCH_{2}OH$	$1.5 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$
40	$ CH_{3}CHCH_{2}OH \longrightarrow CH_{3}CH_{2}CHO + HO_{2}.$	0.001 min ¹
41	$\begin{array}{ccc} OO \cdot & O \cdot \\ \\ CH_{1}CHCH_{2}OH + NO \longrightarrow CH_{3}CHCH_{2}OH + NO_{2} \end{array}$	6 ppm ⁻¹ min ⁻¹
	0.	• • • •
42	$CH_3CHCH_2OH + O_2 \longrightarrow CH_3CHO + HOCH_2O_2$	3000 min ^{-1a}
43	$HOCH_2O_2 \cdot + NO \longrightarrow HOCH_2O \cdot + NO_2$	4 ppm ⁻¹ min ⁻¹
44	$HOCH_2O_2 \rightarrow HCHO + HO_2$	0.001 min ⁻¹
45	$HOCH_2O \rightarrow HCHO + OH \rightarrow$	3000 min ⁻¹
	Mechanism 2	
	OH OH	
46	$C_{3}H_{6} + OH \cdot \longrightarrow CH_{3}CHCH_{2}O_{2} \cdot$	104 ppm ⁻¹ min ⁻¹
	OH 	
47	$CH_{3}CHCH_{2}O_{2} \longrightarrow (CH_{3})_{2}CO + HO_{2}$	0.001 min ⁻¹
	OH OH	
48	$CH_{3}CHCH_{2}O_{2} + NO \longrightarrow CH_{3}CHCH_{2}O + NO_{2}$	6 ppm ⁻¹ min ⁻¹
ус. 		
49	OH	3000 min-1*
50	$CH_{3}CHO_{2} \rightarrow CH_{3}CHO + HO_{2}$	0.001 min ⁻¹
	ОН ОН 	
51	$CH_3CHO_2 \cdot + NO \longrightarrow CH_3CHO \cdot + NO_2$	6 ppm ⁻¹ min ⁻¹
	OH	
52	$CH_{s}CHO + O_{2} \longrightarrow CH_{s}COOH + HO_{2} \cdot OH$	1000 min ^{-1a}
53	$CH_{3}CHO \cdot \longrightarrow CH_{3}CHO + OH \cdot$ Mechanism 3	2000 min ⁻¹
54	$C_{3}H_{4} + OH \rightarrow CH_{2} = CHCH_{2} + H_{2}O$	5000 ppm ⁻¹ min ⁻¹
Pseudo-first-order value.		

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Table IV. The Formation and D	estruction of Pernitrates	
Reaction	Rate constant	Ref.
$CH_3CO + O_2 \longrightarrow CH_3(CO)O_2$	$3 \times 10^6 \text{ min}^{-1^a}$	
$CH_3(CO)O_2 + NO \longrightarrow CH_3(CO)O + NO_2$	8 ppm ⁻¹ min ⁻¹	
$CH_{3}(CO)O \cdot + NO \longrightarrow CH_{3}\dot{C}O + NO_{2}$	0.1 ppm ⁻¹ min ⁻¹	
$CH_3(CO)O_2 \cdot + NO_2 \longrightarrow CH_3(CO)O_2NO_2$	2.0 ppm ⁻¹ min ⁻¹	
$CH_3(CO)O \cdot \longrightarrow CH_3 \cdot + CO_2$	0.0001 min ⁻¹	
$CH_3(CO)O_2NO_2 + NO \longrightarrow CH_3(CO)O_1 + 2 NO_2$	0.16 ppm ⁻¹ min ⁻¹	Schuck and Stephens (1969)
$CH_3(CO)O_2NO_2 + h\nu \longrightarrow CH_3(CO)O_1 + NO_3$	0.01 min-10	
$CH_3O_2 \cdot + NO_2 \longrightarrow CH_3O_2NO_2$	0.001 ppm ⁻¹ min ⁻¹	
$CH_3O_2NO_2 + NO \longrightarrow CH_3O_2 + 2 NO_2$	0.1 ppm ⁻¹ min ⁻¹	
$CH_3O_2NO_2 + h\nu \longrightarrow CH_3O_1 + NO_3$	0.05 min-10	
$CH_3CH_2O_2 + NO_2 \longrightarrow CH_3CH_2O_2NO_2$	0.001 ppm ⁻¹ min ⁻¹	
$CH_3CH_2O_2NO_2 + NO \longrightarrow CH_3CH_2O_2 + 2 NO_2$	0.1 ppm ⁻¹ min ⁻¹	
$CH_3CH_2O_2NO_2 + h\nu \longrightarrow CH_3CH_2O + NO_3$	0.05 min ^{-1b}	
t-order value. b Depends on the light intensity. The value shown is	that used in the validation studies	
	Table IV. The Formation and D Reaction $CH_3CO + O_2 \longrightarrow CH_3(CO)O_2.$ $CH_3(CO)O_2 + NO \longrightarrow CH_3(CO)O + NO_2$ $CH_3(CO)O_2 + NO \longrightarrow CH_3CO + NO_2$ $CH_3(CO)O_2 + NO_2 \longrightarrow CH_3(CO)O_2NO_2$ $CH_3(CO)O_2NO_2 + NO \longrightarrow CH_3(CO)O + 2 NO_2$ $CH_3(CO)O_2NO_2 + h\nu \longrightarrow CH_3(CO)O + NO_3$ $CH_3O_2 + NO_2 \longrightarrow CH_3O_2NO_2$ $CH_3O_2NO_2 + h\nu \longrightarrow CH_3O_2 + 2 NO_2$ $CH_3O_2NO_2 + h\nu \longrightarrow CH_3O + 2 NO_2$ $CH_3O_2NO_2 + h\nu \longrightarrow CH_3O + 2 NO_2$ $CH_3O_2NO_2 + h\nu \longrightarrow CH_3O + NO_3$ $CH_3CH_2O_2 + h\nu \longrightarrow CH_3O + NO_3$ $CH_3CH_2O_2 + h\nu \longrightarrow CH_3CH_2O_3NO_2$ $CH_3CH_2O_2O_2 + h\nu \longrightarrow CH_3CH_2O_2 + 2 NO_2$ $CH_3CH_2O_2NO_2 + h\nu \longrightarrow CH_3CH_2O_2 + NO_3$ $t-order value.^{b}$ Depends on the light intensity. The value shown is	Table IV. The Formation and Destruction of Pernitrates ReactionRate constantRate constantCH ₃ (CO)O ₂ .3 × 10° min ^{-1a} CH ₃ (CO)O ₂ . + NO \rightarrow CH ₃ (CO)O + NO ₂ 3 × 10° min ^{-1a} CH ₃ (CO)O ₂ . + NO \rightarrow CH ₃ (CO)O ₂ + NO ₂ 3 × 10° min ^{-1a} CH ₃ (CO)O ₂ + NO \rightarrow CH ₃ (CO)O ₂ NO ₂ 2.0 ppm ⁻¹ min ⁻¹ CH ₃ (CO)O ₂ + NO ₂ \rightarrow CH ₃ (CO)O ₂ NO ₂ 0.0001 min ⁻¹ CH ₃ (CO)O ₂ + NO ₂ \rightarrow CH ₃ (CO)O ₂ + 2 NO ₂ 0.16 ppm ⁻¹ min ⁻¹ CH ₃ (CO)O ₂ + NO \rightarrow CH ₃ (CO)O ₂ + 2 NO ₂ 0.16 ppm ⁻¹ min ⁻¹ CH ₃ (CO)O ₂ + NO \rightarrow CH ₃ (CO)O ₂ + NO ₃ 0.0101 ppm ⁻¹ min ⁻¹ CH ₃ O ₂ NO ₂ + NO \rightarrow CH ₃ O ₂ NO ₂ 0.001 ppm ⁻¹ min ⁻¹ CH ₃ O ₂ NO ₂ + NO \rightarrow CH ₃ O ₂ NO ₂ 0.001 ppm ⁻¹ min ⁻¹ CH ₃ O ₂ NO ₂ + NO \rightarrow CH ₃ CH ₂ O ₂ NO ₂ 0.001 ppm ⁻¹ min ⁻¹ CH ₃ O ₂ NO ₂ + NO \rightarrow CH ₃ CH ₂ O ₂ NO ₂ 0.001 ppm ⁻¹ min ⁻¹ CH ₃ O ₂ NO ₂ + NO \rightarrow CH ₃ CH ₂ O ₂ NO ₂ 0.001 ppm ⁻¹ min ⁻¹ CH ₃ CH ₂ O ₂ NO ₂ 0.001 ppm ⁻¹ min ⁻¹ CH ₃ CH ₂ O ₂ + NO \rightarrow CH ₃ CH ₂ O ₂ + 2 NO ₂ 0.001 ppm ⁻¹ min ⁻¹ CH ₃ CH ₂ O ₂ + NO \rightarrow CH ₃ CH ₂ O ₂ + NO ₂ 0.001 ppm ⁻¹ min ⁻¹ CH ₃ CH ₂ O ₂ + NO \rightarrow CH ₃ CH ₂ O ₂ + NO ₃ <th colspan="</td>

six-membered ring intermediate,



Alternatively, a secondary hydrogen could be abstracted, and HO_s could split off forming the enol tautomer of propionaldehyde,

 $\begin{array}{c} OO \cdot & OOH \\ | & | \\ CH_3CHCH_2OH \longrightarrow CH_3CHCHOH \longrightarrow \\ CH_3CH=CHOH + HO_2 \cdot \\ | \\ | \end{array}$

Since not much propionaldehyde is observed as a product in propylene smog chamber experiments, Reaction 41 is probably more important than 40. The radical formed in 41 could decompose into acetaldehyde and a radical $HOCH_2$, which probably reacts readily with O_2 to yield $HOCH_2O_2$. (Reaction 42). This radical can react with NO to yield NO_2 (Reaction 43), or simply decompose to give formaldehyde and a hydroperoxyl radical.

CH₃CH₃CHO

The second mechanism (Reactions 46-53) results if the OHadds to the number two carbon atom of C_3H_6 . The steps are analogous to Reactions 39-45. Another likely possibility, Reaction 54, is the abstraction of a hydrogen atom from the number three carbon atom to form an allyl radical and water. The allyl radical has two equivalent resonance bond structures.

 \cdot CH₂-CH=CH₂ \leftrightarrow CH₂=CH-CH₂ \cdot

and a resonance stabilization of 19 kcal/mol relative to CH_{a} . (Huyser, 1970). Employing bond energies at 298 °K, OH attack on the number one carbon atom

 $C_{1}H_{6} + OH \rightarrow CH_{3}CHCH_{2}OH$

has a $\Delta H = -22.3$ kcal/mol, compared to $\Delta H = -30.9$ kcal/mol for Reaction 54. In addition, 54 has a greater overall increase in entropy. Once formed, the allyl radical would probably react with O₂.

Peroxyalkyl radicals might also react with C_3H_6 . Leighton (1961) suggests a direct addition forming a peroxide radical which could then react with O_2 regenerating a peroxyalkyl radical. Leighton also suggests that the intermediate might break at the double bond, forming an aldehyde or ketone and an oxy radical. This reaction would not be expected to be as rapid as the corresponding reaction with OH \cdot .

Oxidation of Propylene by Singlet Molecular Oxygen. It has been suggested that singlet molecular oxygen might be involved in atmospheric oxidation reactions (Pitts et al., 1969). Ackerman et al. (1970) estimated the rate constant for the ${}^{1}\Delta$ form of O₂-tetramethylethylene reaction to be about 10⁸ M^{-1} sec⁻¹. For singlet oxygen attack on propylene, the initial addition product would be a hydroperoxide,

$CH_{2}CH=CH_{2} + {}^{1}O_{2} \longrightarrow CH_{2}=CHCH_{2}OOH$

However, Herron and Huie (1970) have concluded that the oxidation of olefins by singlet molecular oxygen is less important than the reaction with atomic oxygen. Because of this uncertainty we have chosen to omit reactions involving singlet oxygen.

Formation and Destruction of Pernitrates. Pernitrates, especially peroxyacylnitrates (PAN's), have been shown to form in substantial quantities in smog chambers. Pernitrates are of the form $ROONO_2$, where R is an acyl group in the case of PAN's. The most common pernitrate in the propylene- NO_2 system is peroxyacctylnitrate,

O || CH₃COONO₂.

This product begins to accumulate only after the NO is nearly depleted. The series of reactions related to pernitrate formation is shown in Table IV.

The formation of peroxyacetyl radicals (Reaction 55) is the initial step in the pernitrate chain reactions. The principal PAN-forming step is shown in Reaction 58. The delayed formation of PAN can be explained in at least two ways. The peroxyacetyl radical can participate in oxidation of NO to NO₂ (Reaction 56) when there is a substantial quantity of NO in the system. Reaction 56 would then compete with 58 until the NO disappears. The acetate radical formed in 56 can react further with NO, as in Reaction 57, or decompose into a methyl radical and CO₂ as in 59 (Leighton, 1961). The second explanation for the delayed appearance of PAN is its reaction

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	Table V. Aldehy	de Decomposition Reactions	
No.	Reaction	Rate constant	Ref.
68	$HCHO + h\nu \longrightarrow H \cdot + CHO \cdot$	$3.3 \times 10^{-5} \min^{-1^a}$	Leighton (1961)
69	$HCHO + O \rightarrow OH + CHO$	220 ppm ⁻¹ min ⁻¹	Herron and Penzhorn (1969)
70	$HCHO + O_3 \longrightarrow OH + CHO + O_2$	2.45 × 10 ⁻⁵ ppm ⁻¹ min ⁻¹	Leighton (1961)
71	$HCHO + OH \rightarrow CHO + H_2O$	$2.5 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$	
72	$CH_3CHO + h\nu \longrightarrow CH_3 + CHO$	0.0036 min ^{-1a}	Leighton (1961)
73	$CH_{3}CHO + O \longrightarrow CH_{3}CO + OH$	294 ppm ⁻¹ min ⁻¹	Leighton (1961)
74	$CH_3CHO + O_3 \longrightarrow CH_3CO + OH + O_2$	0.0005 ppm ⁻¹ min ⁻¹	Leighton (1961)
75	$CH_3CHO + OH \cdot \longrightarrow CH_3\dot{C}O + H_2O$	2.5 × 10 ⁴ ppm ⁻¹ min ⁻¹	
a Deper	nds on the light intensity. The value shown is that used in the	he validation studies.	

with NO, Reaction 60 (Schuck and Stephens, 1969). The rate constant for this reaction is high enough to prevent PAN from accumulating until the NO is almost completely converted to NO₂. Interestingly, Reaction 60 shows another means of converting NO to NO₂. The photolysis of PAN in Reaction 61 is also a possibility. Pitts (1970) has also recently reported that PAN reacts with water forming singlet oxygen as one of the products in a highly exothermic reaction. This step has not been included.

Although methyl and ethyl pernitrates are not reported as products in the propylenc– NO_z system, formation of trace amounts can be described by Reactions 62–67.

Aldehyde Decomposition. It has been shown how aldehydes, especially HCHO and CH₃CHO, can be formed when propylene is oxidized. Reactions involving aldehyde decomposition are shown in Table V. Both HCHO and CH₃CHO undergo photodecomposition (Reactions 68 and 72). Oxygen atoms react with the aldehydes abstracting a hydrogen atom to form OH- and the corresponding acyl radical (Reactions 69 and 73). O₂ can also abstract hydrogen as in 70 and 74, and OHreacts with aldehydes to give an acyl radical and water, as in 71 and 75.

Other Radical Reactions. Table VI summarizes some radical reactions which may play secondary roles in photochemical smog. We note that in smog chambers initially free of CO, small amounts have been observed to form. This is probably due primarily to Reaction 76. The possible peroxyformyl product of 76 is unstable and has not been observed in smog chambers.

Validation of the Detailed Mechanism

The validation consists of comparing the concentrationtime results from the mechanism to those of an experimental run for the same initial conditions. The fit of the mechanism to the data is achieved by varying rate constants over ranges consistent with the expected order of magnitude for each reaction. The experimental data used for propylene photooxidation were obtained from the Gulf Research Co. (Strickler, 1970). A comparison of the experimental data (solid line) and the detailed mechanism (dashed line) are presented in Figure 1 for the validation rate constants in Tables I–VI. The mechanism curves were generated by numerical integration of the rate equations for all of the species not in a pseudosteady state (all the nonradical species). By use of the numerical integration routine of Gear (1971), 3^{1}_{2} hr of reaction time were simulated in 25 sec on an IBM 360/75.

Because of the large number of unknown rate constants, it is possible to fit the data in Figure 1 closely. Thus, we will not present a large series of comparisons of model predictions vs. data for the detailed mechanism. Perhaps the most important aspect of a detailed mechanism is to aid us in the formulation of a simplified version with far fewer steps and rate constants that gives comparable concentration-time predictions.

A Simplified Mechanism

As we have noted, in an urban atmospheric model it will be necessary to have a kinetic mechanism which not only describes the kinetics accurately over the concentration range of interest but also involves as few steps as possible to minimize computation time. Also, the mechanism should permit simulation of the behavior of a complex hydrocarbon mixture such as exists in the atmosphere. Therefore, it is necessary to achieve a balance between chemical detail and flexibility. In this section we propose a simplified mechanism for photochemical smog.

Simulations carried out with the detailed mechanism reveal that certain reactions are much more important than others. These conclusions are based on the results obtained by systematically varying rate constants and observing the changes in the concentration-time behavior. In addition, inspection of the mechanism shows that many reactions are of the same general type. For example, many free radical reactions can be classed according to the radical type. Thus, to obtain a simplified mechanism we should remove reactions of lesser importance,

No.		Reaction	Rate constant
76	•	$CHO \cdot + O_2 \longrightarrow CO + HO_2 \cdot$	$5.15 \times 10^{5} \text{ min}^{-1^{a}}$
77		$CHO \cdot + OH \cdot \longrightarrow CO + H_2O$	3.6 × 104 ppm ⁻¹ min ⁻¹
78		$CH_{3}O \cdot + CH_{3}O \cdot \longrightarrow HCHO + CH_{3}OH$	3.6 × 10 ⁵ ppm ⁻¹ min ⁻¹
79		$CH_3CH_2O + CH_3CH_2O \rightarrow CH_3CHO + CH_3CH_2OH$	3.6 × 10 ⁵ ppm ⁻¹ min ⁻¹
80		$CH_3(CO)O + CH_3O \rightarrow HCHO + CH_3COOH$	3.6 × 105 ppm ⁻¹ min ⁻¹
81		$CH_3(CO)O_{\cdot} + CH_3CH_2O_{\cdot} \longrightarrow CH_3CHO + CH_3COOH$	3.6 × 10 ⁵ ppm ⁻¹ min ⁻¹

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Figure 1. Comparison of experimental smog chamber concentrations and concentrations predicted by the detailed propylene mechanism

Data for propylene from Gulf Research Co.

combine reactions of similar type, and generalize the reactions involving hydrocarbons. The objective is a compact mechanism capable of accurate description of smog chamber results with different hydrocarbons by adjustment of flexible parameters.

To develop the mechanism let us consider the reaction classes discussed in relation to the propylene mechanism. First, in the NO_z - O_2 -CO- H_2O system we will choose to include the following steps: Reactions 1-4, formation of nitric acid, formation and photolysis of nitrous acid, and reaction of CO and OH radicals. We retain these features to be able to include the effect of water and CO in the simplified mechanism. Thus, the first 10 steps of the simplified mechanism are:

$$NO_{2} + h\nu \xrightarrow{1'} NO + O$$

$$O + O_{3} + M \xrightarrow{2'} O_{8} + M$$

$$O_{3} + NO \xrightarrow{3'} NO_{2} + O_{8}$$

$$O_{3} + NO_{2} \xrightarrow{4'} NO_{8} + O_{2}$$

$$NO_{8} + NO_{2} \xrightarrow{4'} NO_{8} + O_{2}$$

$$NO_{8} + NO_{2} \xrightarrow{5'} 2 HNO_{3}$$

$$NO + NO_{2} \xrightarrow{6'} 2 HNO_{2}$$

$$HNO_{2} + h\nu \xrightarrow{7'} OH + NO$$

$$CO + OH \cdot \xrightarrow{8'} O_{2} + O_{2} \cdot HO_{2} \cdot HO_{2} \cdot HO_{2} \cdot HO_{2} \cdot HO_{2} + OH \cdot HO_{2} \cdot HO_{2} \cdot HO_{2} + OH \cdot HO_{2} \cdot HO_{2} + OH \cdot HO_{2} + OH \cdot HO_{2} \cdot HO_{2} + OH \cdot HO_{2} + OH \cdot HO_{2} \cdot HO_{2} + OH \cdot HO_{2} + O_{2} + OH \cdot HO_{2} + O_{2} + OH \cdot HO_{2} + O_{2} + O_{2}$$

Note that we have combined Reactions 5-7 as 5'. The rate constant of 5' will be that of the rate-determining step 5. In view of the possible importance of HNO_2 as a source of OH when water is present, Reactions 6' and 7' have been retained. In a dry system, Reactions 5' and 6' will not be included. Reaction 10' is included to provide a path for HO_2 . consumption when NO has been depleted.

Next we consider reactions involving hydrocarbons. We introduce a general hydrocarbon species, called HC, which may be taken to represent a single hydrocarbon or a complex mixture of hydrocarbons. If we neglect aldehydes, hydrocarbons present in smog can be divided according to olefins, aromatics, and paraffins. We will consider hydrocarbon attack by O, O_3 , and OH \cdot .

In the case of O attack on olefins the result is the production of two free radicals. For example, the products of O attack on three common olefins are:

ethylene	CH₃· + HĊO	
propylene	$CH_3 + CH_3CO \text{ or } C_2H_5 +$	HCO
isobutylene	$(CH_3)_2CH \cdot + HCO \text{ or } C_2H_5 \cdot$	+ CH₃ĊO

Oxygen atom attack on aromatics in some cases can be as fast as for olefins (Leighton, 1961). The products of the initial aromatic-O reaction are not well-known. Among the products that have been observed from the reaction chain initiated by O attack on aromatics are peroxides, acids, and alcohols (Eventova and Prytkova, 1960; Kemula and Grabowska, 1960). The reaction with paraffins is much slower, the most probable step being hydrogen abstraction (Leighton, 1961),

$$RH + O \longrightarrow R \cdot + OH \cdot$$

Thus, the result of O attack on hydrocarbons is branching, generally to form two free radicals. We will write this step in the general mechanism as

$$HC + O \xrightarrow{\Pi'} \alpha RO_2$$

where RO_2 is a lumped radical species (in general, a peroxyalkyl or peroxyacyl radical) and α is the stoichiometric coefficient—i.e., the number of such radicals produced by this reaction.

Consider now O_8 attack on hydrocarbons. For O_3 attack on olefins the initial products are an aldchyde and a zwitterion. The number of free radicals formed depends on the subsequent zwitterion reaction. For three common olefins, the result of O_8 attack is:

ethylene	$HCHO + CH_2O_2$
propylene	HCHO + $C_2H_4O_2$ or $CH_3CHO + CH_2O_2$
isobutylene	HCHO + $(CH_3)_2CO_2$ or $(CH_3)_2CO + CH_2O_2$

The reactions between O_3 and alkanes and aromatics are slow and can probably be neglected. Summarizing the general hydrocarbon- O_3 reaction, we can write the general step

$$HC + O_3 \xrightarrow{12^{\prime}} \beta RO_2 + \gamma RCHO$$

....

where β and γ are stoichiometric coefficients to be determined by the particular hydrocarbon mix.

Next we consider the general hydrocarbon-OH \cdot reaction. We have proposed three possible mechanisms for the propylene-OH \cdot reaction. In the first two, aldehydes and free radicals are the products, and in the third, the chain reaction is terminated by allyl radical and water formation.

The alkane-OH \cdot reaction has been recently considered by Greiner (1970). The principal products from the hydrogen abstraction are a free radical and water. We might also expect that the branched aromatic-OH \cdot reaction would yield products similar to those of the alkane-OH \cdot reaction.

Combining each of these possible steps we can propose the general hydrocarbon-OH·step,

$$HC + OH \cdot \xrightarrow{13'} \delta RO_2 \cdot + \epsilon RCHO$$

where the stoichiometric coefficients δ and ϵ are determined by the hydrocarbon mix. Since aldehyde formation only occurs for olefins and possibly aromatics (Heuss and Glasson, 1968), ϵ will be less than one.

The remaining reactions in the simplified mechanism describe the oxidation of NO to NO_2 by peroxy radicals and the formation of PAN,

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$$RO_2 + NO_2 \xrightarrow{15} PAN$$

It is important to note that if CO and H₂O are present we treat HO2. and RO2. as separate species. If CO and H2O are not present, we consider only the single species RO2., which includes HO2. within it, since Reactions 5'-10' are omitted. In that case, θ is the fractional product of OH \cdot from Reaction 14'-i.e., the fraction of HO2. in the total lumped radical species RO2 ·.

Many reactions have not been included, for example, the formation of organic nitrates (which can presumably be included in Reaction 15'), reactions involving PAN decomposition (of secondary importance), aldehyde decomposition (can be treated by adjustment of γ and ϵ) and radical-radical recombination (of secondary importance).

The simplified mechanism consists of Reactions 1'-15' and includes the following species: NO, NO2, O3, HC, O, NO3, OH., HO2., RO2., HNO2, HNO3, RCHO, PAN. Differential equations are required for the first four; steady-state relations are written for the next six, and the last three represent products.

Validation of the Simplified Mechanism

In the validation of the simplified mechanism we will consider smog chamber data for the following hydrocarbons:

Propylene (Strickler, 1970; Wayne et al., 1969)

· Isobutylene in the presence and absence of CO (Westberg et al., 1971)

• n-Butane in the presence and absence of CO (Wilson, 1971)

Propylene and n-butane (Wilson, 1971)

These experiments were selected to test the mechanism on both olefins and paraffins, on the effect of different initial reactant ratios, and on the effect of CO.

Let us first discuss the generalized stoichiometric coefficients in the mechanism. Of prime importance is α , the chainbranching factor in the HC-O reaction. In the early stages of reaction, the HC-O reaction is critical in determining the rate of oxidation of NO to NO2. The peak O2 level will depend on how much of the NO is oxidized before the hydrocarbon is consumed. We have found that α should, in some cases, not be taken as constant but rather as a function of the NO to HC ratio throughout the course of the reaction. Large NO to HC



Figure 2. Comparison of experimental smog chamber concentrations and concentrations predicted by the simplified mechanism Data for propylene from Gulf Research Co.

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ratios apparently affect the chain length, and since α governs the chain length directly, it is convenient to reflect this by allowing α to depend on the NO to HC ratio as it changes with time. This dependence should follow the general behavior of a plot of peak O3 concentration vs. initial NO to HC ratio.

The generalized coefficients δ (RO₂· from the HC-OH· reaction) and $\theta(OH \cdot \text{ from the } RO_2 \cdot -NO \text{ reaction})$ are important in simulating the effect of CO. Since OH · attacks both HC and CO and since the products of both reactions are radical species capable of oxidizing one NO to NO2 (HO2. in the former case and $RO_2 \cdot$ in the latter), it is necessary that the number of HO2. radicals formed in the CO-OH. reaction (always equal to one) be greater than the number of RO2. radicals formed in the HC-OH · reaction in the presence of CO. If $\delta\theta > 1$, CO would effectively inhibit the rate of NO oxidation because CO would be scavenging OH. radicals from a reaction with HC capable of generating more radicals able to oxidize NO than the single HO2. formed in the CO-OH. reaction. This can also be seen by examining the differential equation for NO. The terms governing the contribution to the NO oxidation rate from the HC-OH. and CO-OH. reaction both have the quantity $(1 - \delta\theta)$ in the denominator. If $\delta 0 > 1$, the sign of d[NO]/dt will be positive rather than negative. Also, since the term governing the effect of CO has [CO] in the denominator, if $\delta \theta > 1$, CO will inhibit rather than accelerate the oxidation of NO.

Propylene Experiments. The propylene data used are shown in Figures 2 and 3. The data in Figure 2 are the same as in Figure 1 (Strickler, 1970). The data in Figure 3 have been presented by Wayne et al. (1970) from the California Air Resources Board. The photolysis rate for each experiment is $k_1 = 0.37 \min^{-1}$.

Both simulations, shown by the dashed curves, were made with the following rate constants:

k_1'	=	0.37	ks'	-	1800
k_2'		2.76×10^{6}	k10'	=	10
k3'	=	21.8	k11'	=	5×10^4
k_4'	=	0.006	k12'	-	0.0075
k_{5}'	=	0.1	k18'		1000
ks'	=	0.0025	k14'	-	1800
k_{7}'		0.005	k15'	=	10
ks'	==	200			

The initial conditions for Figures 2 and 3 are: $[C_3H_6]_0 = 3.29$. $[NO_2]_0 = 0.088$, $[NO]_0 = 1.612$ and $[C_3H_6]_0 = 1.0$, $[NO_2]_0 =$



Figure 3. Comparison of experimental smog chamber concentrations and concentrations predicted by the simplified mechanism

Data for propylene from the California Air Resources Board



Figure 4. Comparison of experimental smog chamber concentrations and concentrations predicted by the simplified mechanism



0.1, $[NO]_0 = 1.0$, respectively. Each 3-hr simulation was carried out in 3 sec by use of the routine of Gear (1971). Because of the generalized nature of the 15-step mechanism, the "rate constants" for the reactions are more a quantitative expression of the relative importance of classes of reactions than a reflection of the actual rate constants. Consequently, the rate constants for the 15-step mechanism are not identical to those in Tables I-VI, particularly $k_{10}'-k_{10}'$. This feature is a necessary, if undesirable, feature of a mechanism which sacrifices details of chemical reality for conciseness. Similarly, the stoichiometric coefficients must be viewed only qualitatively as true stoichiometric coefficients. Following the dependence of peak O₈ on the NO to HC ratio for ratios from 0.25 to 1 reported by Altshuller et al. (1967), α was determined as

$$\alpha = \begin{cases} 2.45 & [NO]/[HC] < 0.25 \\ 9.8 \frac{[NO]}{[HC]} & 0.25 < [NO]/[HC] < 1 \end{cases}$$

For [NO]/[HC] < 0.25, $\alpha = 2.45$ ensures that a minimum number of free radicals are generated, even when [NO] is very low. For [NO]/[HC] > 1, although we did not have validation data for this range, we would expect α to decrease in accordance with the peak O₃ for such ratios. The values of 2.45 and 9.8 have no significance other than the fact that they give good validation for the experiments shown. The value of β was set



Figure 5. Comparison of experimental smog chamber concentrations and concentrations predicted by the simplified mechanism

Data for isobutylene from Westberg et al. (1971) Initial concentration of carbon monoxide = 100 ppm

at 1.7. The values of δ and θ were set at 0.8 and 0.02, respectively. γ and ϵ were not needed since we did not compute the concentration of aldehydes.

Isobutylene Experiments. Next we consider the isobutylene experiments reported by Westberg et al. (1971) in the presence and absence of CO. Figure 4 presents concentration-time behavior for the following initial conditions: $[C_4H_{sl0} = 3, [NO_2]_0 = 0.04, [NO]_0 = 1.5, [CO]_0 = 0, and k_1' = 0.355 min^{-1}$. Figure 5 shows concentration-time behavior for the same initial conditions except $[CO]_0 = 100$ ppm. The purpose of these trials is to examine the performance of the simplified model for another hydrocarbon and for the effect of CO.

Because isobutylene and propylene are both terminal olefins of similar reactivity, α was kept the same as for the propylene runs. The rate constants and stoichimetric coefficients are the same as for propylene except:

$$\begin{array}{ll} k_{1}{}' &= 0.355 & \beta = 1.9 \\ k_{11}{}' &= 3.1 \times 10^4 & \delta = 0.2 \\ k_{12}{}' &= 0.017 & \theta = 0.22 \\ k_{13}{}' &= 10^4 \end{array}$$

The model results are shown in Figures 4 and 5 by the dashed lines. In the actual experiments, the NO₂ peaks 32 min sooner when 100 ppm CO is present initially (104 min vs. 136 min). In the simulation, the NO₂ also peaks 32 min sooner with 100 ppm CO (105 min vs. 137 min). The model also predicts the more rapid oxidation of isobutylene and accelerated accumulation of O₃ when CO is present.

n-Butane Experiments. We now consider the photooxidation of *n*-butane in the presence and absence of CO, as reported by Wilson (1971). The experimental results in Figure 6 have $[C_4H_{10}]_0 = 3.05 \text{ ppm}, [NO_2]_0 = 0.106 \text{ ppm}, [CO]_0 = 0,$ and $k_1' = 0.4 \text{ min}^{-1}$. For the results in Figure 7, $[C_4H_{10}]_0 =$ 3.25 ppm, $[NO_2]_0 = 0.106 \text{ ppm}, [NO]_0 = 0.50 \text{ ppm}, [CO]_0 =$ 100 ppm, and $k_1' = 0.4 \text{ min}^{-1}$. In both cases the initial NO₂ to C_4H_{10} ratio is about 1:5. The rate constants and stoichiometric coefficients were the same as propylene with the following exceptions: $k_1' = 0.4$, $k_6' = 0.004$, $k_{11}' = 2000$, $k_{13}' =$ 0.001, $k_{13}' = 6000$, $\alpha = 5$, $\beta = 0.5$, $\delta = 1.2$, and $\theta = 0.61$. Note that a constant value of α was used because of the lower reactivity of *n*-butane.

Although O_3 does not react with *n*-butane, we use a nonzero k_{13} because olefins are probably some of the first stable products formed after O and OH attack on butane. Some possible reaction schemes for olefin formation are



Figure 6. Comparison of experimental smog chamber concentrations and concentrations predicted by the simplified mechanism

Data for *n*-butane from Wilson (1971) Initial concentration of carbon monoxide = 0 ppm

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Figure 7. Comparison of experimental smog chamber concentrations and concentrations predicted by the simplified mechanism

Data for *n*-butane from Wilson (1971) Initial concentration of carbon monoxide = 100 ppm

 $C_{4}H_{10} + O \longrightarrow C_{4}H_{9} + OH \cdot$ $C_{4}H_{10} + OH \cdot \longrightarrow C_{4}H_{9} + H_{2}O$ $CH_{3}CH_{2}CH_{2}CH_{2} + O_{7} \longrightarrow C_{3}H_{5} + CH_{2} = CH_{2}$ $CH_{3}CH_{2}\dot{C}HCH_{3} + O_{7} \longrightarrow (CH_{3})_{7}C = CH_{2} + HO_{3} \cdot$

The formation of isobutylene in the butane oxidation may be evidenced by the fact that several products observed in the butane photoxidation—e.g., acetone and PAN (Altshuller, 1969)—are the same as those found in isobutylene photooxidation. The agreement between the model and the experimental results is quite close. It should be noted that the simulations in Figures 6 and 7 are for 6 hr.

Propylene and n-Butane Mixture. Next we consider the photooxidation of a mixture of propylene and n-butane carried out by Wilson (1971). The initial conditions for the experiment are $[C_{3}H_{6}]_{0} = 0.56$ ppm, $[C_{4}H_{10}]_{0} = 3.4$ ppm, $[NO_{2}]_{0} = 0.098$ ppm, $[NO]_0 = 0.48$ ppm, $[CO]_0 = 0$, and $k_1' = 0.4 \text{ min}^{-1}$. Thus, $[NO_z]_0/[C_3H_6]_0 \simeq 1$. The rate constants and stoichiometric coefficients are determined as a linear combination of those for pure propylene and n-butane, where proportionality is given by the initial concentration fraction of each in the mixture, α was set at the constant value of 3.0, with $\beta = 0.67$, $\delta = 1.2$, and $\theta = 0.53$. This method of using a linear combination of the pure hydrocarbon rate constants is similar in nature to the combined-rate approach used by Glasson and Tuesday (1971). They reported that the combined-rate approach predicted a greater oxidation rate than was observed experimentally, and we found the same phenomenon. Changing k_{15} from the combined rate value of 96 to 45, we obtained the results shown by the dashed curves in Figure 8. Aside from this one change, the model effectively predicts the behavior of this mixture with rate constants as average values based on the initial hydrocarbon fractions.

 NO_x Inhibition. Finally, we consider the effect of initial reactant ratios on the maximum O_s concentration attained during the course of the photooxidation. Extensive experimental results reported in the literature indicate that after a certain point, increasing the initial concentration of NO_x will result in a decreasing in the maximum concentration of O_s reached (Glasson and Tuesday, 1970). In some cases, smog chamber results have been presented in the form of O_s concentration after a fixed time of irradiation vs. initial concentration of NO_x at a fixed initial hydrocarbon concentration. Information of this type is useless unless the initial NO_x concentration

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Figure 8. Comparison of experimental smog chamber concentrations and concentrations predicted by the simplified mechanism

Data for propylene and n-butane from Wilson (1971)

is known in terms of both NO and NO2. This is because the time to the NO2 peak and time at which O3 appears are dependent on the individual concentrations of NO and NO2, as well as the total NO_x concentration. We can demonstrate this point quite simply. We have run two cases, in each of which $[HC]_0: [NO_r]_0 = 2:1.1$. In the first case, the NO₂ was composed of 0.1 ppm NO2 and 1.0 ppm NO, while in the second case the NO2 was composed of 0.4 ppm NO2 and 0.7 ppm NO. In the first case the NO2 peaked at 94 min while in the second, it peaked at 57 min. Although the concentration of O₃ ultimately reached about the same maximum level in both cases, after 2 hr the two concentrations were 0.424 and 0.634 ppm, respectively. The peak O₈ formation rate defined and reported by Glasson and Tuesday (1970) as [O3] max/2 11/2, where 11/2 is the time for the formation of one-half of the peak Oa concentration is also highly dependent on the initial mix of NO and NO2. The above points are illustrated in Table VII, in which the simulated results of three runs in which [NOz]o was kept constant but the individual [NO]o was varied are reported. It is clear from Table VII that if smog chamber data are reported in terms of the quantities in either of the last two columns, both the initial NO and NO2 concentrations must be reported.

One of the key requirements that a simplified mechanism for photochemical smog must satisfy is that it demonstrates the inhibitory effect of NO on the maximum concentration of O₃. Altshuller et al. (1967) have reported results on the oxidant level as a function of $[NO_2]_0$ at fixed $[C_3H_6]_0$. Even though the individual $[NO]_0$ and $[NO_2]_0$ were not reported, the irradiation time for each run was 6 hr, ensuring that the peak O₃ level had been reached. Their results are shown by the solid curve in Figure 9. We note a sharp inhibition at $[NO_2]_0$ greater than about 3 ppm for $[C_3H_6]_0 = 2$ ppm. We have simulated these runs using the general 15-step mechanism with $[NO_2]_0 = 0.1$ ppm, the results of which are shown by the dashed curve in Figure 9. It is important to realize that NO inhibition is reflected in the model by the choice of α , so that Figure 9 really

Table	VII. Effor	ect of Ini the Time	tial NO a of Appe	and NO_2 Contrained of Contrained of Contrained of Contrained of Contract o	oncentrations)3
INOL	(NO)	$1_{0} = 2$	pin, [NO	$[O_{3}]_{0} = 1.1 \text{ p}_{1}$	[Oslmar/2 tur
0.06	1 05	0 724	107	0 211	2 20 ~ 10-3
0.05	1.05	0.734	112	0.311	3 28 × 10-3
0.10	0.70	0.741	77	0.424	5 12 × 10-3
0.40	0.70	0.102		0.054	0.12 / 10



Figure 9. Effect of initial NO_x concentration on peak oxidant concentration.

Experimental curve from Altshuller et al. (1967). Model curve based on assumed initial NO2 concentration of 0.1 ppm

only shows that the choice of α is consistent with observed behavior.

Summary

The validation experiments lend strong support to the approach of using a generalized mechanism consisting of a small number of reactions and parameters for mathematical modeling of photochemical smog kinetics. We must stress that the simplified mechanism presented is by no means a unique model for smog formation. Indeed, other mechanisms may also be capable of matching experimental smog chamber data by proper choice of parameters. The mechanism we have developed represents a compact generalized scheme, in which we have strived to retain certain elements of chemical reality. It does not appear that at this point we can suggest firm rules for the selection of rate constants and stoichiometric coefficients. These must be determined by fitting the model to the sets of data available.

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APPENDIX B

MEASUREMENT OF ULTRAVIOLET RADIATION INTENSITY IN PHOTOCHEMICAL SMOG STUDIES

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Abstract

The most widely used technique of measuring ultraviolet radiation intensity in photochemical smog studies is to irradiate NO_2 in a nitrogen atmosphere. In the past a fictitious first-order rate constant, k_d , has been used to characterize the nonlinear NO_2 -time behavior in such a system. The inadequacy in the use of k_d stems from the need to extrapolate the NO_2 -time curve to zero time. The actual photolysis rate constant for NO_2 dissociation, k_1 , provides an unambiguous measure of UV intensity. If the NO_2 photolysis is performed in the usual fashion, we show that k_1 can be computed <u>directly</u> from the NO_2 -time data by the equation,

$$k_{1} = \frac{1}{2\Delta t} \left\{ (1 + R_{1} - R_{2}) \ln \frac{[NO_{2}]_{o}}{[NO_{2}]} + R_{2} \left[\frac{[NO_{2}]_{o}}{[NO_{2}]} - 1 \right] \right\}$$

where the constants R_i are defined in the text. The validity of this equation has been established both experimentally and by computer simulation.

Introduction

It is now widely accepted that among the variable factors in smog chamber experiments, such as temperature, surface to volume ratio, and relative humidity, the intensity of ultraviolet radiation is one of the most critical parameters. The radiation intensity strongly governs the time scale upon which the various processes, such as the rate of conversion of NO to NO_2 , occur. Recently there has been considerable interest in the development of kinetic mechanisms for photochemical smog (Hecht and Seinfeld, 1972 ; Niki et al., 1972; Hecht, 1972). Knowledge of the ultraviolet radiation intensity is vital to the success of computer simulations of smog chemistry, since the correctness of the rate constant for the primary process, the photolysis of NO_2 , determines the validity of the results for nearly all of the subsequent steps.

Physical measurement of UV intensity by various spectroradiometric techniques would, of course, be desirable from the standpoint of comparing the sources of artificial sunlight used in various smog chambers with one another and with the ultraviolet portion of the solar spectrum. However, such absolute measurements require specialized apparatus which is complex and relatively expensive. Since it was first suggested by Tuesday (1961), the photolysis of NO₂ in nitrogen has become more or less universally accepted as the way of calibrating UV sources used in photochemical smog studies. The rationale for this method is that the fundamental photochemical process in smog formation is the photolysis of NO₂:

$$NO_2 + hv \xrightarrow{k_1} NO + O \tag{1}$$

and that the rate of this reaction determines, to a large extent, the rate of the overall process. Thus, it is not necessary to measure the spectral distribution of the radiation, only the first-order decay constant k_1 .

The assumption implicit in smog chamber experiments is that artificial radiation which drives Reaction 1 at a rate comparable to that observed with natural sunlight will also allow the experimenter to simulate all of the other processes which occur in the atmosphere. This assumption is not completely valid, since other species present in smog can also undergo photolysis or photo-excitation and the rates of these processes, in general, have a wave-length dependence different from that of NO₂. To a good approximation, however, these other processes can be neglected and the rate of the primary process can serve as a useful measure of UV intensity within the limitations discussed below.

The key problem in using a system of NO_2 photolysis in N_2 is to determine the photolysis rate constant k_1 from the NO_2 concentration vs. time data. It is well known that the photolysis of NO_2 in N_2 is <u>not</u> a first order process because of a number of side reactions that take place in addition to Reaction 1. Thus, the $ln NO_2$ concentration vs. time data will not lie on a straight line. In spite of this fact, it has been common practice to define a fictitious first-order rate constant k_d for NO_2 disappearance in N_2 . The fictitious rate constant k_d is defined by

$$k_{d} = \frac{\lim_{t \to 0} \frac{-d\ln[NO_2]}{dt}}{dt}$$
(2)

that is, the slope of the NO_2 decay curve extrapolated to time zero. Since k_1 , the desired parameter, has been considered a difficult quantity to measure directly, it has become common practice to use k_d rather than k_1 as the
measure of light intensity in smog chambers. The accuracy of using this approach to calculate k_d is governed by how rapidly and accurately the NO₂ concentration can be determined after the lights are turned on, time being particularly important when the light intensity is strong.

The primary object of this work is to eliminate entirely the quantity k_d in favor of direct measurement and reporting of k_1 , the primary photolysis rate constant. As a result of both experimental and theoretical studies, we have developed a simple method of determining directly the actual rate constant for NO₂ photolysis, k_1 , in systems of NO₂-N₂.

Mechanism of NO_2 Photolysis in N_2 and O_2

The mechanism generally employed in interpreting the photolysis of ppm levels of NO_2 in N_2 and O_2 is presented in Table I. The first ten reactions were proposed by Ford and Endow (1957) for the system free of O_2 -Reaction 11 has been added for the case in which O_2 is present. The primary process, Reaction 1, is dependent on light intensity; all other reactions result from the highly reactive nature of the oxygen atoms formed in Reaction 1.

Ford and Endow (1957) and Schuck et al. (1966, 1969) investigated the mechanism for NO_2 photolysis. When there is no O_2 present initially, it is possible to assume that 0, O_3 , NO_3 and N_2O_5 are in pseudo-steady state. Also under these conditions Reactions 8 and 11 can be neglected. Using these assumptions, Schuck et al. (1966, 1969) derived the following equation for the rate of change of NO_2 concentration:

TABLE I

Reactions and Rate Constants for the Photolysis of Nitrogen Dioxide in Dry Nitrogen and Oxygen

No.	Reaction	Rate Constant	Reference
1.	$NO_2 + hv \longrightarrow NO + 0$	To be Estimated	
2.	$0 + 0_2 + M \longrightarrow 0_3 + M$	$2.33 \times 10^{-5} \text{ ppm}^{-2} \text{min}^{-1}$	Johnston (1968)
3.	$0_3 + N0 \longrightarrow N0_2 + 0_2$	$2.95 \times 10^{1} \text{ ppm}^{-1} \text{ min}^{-1}$	Johnston and Crosby (1954)
4.	$0 + NO_2 \longrightarrow NO + O_2$	1.38 x 10 ⁴ ppm ⁻¹ min ⁻¹	Schuck <u>et al</u> (1966)
5.	$0 + NO_2 + M \longrightarrow NO_3 + M$	$4.50 \times 10^{-3} \text{ ppm}^{-2} \text{ min}^{-1}$	Schuck <u>et al</u> (1966)
6.	$NO_3 + NO \longrightarrow 2 NO_2$	1.48 x 10 ⁴ ppm ⁻¹ min ⁻¹	Schott and Davidson (1958)
7.	$0 + NO + M \longrightarrow NO_2 + M$	$2.34 \times 10^{-3} \text{ ppm}^{-2} \text{ min}^{-1}$	Kaufman (1958)
8.	2 NO + 0 ₂ \longrightarrow 2 NO ₂	$7.62 \times 10^{-10} \text{ ppm}^{-2} \text{ min}^{-1}$	Glasson and Tuesday (1963)
9.	$NO_3 + NO_2 \longrightarrow N_2O_5$	$4.43 \times 10^{-3} \text{ ppm}^{-1} \text{ min}^{-1}$	Schott and Davidson (1958)
10.	$N_2O_5 \longrightarrow NO_3 + NO_2$	1.38 x 10 ¹ min ⁻¹	Mills and Johnston (1951)
11.	$NO_2 + O_3 \longrightarrow NO_3 + O_2$	1.06 x 10 ⁻¹ ppm ⁻¹ min ⁻¹	Johnston and Yost (1949)

$$\frac{-2k_1}{\frac{d \ln[NO_2]}{dt}} = 1 + \frac{k_5[M]}{k_4} + \frac{k_7[M][NO]}{k_4[NO_2]} + \frac{k_2[M][O_2]}{k_4[NO_2]}$$
(3)

where the k's are the rate constants for the corresponding reactions in Table I.

If k, is defined by Eq. (2) then Eq. (3) can be written

$$\frac{2k_1}{k_d} = 1 + \frac{k_5[M]}{k_4} + \frac{k_7[M][NO]}{k_4[NO_2]} + \frac{k_2[M][O_2]}{k_4[NO_2]}$$
(4)

Equation (4) seems complex but it can be readily interpreted. In the absence of any reactions except 1 and 4 all oxygen atoms formed would react with NO_2 to form NO and O_2 . This gives an overall quantum yield of 2 -- two molecules of NO_2 disappear for each photon absorbed. This would give the relationship $k_d = 2k_1$ and would hold if the experiment were run without N_2 at low pressure (M = 0). In the actual case, however, various species compete with NO_2 for the 0 atoms. The effect of this competition is expressed in the last three terms in Eq. (4). These are the ratios of oxygen-atom reaction rates by other pathways to the rate of Reaction 4.

Schuck et al. (1966) analyzed their experimental data using Eq. (4) and obtained values or the various rate constants which they compared to previous determinations, some of which have large uncertainties. These are in good agreement with previous evaluations except for k_4 , for which they derive a value 50% higher than the number generally accepted (Baulch, et al. 1970).

What was apparently not recognized previously is that Eq. (3) may be integrated analytically under the assumption that NO and NO₂ constitute all of the NO₂ at any instant, i.e., that

$$[NO] = [NO]_{0} + [NO_{2}]_{0} - [NO_{2}]$$
(5)

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The result of the integration of Eq. (3) subject to Eq. (5) is the following fundamental expression:

$$k_{1} = \frac{1}{2\Delta t} \left\{ (1 + R_{1} - R_{2}) \ln \frac{[NO_{2}]_{o}}{[NO_{2}]} + R_{2} \left[\frac{[NO_{2}]_{o}}{[NO_{2}]} - 1 \right] + (R_{2}[NO_{0} + R_{3}[O_{2}]) \left[\frac{[NO_{2}]_{o} - [NO_{2}]}{[NO_{2}]_{o}[NO_{2}]} \right] \right\}$$
(6)

where $\Delta t = t(final) - t(initial)$ and

$$R_1 = \frac{k_5[M]}{k_4}$$
 $R_2 = \frac{k_7[M]}{k_4}$ $R_3 = \frac{k_2[M]}{k_4}$

Equation (6) may be simplified if the initial concentrations of NO and $^{\rm O}2$ are zero,

$$k_{1} = \frac{1}{2\Delta t} \left\{ (1 + R_{1} - R_{2}) \ln \frac{[NO_{2}]_{o}}{[NO_{2}]} + R_{2} \left[\frac{[NO_{2}]_{o}}{[NO_{2}]} - 1 \right] \right\}$$
(7)

In the remainder of this paper we establish experimentally the validity of the mechanism in Table I (the Ford-Endow mechanism) for the photolysis of NO_2 in N_2 and verify the assumptions made in the derivation of Eq. (7).

Photolysis of NO_2 in N_2

Experimental System. A long-path infrared system similar to that described by Pitts (1969) was employed. A 90-liter borosilicate glass reactor encloses the sample cell and optics. The reactor is surrounded by twenty 20-watt fluorescent tubes. In the initial experiments ten black-lights and ten sun lamps were used. However, the sun lamps make a relatively small contribution to the rate of NO₂ photolysis because the absorption coefficient is lower for sun lamps than for black-lights and because shorter wavelength ultraviolet is more strongly absorbed by the reactor walls. Thus, in later experiments twenty black-lights were employed to provide a rate of photolysis more nearly comparable to that produced by intense sunlight.

The system is evacuable to 10⁻⁶ torr. The interior metal surfaces, excepting the mirrors, have been coated with a non-porous fluorocarbon resin. The spectrophotometer is a Perkin-Elmer Model 521 equipped with scale expansion which, in effect, allows the maximum optical path length of the cell to be increased electronically from 40 to 800 m. Temperature within the reaction cell is monitored continuously. External forced-air cooling maintains the cell within 2^oC of ambient temperature during irradiation. Trace gases are introduced into the LPIR cell at known pressures (measured with a silicone-oil manometer) from calibrated volumes. The final pressure is brought to one atmosphere with Ultra Pure (Airco 99.998%) grade nitrogen. The NO₂ was purified by pressurizing with O₂ followed by vacuum distillation.

Experimental Results. In the LPIR, we obtain a continuous record of NO_2 concentration as a function of time. Any departure from linearity of the plot of ln (NO_2) <u>vs</u>. time is immediately apparent from the experimental data. Figure 1 shows the results of such an experiment under conditions at which one typically measures k_d . The departure from linearity is appreciable even for short irradiation times. The effect is even more pronounced at high light intensity, such as is present in most environmental chambers.

In our case, the problem of non-linearity is easily overcome by extrapolating back to t = 0 and taking the initial slope of the curve as the value of k_d . For experimental situations where the NO₂ concentration cannot be monitored continuously as a function of time this extrapolation could not be performed.

Two series of experiments were performed to investigate the validity of Eq. (4). This equation may be simplified under certain experimental conditions. If the 0_2 concentration is below 50 ppm, the last term is small and may be ignored. Further, at the beginning of photolysis no NO is present so the second to last term is also negligible since the NO₂ decay rate is extrapolated to zero time.

The first series of experiments involved varying the pressure of M in the k_d determination.Eq. (4) predicts that at zero pressure of added N_2 , $k_1 = k_d/2$. Therefore, this approach should give the best value of the absolute light intensity in terms of k_1 . Figure 2 shows the results of these experiments which were run with varying amounts of added N_2 , corresponding to 0, 0.1, 0.4, 0.7 and 1.0 atm N_2 . If one neglects the datum for no added N_2 , the least squares line of the remaining points extrapolates to $k_1 = 0.144 \text{ min}^{-1}$ at $P_{N_2} = 0$. From the slope of the line a value of $k_5/k_4 = 0.27 \times 10^{-6}$ can be calculated directly. The experimental point at [M] = 0 ($k_d^{-1} = 5.0 \text{ min.}$) is probably not valid, since at this pressure (5 millitorr) diffusion to the walls is rapid: those reactions which require a third body at higher pressures would be expected to occur, instead, on the walls. At pressures above 0.1 atm, wall effects are negligible. In these experiments it was necessary to correct for deviation from the Beer-Lambert Law since the IR absorption of NO_2 is strongly pressure dependent.

In another series of experiments, varying amounts of NO were added to the NO_2 before photolysis. Assuming the last term in Eq. (4) is small it may be rearranged to the form

$$\frac{1}{k_{d}} = \frac{1 + R_{1}}{2k_{1}} + \frac{R_{2}[NO]}{2k_{1}[NO_{2}]}$$
(8)

Thus, a plot of k_d^{-1} <u>vs</u>. [NO]/[NO₂] for these experiments would be expected to be linear. This is shown in Figure 3. The linearity is excellent and the following relationships can be derived:

$$R_2 = 2k_1 \times \text{slope}$$
(9)

$$intercept = \frac{1 + R_1}{2k_1}$$
(10)

Since k_1 is known from the first series of experiments a value of R_2 can be calculated from Eq. (9). The result is $R_2 = 0.16$, Eq. (10) may be used to check on the internal consistency of the data with the mechanism. From the values of k_1 and R_1 found in the first series of experiments a value for the intercept in Figure 3 may be predicted. The predicted value is 4.41 min. while the actual intercept is 4.28 min.

Validation of the Ford-Endow Mechanism and Estimation of k_1 . A computer simulation of the Ford-Endow mechanism for the photolysis of NO₂ yields results which are in excellent agreement with the experimental results over a wide range of initial conditions. A comparison for two typical runs is shown in Figure 1. The curves are from the simulation and the points indicate experimental data. Optimum agreement was obtained using the rate constants of Schuck and Stephens (1969), including the larger value of k_4 discussed above. The curves in Figure 1 can also be generated from the integrated form of the rate expression, Eq. (7). The latter are identical to the computer simulation.

The simulation also computed the concentrations of all nitrogen-containing species appearing in the mechanism. The results indicate that the assumptions made in deriving and integrating Eq. (3) are indeed valid.

Table II shows the results of the estimation of k_1 by Eq. (7) for two types of systems: varying initial NO₂ concentrations with zero initial NO concentration, using 20 blacklight fluorescent lamps, and fixed NO₂ and varying NO using 10 lamps. The estimated value of k_1 is a constant in each case, values of k_1 differing only because the UV intensity was different for the two sets of experiments. The estimated value of k_1 for 10 lamps (avg, 0.143 min⁻¹) is in excellent agreement with the experimental value of k_1 (0.144 min⁻¹) shown in Figure 2 determined by reducing the pressure of the system.

[NO2]0(ppm)	[NO] _o (ppm)	k ₁ (min ⁻¹)	No. of Lamps
1.00	0,0	0.319	20 BL
3,11	0.0	0.312	20 BL
4,92	0.0	0.325	20 BL
5.00	0.0	0.322	20 BL
6.99	0.0	0.312	20 BL
5.02	0.0	0.147	10 BL
5.04	19.8	0.140	10 BL
5.04	50.7	0.141	10 BL

<u>Discussion of the Experimental Results</u>. A study has recently been published (Laity, 1971) comparing blacklight fluorescent lighting to natural sunlight for several synthetic smog mixtures. No significant difference in the rates of reaction or in the products was found, thus further establishing the usefulness of the NO₂ photolysis method of measurement of light intensity.

Dimitriades (1970) reported that the temperature of blacklight fluorescent lamps must be carefully controlled if their ultraviolet output is to remain constant. Most lamps yield maximum UV at an ambient temperature of about 70°F (22°C). Our experience indicates that a rise of 30°F in the temperature of the air surrounding the lamps results in a 40% decrease in UV output, as measured by a photoresistor sensitive to light in the 300-400 nm range. Moreover, some lamps exhibit a warm-up period of several minutes over which the intensity

Table II

Summary of NO₂ Photolysis Data and

gradually increases to the maximum value. It is important that the light intensity be constant or at least well defined during the k_1 measurement. This may not be the case if the lamps are switched on to initiate photolysis. The lamps used in this study achieved constant intensity immediately.

Algebraic analysis of Eq. (4) allows one to deduce values of R_1 , R_2 and R_3 but not of the individual rate constants contained in these terms. Our values of these terms along with those of Schuck et al.(1966) are shown below.

Rate - constant ratio	This work	<u>Shuck et al. (1966)</u>		
R ₁	0.27	0.33		
R ₂	0.16	0.18		
R ₃	not determined	0.00115		

The concentration range investigated in this study is the most useful for k_1 studies in environmental chambers. Much additional work has been conducted at higher NO₂ pressures (<u>ca</u>. 1000 ppm) in the past. The results of these earlier studies are not conclusive and the mechanism for photolysis at these higher concentrations is not satisfactorily established. It is probable that reactions not included in the Ford-Endow mechanism are important at higher NO₂ partial pressures. For example, photoexcited states of NO₂ produced by radiation of wavelength greater than about 385 nm (the midpoint of the dissociation region) are important at higher NO₂ concentrations. However, we have estimated the contribution from these processes at the NO₂ pressures used in this work and find it to be negligible as a result of rapid collisional deactivation by N₂. Finally, we wish to stress that the use of k_d rather than k_1 should henceforth be avoided in all light intensity determinations. Figure 4 shows the apparent value of k_d as a function of Δt where Eq. (2) has been approximated by

$$k_{d} = -\frac{1}{\Delta t} \ln \frac{[NO_{2}]}{[NO_{2}]}$$

When determined by this formula, k_d varies strongly with Δt , particularly at k_1 values typical of normal bright noonday sun in Los Angeles (about 0.3^2 min^{-1}). The error in assuming that the NO₂-time curve is linear for even a few minutes is quite significant. The determination of k_1 from Eq. (7) eliminates the need to extrapolate the curve to zero time and provides a direct means of calculating k_1 .

Effect of 0_2 on NO_2 Photolysis in N_2

The above experimental results have been obtained for a system initially free of 0_2 . Often there may exist small amounts of 0_2 as an impurity in the N_2 or as a result of inadequate purging of the chamber. It is of importance, therefore, to assess the effect of the presence of 0_2 on the value of k_1 calculated from Eq. (7) assuming no 0_2 is present. In Table III we show the effect of initial 0_2 concentration on the calculated value of k_1 from Eq. (7), assuming no 0_2 is present. We see that up to 20 ppm, the presence of 0_2 has little effect on the calculated value of k_1 at $k_1 = 0.4 \text{ min}^{-1}$. We recommend, therefore, that experimenters use a grade of N_2 containing below 20 ppm of 0_2 or take precautions to remove 0_2 before performing the $N0_2$ photolysis. For those 0_2 concentrations for which Eq. (6) is valid, Eq. (6) can be used directly to compute k_1 from $N0_2$ vs. time data when 0_2 is present. To assess the validity of Eq. (6), we have compared the predicted k_1 values from Eq. (6) with the actual value of 0.4 min⁻¹ as in Table III, as obtained by a numerical solution of the mechanism in Table I. We see that Eq. (6) is valid up to about 1000 ppm of O_2 , at which point the assumption that O_3 is in steady state begins to be in error. We note that the data from which k_1 has been calculated were obtained by numerically integrating the mechanism in Table I using the rate constants in Table I, whereas the calculated values of k_1 from Eqs. (6) and (7) were obtained using the experimentally obtained values of R_1 and R_2 . This accounts for the discrepancy between the actual and calculated k_1 values at 0 ppm of O_2 .

Photolysis of NO_2 in air has been considered by Bufalini and Stephens (1965). Because of several experimental problems, such as removing water, CO and hydrocarbon impurities present in air, this represents a less desirable means of computing k_1 than does NO_2 photolysis in N_2 .

Table III. Effect of O_2 on the Calculated Value of k_1 from Eqs. (6) and (7). Actual Value of $k_1 = 0.4 \text{ min}^{-1}$

[0 ₂], ppm	0	20	50	100	200	500	1000	100
Apparent value of k ₁ , min ⁻¹ , Eq. (6)	0.38	0.38	0.38	0.38	0.39	0.41	0.44	
Apparent value of k ₁ , min ⁻¹ , Eq. (7)	0.38	0.37	0.35	0.33	0.29	0.23	0.18	

Conclusions

As a result of this study we recommend that the fictitious parameter k_d henceforth be abandoned as a measure of the light intensity in a smog chamber in favor of k_1 , the absolute photolysis rate of NO₂. The data needed to calculate k_1 from the irradiation of NO₂ in N₂ by Eq. (7) are no different than those previously used to calculate k_d , so that the experimental technique remains unchanged. We have demonstrated the feasibility of using this method in the ranges of 1-7 ppm of NO₂ and 0-50 ppm of NO.

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- Figure 2. Pressure Dependence of k_d Determination (Photolysis of 5 ppm NO_2 at varying Pressure of N_2)
- Figure 3. Variation of k_d with Added NO (Photolysis of Mixtures of 5.0 ppm NO₂ and Varying NO)
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Figure 4

Appendix C

THE DETERMINATION OF k, IN AIR

In Chapter IIJ we described a method for determining k_1 in an inert atmosphere. However, there is a great need for a general method of computing k_1 from the NO2 concentration vs. time data collected during the photolysis of a given mixture of NO_2 , N_2 and O_2 (such as NO_2 in air). This need arises for two reasons. First, it is often difficult to purge all the O2 from a system of NO2 and N_2 , and thus it is of interest to know at what level of O_2 impurity deviations from the behavior of a pure NO2-N2 system begin to appear. Second, with the advent of large outdoor irradiation chambers, it will be impractical to determine k_1 in an NO_2-N_2 system; rather, one must be able to estimate k_1 from an NO₂-air system. We present in the appendix a general method for directly and accurately determining k1 from the NO2 concentration-time data gathered during the photolysis of a mixture of NO₂, NO, N₂ and O₂ of any initial concentration.*

The method is the following. One irradiates NO_2 or NO_2 and NO in N_2 and O_2 (e.g. dry air), noting the initial concentrations and thereafter recording the NO_2 concentration in the system at several times over the course of the irradiation, for example, every minute or so for a period of ten minutes. The experimental data obtained can be denoted by $NO_2^{exp}(t_i)$, i = 1, 2, ..., R, where R is the number of data points. Since the reaction mechanism of a system consisting of NO_2 , NO, O_2 and is known, and all the rate constants except

^{*} It is important to point out that the validity of this approach is subject to experimental confirmation under a range of conditions. Such verification is necessary to guarantee that the mechanism in Table 1 (presented in Chapter III) completely describes the chemistry of NO_x in the presence of O_2 .

 k_1 are known (see Table 1), one can numerically integrate the differential rate equations governing the system, given any assumed value of k_1 . Let us denote the result of this integration by $NO_2^{calc}(t)$. The objective, then, is to determine that value of k_1 which produces the closest match between the calculated NO_2 concentrations, $NO_2^{calc}(t_i)$, and the experimental concentrations, $NO_2^{exp}(t_i)$.

A useful way to quantify the stated problem is as follows: Find that value of k_1 which minimizes the unweighted least squares objective function

$$S = \sum_{i=1}^{R} [NO_{2}^{exp}(t_{i}) - NO_{2}^{calc}(t_{i})]^{2}$$
(1)

(If we suspected that some data points were subject to more experimental error than others, we might weight the residuals so as to reflect these differences.) We thus wish simply to estimate a set of constant parameters (in this case, only one) in a system of ordinary differential equations, given a set of experimental data, a problem that has received an enormous amount of attention in the literature, particularly with regard to chemical kinetics (for example, see Bard and Lapidus, 1968) . A particularly efficient technique for carrying out the minimization of S is called quasilinearization, a procedure which essentially involves an extension of the Newton-Raphson method to systems governed by ordinary differential equations. For details of the method we refer the reader to Lee (1968) and Seinfeld (1970). In order to estimate k_1 using this technique we need first to formulate the differential equations for the species in the mechanism in Table 1. A differential equation is not needed for oxygen atoms, as the concentration of this species is at steady state. Let $[NO_2] = z_1$, [NO] = z_2 , $[O_3] = z_3$, $[NO_3] = z_4$, $[O_2] = z_5$, $[N_2O_5] = z_6$ and the desired parameter $k_1 = z_7$. Using the steady state relation,

$$[0] = z_1 z_7 / (k_2 z_5 [M] + k_4 z_1 + k_5 z_1 [M] + k_7 z_2 [M])$$
(2)

in the rate equations for z_1 to z_6 , we can write the rate equations in the form

$$\frac{dz_i}{dt} = g_i(z_1, \dots, z_7) \quad i = 1, 2, \dots, 6$$
 (3)

In addition, since k₁ is constant,

$$\frac{dz_7}{dt} = g_7 = 0$$
 (4)

The g_i are obtained directly from Table 1. The differential equations (3) can be integrated easily on a digital computer.

We now summarize the digital computer algorithm for estimating k_1 (the derivation of the algorithm may be found in Lee (1968)):

- 1. Make an initial guess for $k_1(z_7)$ and integrate Equations (3) from t = 0 to $t = t_R$. Denote this solution by $z^{(0)}(t) = [z_1^{(0)}(t), \dots, z_7^{(0)}(t)]$.
- 2. Solve the six homogeneous equations

$$\frac{\mathrm{d}\phi_{\mathbf{i}}}{\mathrm{d}\mathbf{t}} = \sum_{\mathbf{j}=1}^{7} \left(\frac{\partial g_{\mathbf{i}}}{\partial z_{\mathbf{j}}} \right)_{z} (0) \phi_{\mathbf{j}}; \phi_{\mathbf{i}} (0) = 0$$

$$i = 1, 2, \dots, 6$$
 (5)

from t = 0 to t = t_R with $\phi_7 = k_1^{(0)}$, the initial guess.

$$\frac{dp_{i}}{dt} = g_{i}^{(0)}(t) + \sum_{j=1}^{7} \left(\frac{\partial g_{i}}{\partial z_{j}}\right)_{z^{(0)}} (p_{i} - z_{i}^{(0)})$$
 (6)

$$p_i(0) = z_i(0) i = 1, 2, \dots 6$$

from
$$t = 0$$
 to $t = t_p$. Note that $p_7(t) = 0$.

4. Compute an improved estimate of k_1 from

Ŧ

$$k_{1}^{(1)} = \frac{\sum_{r=1}^{R} [NO_{2}^{exp}(t_{r}) \phi_{1}(t_{r}) - p_{1}(t_{r}) \phi_{1}(t_{r})]}{\sum_{r=1}^{R} \phi_{1}^{2}(t_{r})}$$
(7)

5. Generate improved values of
$$z_i(t)$$
 from
 $z_i^{(1)}(t) = k_1^{(1)} \phi_i(t) + p_i(t)$ i = 1,2,...,6
 $z_7^{(1)}(t) = k_1^{(1)}$ (8)

- 6. Return to step 2 using $z^{(1)}$ in place of $z^{(0)}$.
- 7. Continue to iterate until a subsequent estimate of k_1 does not change by more than some preset criterion (e.g., 0.001),

$$\frac{\left|k_{1}^{(\ell+1)}-k_{1}^{(\ell)}\right|}{k_{1}^{(\ell)}} < \varepsilon$$

Although we have not obtained experimental data with which to test the algorithm, we have been able to assess theoretically the effect of 0, on the decay rate of NO, in sunlight. Figure 1 shows the effect of the level of 0, on the NO₂ behavior during irradiation, based on the mechanism shown in Table 1. We note that, as the amount of oxygen present increases, the initial rapidity of disappearance of NO, increases, but the total amount of NO, lost over a fixed time of irradiation decreases. Thus, two potential measurement problems exist in such an experiment. First, small changes in NO2 concentration must be detected. For example, upon irradiation of 1 ppm of NO2 in air, only 10% of the initial charge is lost over a fiveminute interval. Second, since the greatest change in NO, concentration occurs in the first minute, measurements must be carried out rapidly. Instrument response time is important in this regard. Both problems might be circumvented by measuring the accumulation of NO instead of the depletion of NO2, since NO can be measured more accurately and quickly than NO2 (e.g., by chemiluminescence). The algorithm presented requires only minor modification if NO, rather than NO2, is to be measured.

We have tested the algorithm for estimating k_1 for the $NO_2-N_2-O_2$ system by generating NO_2 vs. time data for $[NO_2]_0=1$ and 10 ppm and $k_1 = 0.4 \text{ min}^{-1}$ through numerical integration of the mechanism in Table 1. Five data points, collected over a period of 1.5 minutes, were selected as "experimental data" with which to estimate k_1 using the algorithm. The results of the computer experiments are summarized in Table 2. The algorithm rapidly converged to the "true" value of



 k_1 , and, as can be seen in Figure 2, the final predicted decay of NO₂ in air (solid line) agrees very well with the data used for the estimation (triangles).

It is important to emphasize again that, although we have demonstrated the applicability of the algorithm for estimating k_1 using the mechanism shown in Table 1, the validity of this mechanism has yet to be established experimentally.

Table 2. Estimation of k_1 from NO₂ Photolysis in Air

NO _{2 o} (ppm)	$k_1^{(0)}(min^{-1})$	Iterations	$k_1^{(final)}(min^{-1})$
1.0	0.2	13	.400
1.0	0.35	10	.400
10.0	0.35	12	. 399



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Appendix D

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Radical Attack on Propylene as Studied by Electron Spin Resonance

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Abstract: The reactions of propylene with hydroxyl, phenyl, and *tert*-butoxyl radicals have been studied in liquid propylene or mixtures of propylene with ethyl ether. Hydroxyl radicals add to either side of the olefinic linkage, phenyl radicals add predominantly to the terminal carbon atom to give alkyl radicals, and *tert*-butoxyl radicals abstract hydrogen to form allyl radicals. The different behavior of these and other radicals reported in the literature toward propylene is discussed in terms of their electron affinities, and some consequences regarding the formation of aerosols in polluted air are presented.

Propylene, released into the air in auto exhaust, plays an important role in the formation of photochemical smog, and is typical of many of the reactive hydrocarbons present in polluted air.¹ While the initial products of the bimolecular reactions between oxygen atoms (produced by the photodissociation of NO_2 in sunlight) and olefins have been determined,² the reactions between hydroxyl and other free radicals present in polluted atmospheres are still far from being understood in complete detail. Three routes for the radicalpropylene reactions appear possible: addition to either side of the olefinic linkage or abstraction of a hydrogen atom, leading to alkyl radicals in the first two cases or to allyl radicals in the third case. Recently,

 $R \cdot + CH_2 = CH - CH_3 \longrightarrow R - CH_2 - CH_3$ (1)

$$\mathbf{R} \cdot + \mathbf{CH}_2 = \mathbf{CH} - \mathbf{CH}_3 \longrightarrow \cdot \mathbf{CH}_2 - \mathbf{CH}(\mathbf{R}) - \mathbf{CH}_3 \qquad (2)$$

$$\mathbf{R} \cdot + \mathbf{CH}_{2} = \mathbf{CH} - \mathbf{CH}_{3} \longrightarrow \mathbf{RH} + \mathbf{CH}_{2} = \mathbf{CH}_{2} = \mathbf{CH}_{2} \quad (3)$$

5

it was reported that triethylsilyl radicals, methylthiyl

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radicals, and *tert*-butylthiyl radicals add to propylene according to reaction 1 in the liquid phase at low temperatures.³ Under the same conditions, however, *tert*-butoxyl radicals abstract hydrogen from propylene according to reaction 3⁴ while no reactions with alkyl radicals were observed.³ Of particular importance for the formation of smog products are reactions with hydroxyl radicals, whose most likely sources in the atmosphere are hydrogen abstraction from hydrocarbons by oxygen atoms

$$O + RH \longrightarrow R \cdot + \cdot OH \tag{4}$$

photolysis of nitrous acid

$$NO + NO_2 + H_2O \longrightarrow 2HONO$$

HONO
$$\longrightarrow OH + NO$$

and reactions between hydroperoxy radicals and nitrous oxide

$$HO_2 \cdot + NO \cdot \longrightarrow \cdot OH + NO_2$$
 (6)

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Figure 1. Esr spectra of radicals produced by photolysis of H2O2 in ethyl ether-propylenc at -80°.



Figure 2. Esr spectra of radicals produced by photolysis of H₂O₂ in ethyl ether-propylene after 40 min of irradiation at -80° .

In a mass spectrometric study of OH-propylene reactions in a discharge flow system, Morris, et al.,5 found mass peaks corresponding to OH adducts suggesting that addition might be the preferred route. They encountered difficulties in the product analysis, however, because of the transient nature of the products. Griffiths, et al.,6 studied the reactions of amino and hydroxyl radicals with propylene in acidified aqueous solutions at room temperature by esr using a rapid flow-mix technique and reported the addition of these radicals to the olefin according to reaction 1.

In our study we have reexamined the reactions of hydroxyl radicals with propylene to determine whether addition occurs exclusively to the terminal carbon atom (eq 1). Furthermore, the reactions with tert-butoxyl, phenyl, and α -ethoxyethyl radicals were studied in degassed and oxygen-saturated solutions of pure propylene or mixtures of propylene and ethyl ether at low temperatures, and the short-lived intermediates were identified by esr.

Experimental Section

The esr experiments were carried out at temperatures between -60 and -90° with static samples which were irradiated with uv light in the cavity of an esr spectrometer. The light source and other details of the apparatus have been described previously.7

The primary radicals were produced by photolysis of tert-butyl peroxide (Matheson Coleman and Bell), tert-butyl perbenzoate (Ram Chemicals), and tert-butyl hydroperoxide (MCB) in liquid propylene, and 80% aqueous hydrogen peroxide (Food Machinery Corp., Becco Division) in a mixture of equal amounts of ethyl ether and propylene. The samples were free of oxygen, if not stated otherwise, and those containing ether and hydrogen peroxide were dried over sodium sulfate for at least 24 hr before use to remove water.

Products were identified by comparison of their glpc retention times with those of authentic samples.

Results

Irradiation of propylene without added peroxide gave no esr signals. Hydroxyl radicals were produced

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Figure 3. Esr spectra of radicals produced by photolysis of tertbutyl perbenzoate in propylene at -90°.

from hydrogen peroxide and tert-butyl hydroperoxide, tert-butoxyl radicals from tert-butyl peroxide, tert-butyl hydroperoxide, and tert-butyl perbenzoate, and phenyl radicals were generated from tert-butyl perbenzoate. As in earlier studies these initially formed radicals were not observed by esr.8

Hydrogen Peroxide. Since hydrogen peroxide is insufficiently soluble in liquid propylene, mixtures of approximately equal amounts of ethyl ether and propylene were used as solvent. Hydroxyl radicals produced by photolysis of hydrogen peroxide can attack both the ether and the propylene. Figure 1 shows the esr spectrum of a solution of 0.2 M H₂O₂ in etherpropylene at -80° . The center of the spectrum was recorded after 7 min of irradiation. Under continuous irradiation (40 min) the spectrum shown in Figure 1 was converted rapidly into the broad line spectrum of Figure 2. Some of the lines in Figure 1 can be assigned to radical 1 which is derived from ether by abstraction

CH3CHOCH2CH3 1

of an α -hydrogen atom by a hydroxyl radical. In the absence of propylenc only 1 was observed. Its hyperfine splitting parameters, $a_{\rm H}^{\rm CH} = (13.75 \pm 0.1)$ G, $a_{\rm H}^{\rm CH_3} = (21.50 \pm 0.1)$ G, and $a_{\rm H}^{\rm CH_2} = (1.58 \pm 0.05)$ G agree well with those obtained in acetone⁹ and water¹⁰ at higher temperatures. The other lines in Figure 1 are presumably due to short-lived radicals derived from propylene. In contrast, the radicals of Figure 2 were relatively stable; their half-life at -80° was about 30 min. Ice crystais were visible in the system after prolonged irradiation.

tert-Butyl Peroxide. tert-Butyl peroxide decomposes into two tert-butoxyl radicals which attack the solvent or fragment into acetone and methyl radicals.11 In pure propylene at -80° we observed only allyl radicals (2) resulting from hydrogen abstraction by tert-

CH2===:CH2===CH2

butoxyl radicals from propylene as reported previously by Kochi and Krusic.⁴ No additional lines were observed in the spectra when the irradiation was continued for 1 hr. Comparison with Figure 1 showed that no allyl radicals were present in the spectra obtained by photolysis of hydrogen peroxide. When tertbutyl peroxide was photolyzed in a mixture of equal amounts of ether and propylene at -80° only radicals

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only methyl radicals during the first few minutes of irradiation.

1 were observed. This indicates that these radicals are too stable to attack propylene rapidly.

The additional lines in Figure 1, therefore, are expected to be due to radicals 3 and 4, generated in reac-

tions 1 and 2. For comparison, radical 4 was produced by photolysis of hydrogen peroxide in a mixture of isopropyl alcohol and propylene at -80° , which yielded also acetone ketyl radicals derived from α hydrogen abstraction from the alcohol. Its spectrum exhibited a doublet of triplets of relatively broad lines with 1.2-G line width and the coupling constants $a_{\rm H}^{\rm CH} = (26.2 \pm 0.1) \, \rm G \text{ and } a_{\rm H}^{\rm CH_2} = (21.85 \pm 0.1) \, \rm G,$ which differ slightly from those obtained earlier by Livingston and Zeldes¹² in a mixture of water and isopropyl alcohol at -5° ($a_{\rm H}^{\rm CH} = 24.38$ G, $a_{\rm H}^{\rm CH_2} =$ 22.06 G). The broad lines in Figure 1 can be assigned to radical 4 and the remaining sharp lines to radical 3 with the coupling constants $a_{\rm H}^{\rm CH} = (21.8 \pm 0.1)$ G and $a_{\rm H}^{\rm CH_2} = a_{\rm H}^{\rm CH_2} = (24.7 \pm 0.1)$ G as indicated by the computed spectra. The equivalence of the methyl and methylene protons in radical 3 indicates that rotation of the methylene group around the C_{α} - C_{β} bond axis is not hindered by the hydroxyl group. Little or no hindrance was also found in earlier studies on a series of radicals of the type $X\dot{C}HCH_2OH$ (X = CO_2H , CO₂CH₃, CO₂C₂H₅, and CN).¹³ However, in water the coupling constant of the methylene protons was found to be only 19.8 G⁶ indicating that in this solvent rotation might be hindered by interaction with the polar water molecules.

tert-Butyl Hydroperoxide. Since it was found that tert-butoxyl radicals exclusively abstract hydrogen from propylene while hydroxyl radicals add to the double bond it was expected that the photolysis of tert-butyl hydroperoxide in propylene would result in the superposition of the spectra of allyl radicals and radicals 3 and 4. However, photolysis of 0.2 M tertbutyl hydroperoxide in propylene produced only the tert-butylperoxy radical, probably formed by hydrogen abstraction from tert-butyl hydroperoxide by the initially generated hydroxyl and tert-butoxyl radicals14 (eq 7--9).

$$(CH_3)_3COOH \longrightarrow (CH_3)_3CO + OH$$
 (7)

$$(CH_{s})_{s}COOH + \cdot OH \longrightarrow H_{2}O + (CH_{s})_{s}COO \cdot$$
(8)

(CH₂)₂COOH + ·OC(CH₂)₂ →

 $(CH_3)_3COH + (CH_3)_3COO \cdot (9)$

After prolonged irradiation at -65° the peroxy radicals gradually disappeared with decreasing peroxide concentration and a broad line spectrum, as in Figure 2, emerged.

tert-Butyl Perbenzoate. tert-Butyl perbenzoate is photolyzed to give tert-butoxyl and benzoyloxy radicals.8 In our samples with 0.2-0.5 M tert-butyl perbenzoate in propylene, a strong evolution of gas indicated that the benzoyloxy radicals probably decarboxylated into CO2 and phenyl radicals which were not observed

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because of their short lifetime.8 Figure 3 shows the

$$\begin{array}{c} 0 \\ \text{PhCOOC(CH_{2})_{3}} \xrightarrow{h_{\nu}} & \begin{array}{c} 0 \\ \text{PhCOOC(CH_{3})_{3}} \end{array} \end{array} \xrightarrow{(h_{\nu})} & \begin{array}{c} 0 \\ \text{PhCOOC(CH_{3})_{3}} \end{array} \end{array}$$
 (10)

$$h CO_2 \longrightarrow CO_2 + Ph$$
 (11)

spectrum obtained at -90° . It is assigned to allyl radicals (2) and radical 5 whose coupling constants CH₂CHCH₂Ph

р

are $a_{\rm H}^{\rm CH} = (22.0 \pm 0.1)$ G, $a_{\rm H}^{\rm CH_3} = (25.4 \pm 0.1)$ G, and $a_{\rm H}^{\rm CH_2} = (17.8 \pm 0.1)$ G. Two additional broad lines, indicated by arrows, are tentatively assigned to radicals 6. The lines of the allyl radical in Figure 3 are

·CH2CH(Ph)CH3

strongly distorted because of the high modulation which was required to obtain a reasonable signal-tonoise ratio for radical 5. They appeared more clearly when the modulation amplitude was below 100 mG. From the relative line intensities it is estimated that allyl radicals and radicals 5 are present in approximately equal concentrations.

The coupling constants of radical 5 for the α proton and the methyl protons agree well with those of radical The methylene protons of radical 5, however, have 3. coupling constants of only 17.8 G compared to 24.7 G in radical 3. This shows that in radical 5 rotation of the methylene group around the $C_{\alpha}-C_{\beta}$ bond axis is hindered by the bulky phenyl group.

The structure of the spectra did not change under continuous irradiation for 1 hr.

Products. In order to confirm the results obtained by the esr experiments and to reveal the nature of the species causing the broad line spectrum of Figure 2, a qualitative product analysis of irradiated samples of hydrogen peroxide in ether-propylene was carried out by glpc. In addition to water and a large number of mostly unidentified products already obtained in samples of hydrogen peroxide in ether alone, the major products were n-propyl, isopropyl, and allyl alcohols, and acetone. These four products are expected from bimolecular reactions among the radicals 1, 3, and 4. 1,5-Hexadiene, which is expected to be formed by dimerization of allyl radicals, could not be detected, probably indicating that no allyl radicals were present in this system. No polymeric products were found.

Because no polymerization was observed at the low temperatures employed, the broad line spectrum of Figure 2 was interpreted as predominantly due to radicals 3 and 4 trapped in ice crystals. This is in agreement with the high stability of the radicals, their large line widths, and the fact that the broad line spectra developed faster when the solutions of hydrogen peroxide in ether-propylene were not dried before use but initially contained small amounts of water. The water in the originally dry solutions is due to hydrogen abstraction by OH radicals from ether in the case of etherpropylenc solutions or from tert-butyl hydroperoxide in the case of solutions of tert-BuOOH in propylene.

A product analysis of an irradiated sample of tertbutyl perbenzoate in propylene showed tert-butyl alcohol, 1,5-hexadiene, n-propylbenzene, allylbenzene,

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benzene, and small amounts of cumene among the products. tert-Butyl alcohol is the expected product of hydrogen abstraction from propylene by tertbutyoxyl radicals, while 1,5-hexadiene, n-propylbenzene, allylbenzene, and cumene are formed in bimolecular reactions of the radicals 2, 5, and 6. The formation of benzene indicates that phenyl radicals might also abstract hydrogen from propylene; however, benzene could also be formed as a secondary product by hydrogen abstraction from the tert-butyl alcohol already present.

Oxygen-Saturated Samples. Samples saturated with oxygen are expected to give the esr spectra of peroxy radicals resulting from the reaction

$$R \cdot + O_2 \longrightarrow ROO \cdot$$
 (12)

where $R \cdot = 1-6$. The g values of alkyl peroxy radicals are known to fall in the range from 2.014 to 2.019.14-16

Solutions of hydrogen peroxide in ether-propylene exhibited one line with 8-G line width and g = 2.0152 ± 0.0003 . The line appeared to be split into a doublet with a spacing of 3.7 G which could be due to interaction with an α proton. The signal should be due to the peroxy radicals formed by addition of oxygen to 1, 3, and 4. The peroxy radical from 1, which was produced in oxygen-saturated solutions of hydrogen peroxide or tert-butyl peroxide in ether, gave a line width of only 3.5 G and a g value of 2.0151 ± 0.0003 . In these systems radical 1 was also observed.

In solutions of tert-butyl perbenzoate in propylene, two broad esr lines were found. One, with a line width of 3.5 G and $g = 2.0159 \pm 0.0005$, is clearly due to alkylperoxy radicals, probably the peroxy derivatives of the radicals 5 and 6. The other line had a line width of 10 G and a g value of 2.0038 ± 0.0003 . In solutions of tert-butyl peroxide in propylene only one broad line with a line width of 10 G and a g value of 2.0037 ± 0.0003 was found which should be due to the same species.17

Weiner and Hammond¹⁸ observed the broad line of a short-lived radical with similar line width and g value in pure tert-butyl peroxide and attributed the signal to tert-butoxyl radicals. However, Symons¹⁹ suggested that this signal might be due to the "ozonide" radical 7 whose g value is expected to be close to 2.004.

(CH₃)₃COOO · 7

Since in our experiments the signal was found only in oxygen-saturated solutions, we believe that it is due to the "ozonide" radical 7. The signal was not found in oxygen-saturated solutions of tert-butyl peroxide in ether, which shows that tert-butoxyl radicals react more rapidly with ether to form radicals 1 and tert-butyl alcohol than with oxygen to form radical 7. Thus, it seems that no allyl radicals are formed during photolysis of tert-butyl peroxide in propylene in the presence of oxygen, and it is not known whether allyl radicals react with oxygen to form alkenylperoxy radicals.

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Discussion

Our experiments have shown that hydroxyl radicals not only add to the terminal carbon atom of the double bond of propylene (eq 1) but also to the central carbon atom (eq 2). Phenyl radicals react preferably by addition rather than abstraction with propylene, while tert-butoxyl radicals exclusively abstract hydrogen from its methyl group. The behavior of the three radicals in reaction with propylene is interesting and somewhat surprising. We learn that even a very simple molecule can react predominantly in one way with one radical and show entirely different preference with another. Almost surely there can be no single reactivity variable which will account for the fact that both phenyl and hydroxyl radicals add whereas the tertbutoxyl radical abstracts hydrogen from propylene. As a broad generalization, there seems to be an increasing preference for hydrogen abstraction in preference to addition to a carbon-carbon double bond as the electron affinity of the attacking radical is increased. Thus, on the average, π -electronic carbon radicals, whose electron affinities in the gas phase are around 1 eV or less, 20, 21 have a tendency to add, as in vinyl polymerization. Amino and methylthiyl radicals, whose electron affinities are reported to be 1.1 and 1.3 eV, respectively,²² also add to propylene^{8,6} and so does the tricthylsilyl radical,³ which is expected to have an even lower electron affinity. Chlorine atoms, however, usually abstract hydrogen as in photochlorination in accordance with their high electron affinity of 3.62 eV.²³⁻²⁶ Between these two extremes we find hydroxyl, alkoxy, and probably phenyl radicals. The electron affinity of the hydroxyl radical was determined by several different methods to be between 1.8 and 1.9 eV.^{20, 27-30} In an electron impact study in a mass spectrometer the electron affinities of alkoxy radicals were recently found to fall in the range 1.7-1.9 eV, 29 although an earlier study using the magnetron method resulted in values between only 0.4 and 0.7 eV.22.31 Finally, the electron affinity of the phenyl radical was determined by Gaines and Page with the magnetron method to be 2.2 eV.32 This method uses the formation of negative ions by the surface ionization of gases on hot metallic filaments; in this study benzene, benzil, and diphenylmercury were used to produce phenyl ions. However, in a mass spectrometric study under similar conditions the dissociative ionization of benzene was not found to result in the formation of phenyl ions but the fragments C2H-, C2-, and CN-,33 the electron

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affinities of the corresponding radicals being 2.1, 3.3,34 and 3.2 eV,35 respectively. Thus the high value reported for the phenyl radical might be somewhat uncertain.

Our results indicate that hydroxyl and alkoxy radicals as a class may be fairly delicately balanced in a borderline region of relative reactivity. If so, there are any number of reasons (steric hindrance, differences in polarizability, etc.) which could be cited as sources of the interesting difference between the reactivity of hydroxyl and tert-butoxyl radicals. Based on this discussion we would expect acyloxy radicals to abstract hydrogen from propylene rather than add to the double bond.36

The allyl 2 and alkyl radicals 1 and 3-6 do not add to the double bond of the olefin at the low temperatures employed; thus, no polymerization was observed. The alkyl radicals react rapidly with oxygen to form relatively stable alkylperoxy radicals, whereas the fate of the allyl radicals in the presence of oxygen remains unknown. Although in our experiments allyl radicals were probably not formed in the presence of oxygen, this should be the case at high temperatures where the highly unstable "ozonide" radical 7 is expected to be in equilibrium with the alkoxy radical. Similar be-

$$(13)_{3}CO + O_{2} \rightleftharpoons (CH_{3})_{3}COOO + (13)_{3}COOO + (13)_{3}COO + (13)_{3$$

havior should hold for other alkoxy radicals.

Finally, it was shown in this study that the bimolecular termination reactions of the radicals formed with propylene lead partially to unsaturated compounds such as allyl alcohol, allylbenzene, and 1,5-hexadiene.

Although this work was carried out at low temperatures and, consequently, was a study only of reactions

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with very low activation energies, some interesting possibilities for the formation of photochemical smog are presented. We have seen that there are two distinct types of radical species, those which add to the double bond leading to an alkylperoxy radical in air, and those which abstract a hydrogen atom leading to the formation of an allyl or an alkenylperoxy radical in air. The latter two species are particularly significant because they (as the alkenyloxy counterpart) can enter into reactions with other olefins, aromatics, or free radicals in polluted air resulting in larger products but still retaining a reactive double bond. It has been found that monoolefins of six carbon chains or more lead to organic aerosol formation in smog chambers.38 In polluted air, however, in which hundreds of free-radical species are present, the chance of abstraction vs. addition to olefins increases substantially, and with it the possibility that unsaturated free radicals are formed which can serve as the nuclei for organic aerosol formation in polluted air.

A rather important, and disconcerting, conclusion of the work reported here relates to atmospheric chemical modeling studies. Reduction in the number of steps included in a mechanism is required to produce manageable computer programs. The task would be greatly simplified if one could assume that all radicals react predominantly in a single way with a molecule as simple as propylene. However, our study shows that such a simplification is not possible.39

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