PHOTOLYSES OF PHENYL ESTERS

Thesis by

James Wilfred Meyer

In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1971

(Submitted August 6, 1970)

To my Father and Mother

ACKNOWLEDGEMENTS

I am very grateful to Professor G. S. Hammond for the advice and guidance he gave me throughout the course of this work. His enthusiasm, patience, and friendship are very deeply appreciated.

My association with the members of the Hammond Group has been both enjoyable and scientifically rewarding. Several of the members have contributed directly to this study. In particular, I wish to thank Dr. Carl C. Wamser for performing many of the flash spectroscopy experiments, and Dr. S. A. Wiener for conducting the EPR experiment.

A number of other members of the chemistry department have also made contributions to this work. I am grateful to Dr. Norman Davidson for his helpful suggestions concerning the design of the flow system. Professor Aaron Kuppermann graciously permitted us the use of his gas chromatograph - mass spectrometer for which I express my thanks. The work and counsel of Professor Dov Elad of the Weizmann Institute of Science is gratefully acknowledged. Mr. James H. Prestegard obtained a 220 MHz nmr spectrum for one of the photoproducts. I wish to thank him for this and the countless helpful discussions we have had over the last several years.

Finally, I am most deeply indebted to my wife, Jenny. Not only has she typed this thesis with a sense of real dedication, but she has been a constant source of strength and comfort to me throughout my graduate studies. Her presence during my times of despair helped me to keep things in their proper perspective, and during the times of joy, gave me someone important to share them with.

I would also like to thank the Department of Health Education and Welfare for the financial support provided in the form of an NDEA Fellowship.

TABLE OF CONTENTS

LIST OF TABLES

TABLE OF FIGURES

ABSTRACT

The photochemical reactions of phenyl esters have been studied in both solution and gas phases. The irradiation of phenyl esters in the gas phase with ultraviolet light results in their photolyses. The photolysis of phenyl acetate in the vapor phase produces mainly phenol with lesser amounts of o- and p-cresols and o- and p-hydroxydiphenyl ethers. In addition to these compounds, p-benzoquinone was also isolated, however it is believed to be formed from the secondary photolysis of p-hydroxydiphenyl ether. These products are explained with a mechanism involving the photolysis of phenyl acetate into phenoxy and acyl radicals followed by decarbonylation of the acyl radical to give carbon monoxide and methyl radicals. The reactions of methyl and phenoxy radicals produce the observed products. Although attempts at scavenging the acyl radical failed, the detection of products from the decomposition of butyryl radicals in the irradiations of phenyl n-butyrate indicates a similar mechanism is operating in solution. These results are taken to indicate that the photo-Fries Rearrangement results from the cage recombination of phenoxy and acyl radicals rather than by means of a molecular rearrangement. The quantum yields of phenyl benzoate were measured in ether: $\Phi_{-ester} = 0.85$, $\Phi_{\underline{o}} = 0.30$, $\Phi_{\underline{p}} = 0.28$, $\Phi_{\phi OH} = 0.14$.

The emission spectra of several different phenyl esters were recorded and discussed in terms of the excited state leading to reaction.

The irradiations of 1-butanethiol in solution and _o_-hydroxyacetophenone in the vapor phase were briefly studied. 1-Butanethiol gives hydrogen sulfide, butyldisulfide and dibutyl sulfide. Irradiations of _o_-hydroxyacetophenone appears to give phenol at low pressures and salicylaldehyde at about 1000 mmHg.

ABSTRACTS OF PROPOSITIONS

Proposition 1.

A study of triplet energy transfer from organic sensitizers to transition metal carbonyls is proposed to gain information about the excited states responsible for their photoreactions.

Proposition 2.

A method is described which will assess the importance of $d_\pi - p_\pi$ type interactions between mercury and cyanide.

Proposition 3.

A direct chemical probe is presented to determine the nature of energy transfer in the fluorescence quenching of aromatic hydrocarbons.

Proposition 4.

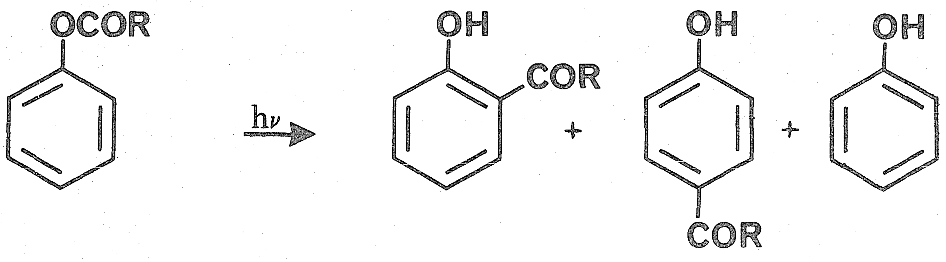
A system if proposed in which a 1,2 free radical shift of silicon could be observed.

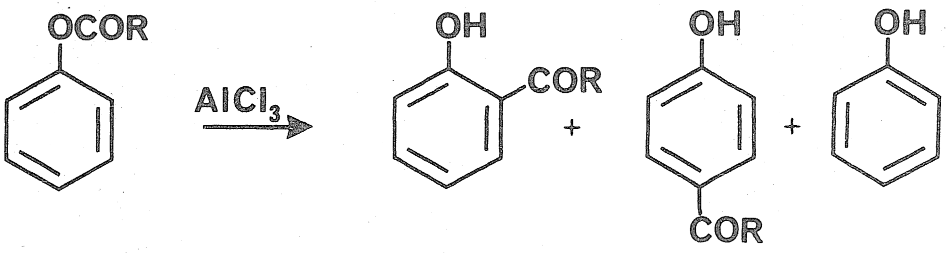
Proposition 5.

An experimental method is proposed which would permit the direct detection of free radicals and other unstable species resulting from photochemical processes in the gas phase.

I. INTRODUCTION

The photochemistry of phenyl esters has been the subject of numerous investigations in recent years. The discovery of the photochemically induced rearrangement of phenyl esters to o- and p-hydroxyphenones was reported simultaneously by Kobsa[1], and Anderson and Reese[2] around 1960. The analogy of the photochemical transformation to that of the well-known Lewis acid catalyzed Fries-Rearrangement led to the name, photo-Fries rearrangement. In addition to the thermal and photochemical means, high energy γ-irradiation has also been reported to affect this transformation.[3-5] However, this discussion will focus primarily on the photochemical process.





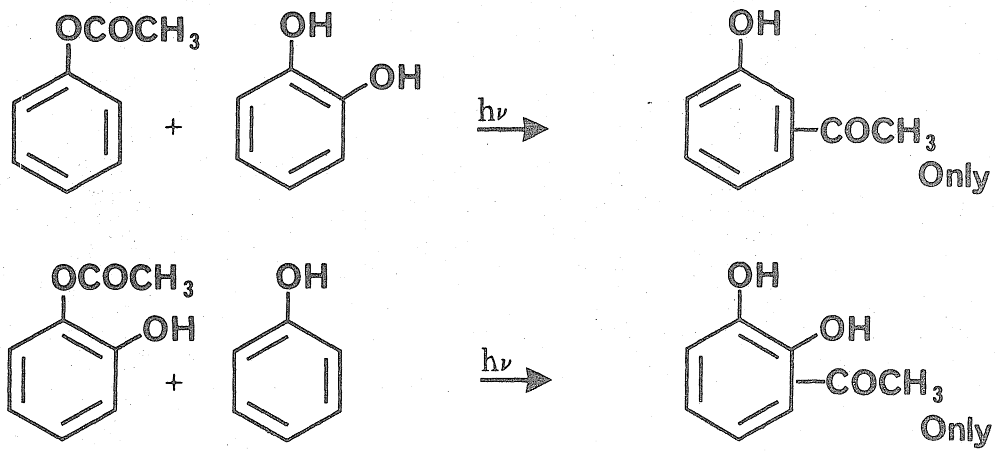
Interest in the photo-Fries rearrangement and the photochemistry of phenyl esters in general, has continued for nearly a decade. In that time, the reactions have been the subject of a great deal of study, and two reviews of the subject are available.[6,7] Motivation for these studies has come from a variety of sources. A large number of the investigations have been aimed at determining the synthetic utility of these reactions. Other contributions have been made as a result of interest in the photochemistry of these compounds due to their applications in commercial polymerizations. Still others have embarked on the studies of phenyl ester photochemistry purely to determine the mechanisms by which the reaction takes place. Our interest in the photo-Fries rearrangement falls into the last category, since this study was undertaken in an attempt to clear up some of the confusion concerning the mechanism of this rearrangement.

Scope of the Rearrangement

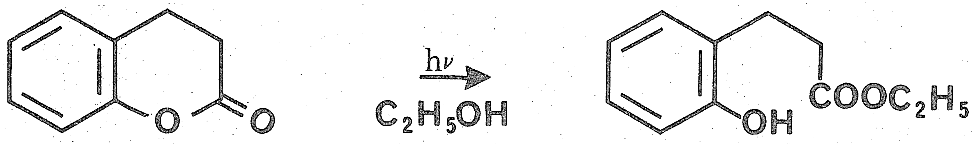
As noted earlier, the photo-Fries rearrangement received its name because of the similarity between it and the well-known thermal rearrangement. However, as a result of the detailed studies of the photochemical reaction, many significant differences between it and its thermal analog have been revealed.

For example, the photo-Fries rearrangement gives usually higher ratios of *o*-/*p*-hydroxyphenones than its thermal counterpart at low temperatures.[8-10] Since higher values of the *o*-/*p*- ratio can be obtained from the thermal reaction only at high temperatures,[11] the photo-Fries rearrangement provides a potentially milder synthetic route to o-hydroxyphenones.

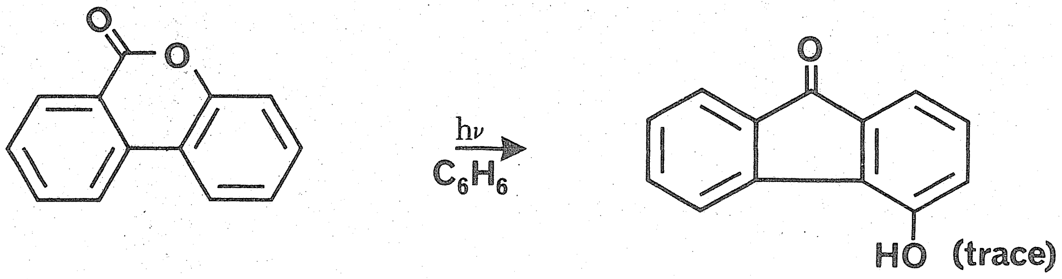
Several experiments indicate that the photochemical rearrangement proceeds by strictly an intramolecular pathway. For example, cross products were not detected when phenyl esters were photochemically rearranged in the presence of different phenols.[2] A similar result was reported by Finnegan and Mattice from the irradiation of p-chlorophenyl benzoate in the presence of phenyl p-chlorobenzoate.[13] Again no cross products were detected confirming the conclusion of Anderson and Reese that the photo-Fries rearrangement was strictly an intramolecular process. In contrast, the same type of experiments performed with a Lewis acid catalyst instead of ultraviolet light, produced all possible cross products.[11-12]



Another feature of the photo-Fries rearrangement not shared by the thermal rearrangement is the extreme resistance to forming the meta- product. Under no conditions, where the acyl group is unrestrained, have m-hydroxyphenones been formed via the photochemical reaction. Even the irradiation of dihydrocoumarin in ethanol failed to yield rearrangement, and only the solvolysis product resulted.[8]



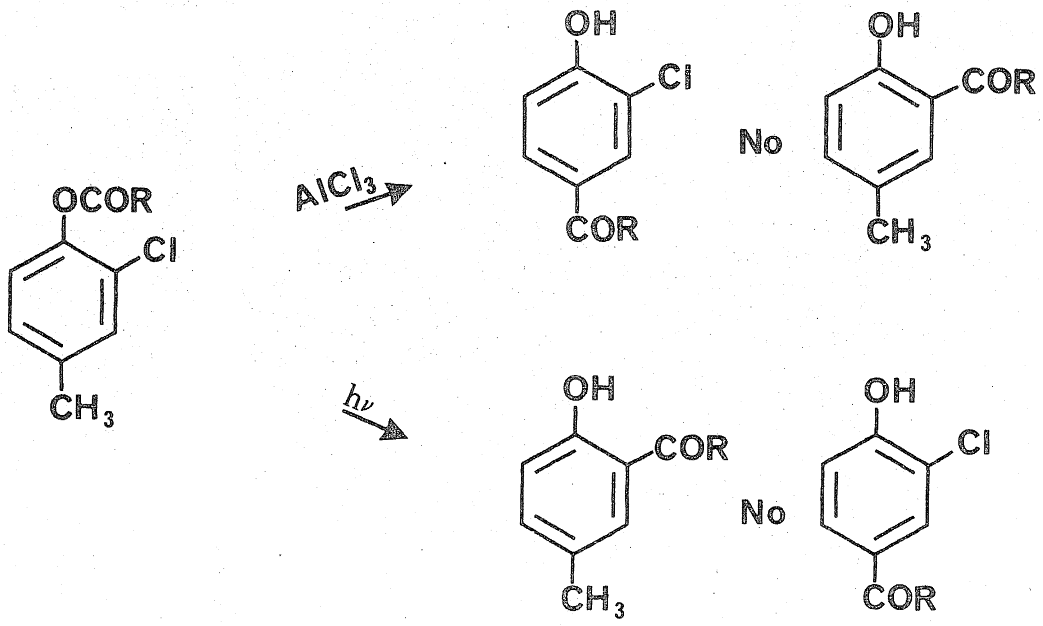
This compound, of course, is sterically restrained so that rearrangement can only occur at the meta- position. Attempts at rearrangements of 3,4-benzocoumarin in benzene reflect a similar reluctance to rearrange. Only under extreme conditions, involving high intensity and very long irradiations, was a small amount of the hydroxyfluorenone



produced.[13] On the other hand, meta- rearrangement products, although fairly rare, are observed in the thermal rearrangement.[11, 14, 15]

Substituent effects in the photo-Fries rearrangement have been extensively studied and are substantially different from those observed in the Lewis acid catalyzed rearrangement.[15] Perhaps the most striking difference is the apparent reversal of effects caused by the presence of alkyl groups or chlorine atoms in the *o*- or *p*- positions of the phenyl moiety.

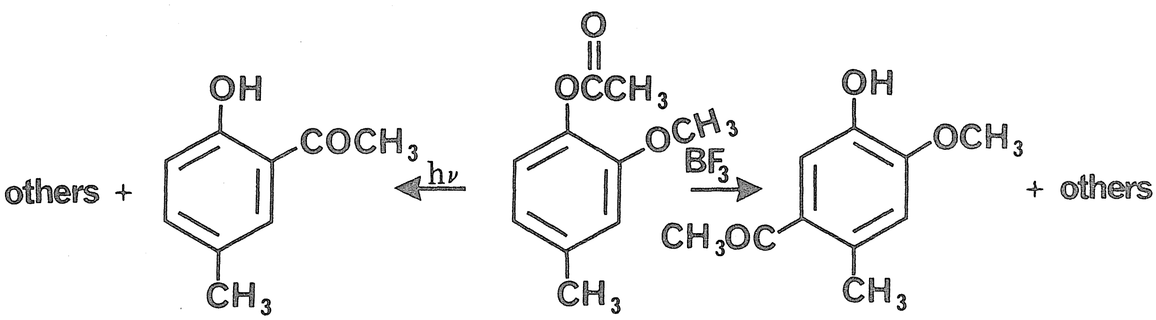
In the acid catalyzed rearrangement of *o*- or *p*-alkylated phenyl esters, rearrangement to the *o*- or *p*-positions is not inhibited by the presence of these groups, and in fact, the alkyl group is displaced yielding unsubstituted hydroxy ketones.[10,16-18] On the other hand, the presence of chlorine atoms in the same positions, effectively blocks thermal rearrangement to those locations, and only chloro- substituted hydroxyketones are formed provided an unchlorinated *o*- or *p*- site exists in the ring.[1,10,11]



The reverse is true when the rearrangement is carried out by photochemical means. Kobsa found that the *p*-*t*-butyl group on the phenoxy ring of *p*-*t*-butyl phenyl benzoate was not replaced by the acyl group, and instead only rearrangement to the ortho- position was observed.[1] Many similar observations with alkylated phenyl esters have established that such behavior is a general phenomenon of the photo-Fries rearrangement.[13,19-22]

On the other hand, the presence of an o- or p- chlorine atom on the phenoxyl moiety of phenyl esters leads to rapid photo substitution of the halogen by the migrating acyl group. A number of studies have documented this behavior,[1,13,23] however, it is still unclear whether the substitution involved a simple displacement[1] or a predissociation of the chlorine.[23]

In like manner, o- and p- methoxy groups are replaced photochemically but not thermally.[20,24] Instead, the only apparent influence of a methoxy group on thermal rearrangement is in directing acyl substitution on the phenyl ring. As an example, Bradshaw, et al. have shown that the presence of a methoxy group in 2-methoxy-4-methylphenyl acetate is capable of causing rearrangement to the unlikely meta- position when catalyzed by BF_3.[20] Photochemically none of this compound is formed and instead only rearrangement to the ortho- positions and side reactions are observed.[20]



Substituent effects from nitro-substitution on the phenyl ring have been studied, however they appear to undergo localized photochemistry of their own, partially preventing the photochemical Fries rearrangement.[1,23,25] Various investigators have looked at the effect of substituents on the rates of rearrangement in terms of linear free energy correlations. Plots involving variation of substitutents spanning a considerable range of σ values on both the phenol and acid portions of the ester have been made.[1,23,26] The trends seem to indicate that electron donating groups on the phenoxy portion tend to give slightly increased quantum yields for photochemical rearrangement as do electron withdrawing groups on the acid portion. However the results of such studies must be considered carefully. In view of the fact that electronic excitation of the ester provides it with energy in excess of that required for C-O bond breaking, the barrier to reaction must be small. Thus, any substituent effects would involve small perturbations on very fast reactions, and alteration of a substituent in the Hammett sense would be expected to have only a trivial, if measurable, effect on the rates of reaction. Results of isotope effect measurements tend to support this opinion. Within experimental error, no isotope effect could be detected for the photo-Fries rearrangement of carbonyl C^{14} labeled p-methoxyphenyl acetate.[27]

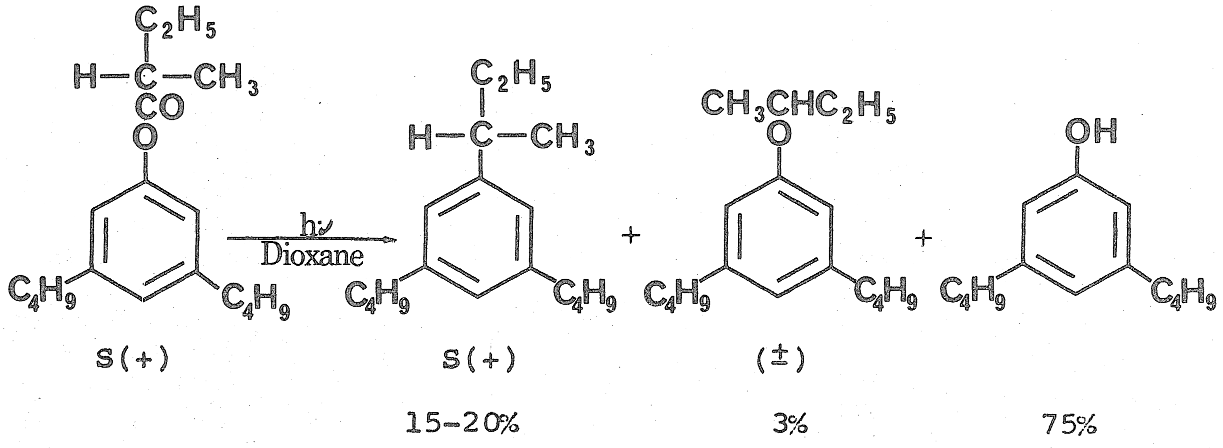
From the large number of photochemical Fries rearrangements that have been carried out in many different solvents, a rather general solvent effect on the rearrangement has been noted.[9,21,28] Rearrangement proceeds more quickly and with higher relative yields of the rearranged products in the polar alcohol solvents. There has been at least one indication that increased solvent polarity favors a higher o-/p- ratio in the rearranged products, and lower overall yields of phenol.[9] However, these results should be interpreted with some caution since they reflect values obtained over wide variations of total conversion, making them questionable indicators of relative quantum yields. Nonpolar solvents not only tend to give lower yields of rearrangement, but in many cases increase the amount of decarboxylation side reaction.[21,28]

Side Reactions

Esters with considerable steric hindrance to rearrangement like esters of 2,5-di-t-butylphenol, mesitol and others, prefer to undergo decarboxylation in nonpolar solvents.[13,22,29,30]

Bradshaw, *et al.* have suggested the solvent effect on decarboxylation may imply that there is considerable polar character in the intermediate stages of reaction.[20] Hageman has proposed that the solvent and substituent effects on decarboxylation may best be explained by rearrangement and decarboxylation proceeding from separate intermediates.[21]

Hageman's proposal gains at least some support from the elegant work of Finnegan and Knutson involving the irradiation of (S)-(+)-3,5-di-t-butylphenyl-2-methylbutanoate.[30] Some decarboxylation of this compound was observed and isolation



of (+)-2-(3,5-di-t-butylphenyl)butane revealed the reaction had taken place with retention of stereochemistry. This requires the reaction path for decarboxylation to be concerted, and since the mechanism for rearrangement may involve a nonconcerted process, Hageman's suggestion does have some merit. (S)-(+)-3,5-di-t-butylphenyl-2-methyl-butanoate also gives some decarboxylation on irradiation.

The 3,5-di-t-butylphenyl 2-methylbutyl ether isolated from the irradiation is racemic. This finding demands a mechanism in which the alkyl group is free to racemize during the loss of carbon monoxide, and is most easily accomodated by a radical recombination step. Diffusion of the radical pair out of the solvent cage would also explain the high yields of phenol obtained in this study. Such a mechanism is also consistent with the findings of others concerning the phenol formation which accompanies the photo-Fries rearrangement.

Barton and coworkers, interested in developing photochemically removable protecting groups for phenols involved in synthetic schemes, studied the phenol forming reaction.[31, 32] In attempting to maximize the yield of the phenol, they noted that the structure of the acid group exerts great influence on the amount of cleavage the ester undergoes. By measuring the amount of carbon monoxide produced in the reaction, it was determined that more phenol was formed from those esters in which decarbonylation of the acyl fragment produced stable free radicals. In these studies, the greatest amount of decarbonylation was obtained from aryl esters formed from fluorene-9-carboxylic acid which upon photolysis yields the stable fluorenyl radical, carbon monoxide, and the phenol in about 60% yield.

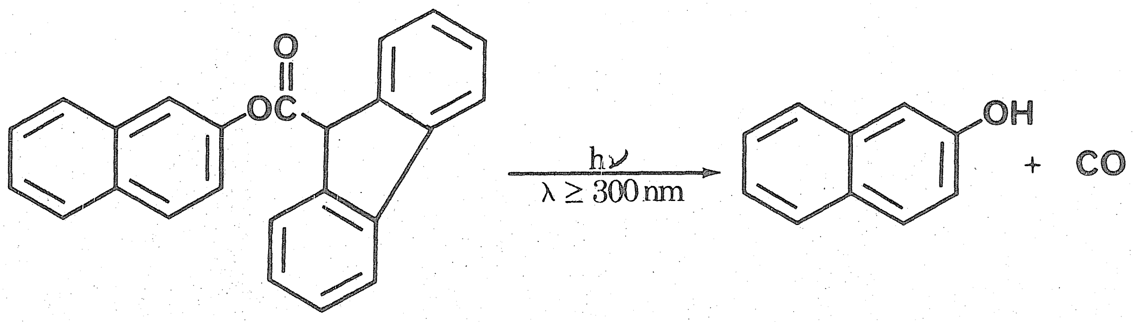
In a similar study aimed at maximizing the phenol formation as a possible source of phenoxy radicals, Horspool and Pauson investigated the photochemistry of carbonates, formates, and oxalates of phenol and p-t-butylphenol.[33] Rearrangement was found to be the major reaction pathway when carbonate was the acid residue. However both the formates and the oxalates gave chiefly phenol when irradiated, and no rearrangement product could be isolated. The photolysis of p-t-butylphenyl formate in ethanol gave the best yields of phenol. The detection of considerable amounts of acetaldehyde, indicated that radicals, formed as intermediates, were abstracting hydrogen from the solvent. Similarly, photolysis of this compound in benzene gave biphenyl and 2,2'-dihydroxy-5,5'-di-*t*-butylbiphenyl, which likewise suggests that irradiation of the formate involves fission into phenoxy and acyl radicals. As with the work of Barton, *et al*. it seemed clear from this study that the nature of the acid group clearly exerted a profound influence on the extent of cleavage observed in the photochemistry of phenyl esters.

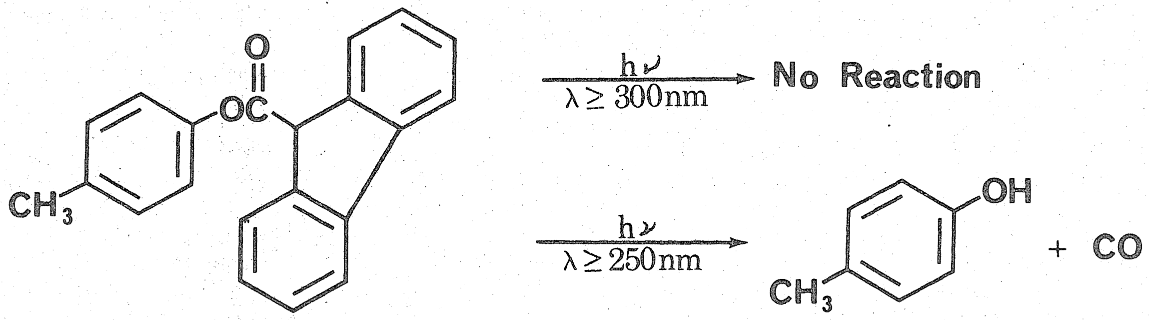
Mechanistic studies

There has been considerable speculation over the details of the activation process in which ester molecules are raised to an energy level sufficient for bond breaking and rearrangement. Although a number of questions still remain, some of the facts about the mechanism of light absorption and promotion to excited states have emerged.

The work of Barton, *et al*. may have established the aryloxy group as the active chromophore leading to reaction since irradiation of β-naphyl fluorene-9-carboxylate through pyrex results in the cleavage of the acyl-oxygen bond.[31] In contrast, the irradiation of *p*-cresyl fluorene-9-carboxylate under the same conditions gives no reaction despite the fact that the fluorene chromophore absorbs strongly in this spectral region. The *p*-cresyl ester does however react when light of shorter wavelength is absorbed by the cresyl group.

Hence it would seem that light absorption by the acid group does not lead to bond cleavage in aryl esters.





When the light is absorbed by an aryl ester, it undoubtedly promotes the molecule to an excited singlet state. The bond cleavage reaction may proceed from this state or alternatively, the molecule might first intersystem cross with a spin flip to an excited triplet state from which the bond breaking step is initiated. A number of investigators have studied this aspect, and to date, there still appears to be some question as to the excited state responsible for reaction.[21,34-37]

Attempts at triplet sensitization of the rearrangement of p-cresyl acetate with acetophenone produced no reaction. However, the triplet level of the ester is probably well in excess of the 74 kcal energy of acetophenone making energy transfer very endothermic and therefore not possible. A sensitizer with a triplet energy of about 85 kcal is probably required for exothermic energy transfer with phenyl esters.

Quenching experiments likewise have been performed with triplet quenchers like napthalene, Fe^{II} acetoacetonate, piperylene, and cyclohexadiene with several different phenyl esters. In all cases, no decrease in the quantum yields of either the rearranged hydroxyphenones or the phenol formation was observed despite this being an energetically-allowed process. These quenching experiments are in agreement with the general observation that oxygen does not appear to affect the rates of reaction in any way. These results indicate that either the reaction does not proceed through a triplet, or that if it does, the rate constant for reaction from the triplet is greater than that for diffusion in solution.

Recently Plank has reported that, although both phenyl acetate and phenyl benzoate do not interfere with the photoreduction of xanthone ($E_T = 74$) in isopropyl alcohol, he claims to have obtained some indirect evidence for energy transfer from triphenylmethane ($E_T = 81$).[36] The times required for 40% disappearance of phenyl benzoate were monitored in the presence and absence of triphenylmethane, and no difference in the times was observed. Since the quantity of triphenylmethane in these experiments was sufficient to absorb 20% of the light, Plank argues that the triphenylmethane is excited and intersystem crosses (apparently with very high efficiency) to the triplet which then sensitizes some phenyl benzoate. The apparent equal rates of disappearance with and without triphenylmethane is attributed to the direct and sensitized photo reactions proceeding from the same excited state, namely the triplet. This obviously requires that the ester intersystem crosses prior to reaction.

Because this study deals with yields based on a rather large fractional conversion and thus neglects to measure quantum yields at low conversion, one cannot be sure of the result. In addition it seems as though Plank has ignored the likely possibility for singlet energy transfer from triphenylmethane to phenyl benzoate resulting in singlet reaction.

In view of the fact that fluorescence has not been observed from phenyl esters of aromatic acids, the first excited singlet state remains a strong candidate for initiating the photochemistry.[1,26] With reference to the strong fluorescence of phenol,[38] it is likely that in most of these phenyl esters the rate constant for bond cleavage and rearrangement is considerably greater than the rate constant for fluorescence. Alternatively, Shizuka has suggested that excitation of phenyl acetate leads to the first singlet excited state which then crosses to a dissociative $^3\sigma^*$ excited state in which the acyl oxygen bond is severed.[37]

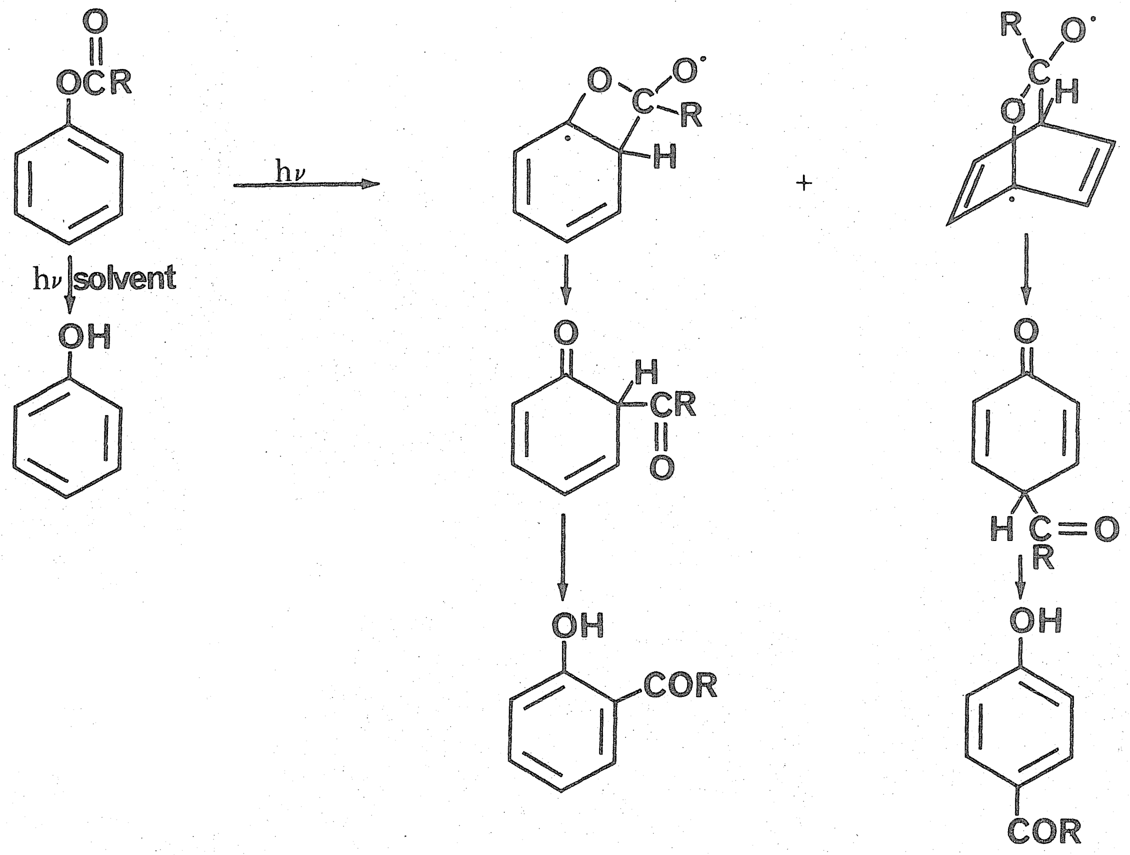
Experiments have as yet not clearly distinguished between singlet and triplet excited states as the precursor to bond breaking of phenyl esters. However, it appears that the majority of evidence is in favor of the excited singlet as the reactive state. Generally most investigators have assumed that the same excited state is responsible for both phenol formation and rearrangement. In contrast, Plank has suggested that the influence of solvent polarity may cause partitioning of the original excited state into two separate excited intermediates.[9] One of the excited intermediates is depicted as a charge transfer excited state which is favored by polar solvents, and leads to the rearrangement products. The other excited state, favored by nonpolar solvents, leads to phenol. Recently, in a preliminary comment in his latest publication, Plank has suggested he may have successfully quenched the phenol formation by 50% without affecting the yield of the rearrangement product.[36] The experiment involved irradiating p-cresyl benzoate to 40% conversion with light of 3500 Å in the presence of 0.3M napthalene. The results of this experiment, however, are unclear since at this wavelength both napthalene and the ester do not absorb appreciably, and in any case, the best comparison would be in terms of quantum yields taken early in the reaction.

In addition, the amount of napthalene seems unusually high for triplet quenching and singlet interference seems likely.

One other paper has just been published which includes a scheme involving a partitioning of excited states to explain the general solvent and substituent effects on the reaction.[21] A partitioning between _s-cis_ and _s-trans_ conformeric forms of the excited singlet state of substituted phenyl acetates is proposed to explain the solvent and substituent control of the ratio of decarboxylation to rearrangement. In this scheme, _s-cis_ and _s-trans_ forms of the ester are in equilibrium, and exposure to ultraviolet light excites each to a _s-cis_ and _s-trans_ conformation of the first excited singlet state respectively. Both excited singlet conformers lead to unique, unspecified intermediates with the one coming from the _s-cis_ form causing decarboxylation and the one from the _s-trans_, rearrangement. Variations in solvents and substituents on the phenyl ring are seen to affect the conformational equilibrium and thus produce a variation in the rates of rearrangement and decarboxylation. However, this interesting hypothesis still remains to be tested.

Following the primary activation process, the excited ester molecule begins the appropriate nuclear motions which will eventually transform it into the products. Taken collectively, all subsequent travel across the reaction potential surface describing the chemistry is referred to as the secondary process in the mechanism. The majority of the research effort on the photo-Fries rearrangement has been concerned with the elucidation of the secondary process. Despite almost a decade of work on this problem, description of the reaction pathway has remained largely controversial. Basically, two conflicting hypotheses have been advanced to explain the photochemistry of aryl esters. As a result, each has enjoyed rather widespread popularity in the literature, and two divergent lines of argument have developed based on a number of different experimental results.

The very first studies of the mechanism which accompanied the discovery of the rearrangement by both groups dealt with investigating the nature of the secondary process. Anderson and Reese after having determined that o- and p-hydroxyphenones were the primary products of the reaction, and were stable under the reaction conditions, proposed a mechanism which has in a general way continued in popularity. Based on the higher proportion of o- substituted products when compared to the acid catalyzed rearrangement, the extreme resistance to meta- substitution, and the high degree of intramolecularity of the photo-reaction, Anderson and Reese proposed a mechanism involving a concerted formation of the rearranged products.[8] The major concept in their mechanism implies that the timing of bond breaking and bond formation is synchronized. Specifically, the reaction is seen as proceeding through a pair of bridged biradicals, one involving attack on the ortho position of the phenyl ring, the other involving para attack.



Intermediate between the stages of bridged biradicals and products is the formation of acyl cyclohexadienones. These compounds under the conditions of reaction, would be expected to enolize very quickly giving the phenolic products. It is important to note that there is no provision in this concerted scheme for the formation of phenol which has been shown to accompany rearrangement. To explain the dilemma Anderson and Reese suggested that the phenol results from a competing photo reaction of the phenyl ester with ethanol as was observed in the irradiation of dihydrocoumarin. However, the expected ethyl ester, which should accompany the phenol was not detected.

In the considerable amount of literature which has followed this work, several papers have appeared favoring similar molecular rearrangement type mechanisms.[9,20,26,34,35]

Coppinger and Bell studied the photochemistry of substituted phenyl 3,5-di-t-butyl-4-hydroxybenzoates in polyethylene films.[26] The only reaction they observed was rearrangement to the ortho position; fragmentation to give phenol was not detected. When the ortho positions were blocked as in the o,o-dimethylphenyl ester no reaction at all was observed. From studies of the substituent effects on this series it was found that both molecular complexity and electron withdrawal from the phenyl group tends to depress the quantum yield. A charge transfer mechanism was proposed to correlate these results. Bond breaking of the C-O bond is accompanied by strong polarization which keeps the two portions of the molecule in close association throughout the rearrangement. Following migration, this charge transfer complex then collapses to the o-dienone which ultimately enolizes to give the observed product.

Based primarily on this work, Plank has suggested that a similar molecular charge transfer mechanism maybe responsible for the photo-Fries rearrangement in solution.[9] It is argued that such an intermediate could explain the solvent effects, since solvents like ethanol would stabilize a charge transfer excited state and thereby favor rearrangement over phenol formation. (The latter, as previously noted, is seen to proceed from a non-polar type "intermediate" in Plank's proposal.)

Another molecular type mechanism has been advanced from the work of Trecker, et al.[34,35] This work involved determining the effect of the solvent environment on the photochemistry of several p-cresyl esters. Specifically, Trecker found no change in the quantum yields for the ortho rearrangement from the irradiation of p-cresyl acetate and benzoate in alcoholic solvents spanning a wide range of solvent viscosities. However, the quantum yield for the phenol (p-cresol) was found to increase with decreasing solvent viscosity. If a concerted molecular rearrangement were responsible for the rearrangement to the o-hydroxyphenone, one would not expect to find a variation in the rearrangement quantum yield. Since none was detected, Trecker has suggested that the rearrangement occurs as a concerted suprafacial shift of the acyl group to the ortho and para positions. Because of the different orbital symmetries of the first and second excited states of phenyl acetate, this model generates the prediction that there should be a wavelength dependence on the ratio of the quantum yields of o-hydroxy and p-hydroxyacetophenone. (Implicit in this model is the assumption that the decay of $S^2 \rightarrow S^1$ is not significantly faster than reaction.) This aspect of the hypothesis, however is still under study.

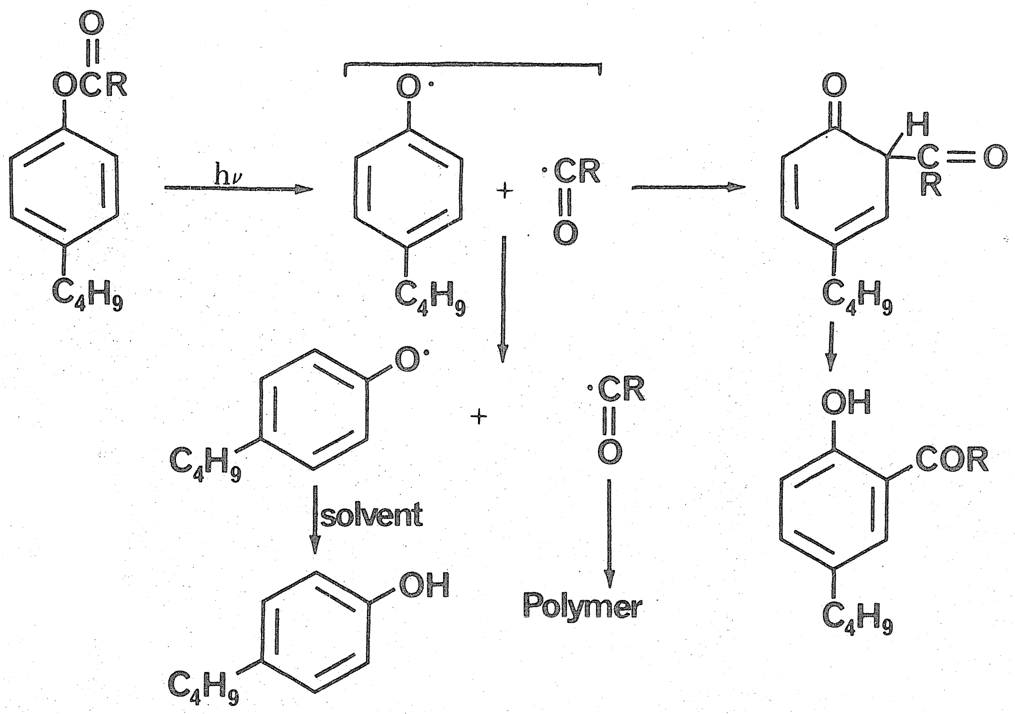
The variation in the quantum yield of the phenol (p-cresol) is explained by proposing a second reaction from the excited state. As an alternative to the concerted rearrangement the excited phenyl acetate may undergo carbon-oxygen bond homolysis. These radical fragments are then able to either recombine to give back mainly the starting material and presumably little or no rearrangement products, or diffuse out into the solvent. In the latter case, the free phenoxy radical abstracts a hydrogen from the solvent and forms the phenol. As has been the case in most studies, the fate of the acyl radical was not determined. In this model, increased solvent viscosity would decrease the ratio of cage escape products to recombination products. Such a scheme thus explains the observed lower p-cresol quantum yields by assuming that a larger proportion of the radical pairs must recombine to give back the starting ester in the very viscous solvents.

Bradshaw, et al. have also favored this type of molecular rearrangement as the mechanism leading to the hydroxyphenones.[20] Although they prefer to hedge a bit as to the precise nature of the intermediate, it is clear that they have chosen a tightly bound one similar to the types discussed above to explain solvent and substituent effects.

Hageman has recently interpreted the absence of isotope effect in the photo-Fries rearrangement of p-methoxyphenyl acetate to be consistent with a molecular rearrangement mechanism in which the C-O bond remains largely intact in the transition state.[21] As pointed out earlier, however, a far more reasonable explanation is simply that photochemical excitation imparts an excess of energy to the ester so that a transition barrier in the thermal chemical sense simply does not exist. The isotope effect experiment in this case does not give any information about the rearrangement pathway.

While all the above papers perhaps do not agree in detail with the original proposal of Anderson and Reese, they do share the common proposal that the rearrangement takes place via a concerted molecular mechanism. It is in this sense that these papers form one side in the nearly ten years of controversy over the mechanism of the photo-Fries rearrangement.

An entirely different concept, first advanced by Kobsa, has been the basis for the other side of this controversy.[1] Kobsa suggested that both the rearrangement and the formation of phenol could be rationalized by a single mechanism. From his investigations of the rearrangement of several substituted aromatic esters the following scheme was proposed. Two observations suggest the initial photodissociation step yielding phenoxy and acyl radicals is quite efficient. First, Kobsa determined the dissappearance quantum yields to be about 0.65 for most of the esters he investigated, and second, there is a total absence of luminescence from these esters. Taken together these facts give strong support



to the hypothesis that the ester dissociates to radicals with nearly unity quantum yield. He proposed that the back reaction, recombination of the radical pairs to regenerate the original ester, occurs about a third of the time and accounts for the 0.65 dissappearance quantum yield.

Unlike the molecular rearrangement mechanisms, the significant point in this scheme is that both the rearrangement product and phenol result from the reactions of the phenoxy-acyl radical pair. The phenoxy and acyl radicals, trapped by neighboring solvent molecules, remain in close proximity for a large number of collisions. As a result there is a high probability that they will recombine. In doing so they may give back starting material, as has already been proposed, or more importantly, they could combine to give a 2-acyl-3,5-cyclohexadien-1-one. The latter possiblity followed by rapid enolization as in other mechanisms, would result in the observed rearrangement product.

Alternatively, the radicals may diffuse out of the solvent cage, become free of each other, and enter into other reactions. Phenoxy radical, for example, must eventually abstract a hydrogen (probably from solvent) and form phenol. Kobsa reports that the amounts of t-butylphenol isolated from the reaction, taken with the yield of rearrangement product are sufficient to account for essentially all the reacted ester. Apparently the free acyl radical goes on to do more complicated chemistry, since no aldehyde is detected among the products. Kobsa believes it is probably involved in polymer formation which inevitably accompanies the rearrangement.

The small substituent effect which was observed from variation of electron donating and withdrawing groups on the carboxylic portion of the ester indicated an enhancement of rearrangement with increased electron withdrawal. This effect is consistent with the proposed scheme. The recombination of phenoxy and acyl radicals is expected to involve little activation energy, and increased electron withdrawal in the acyl group would be expected to slightly accelerate the reaction.

As with the proposal put forth by Anderson and Reese, Kobsa's mechanistic scheme has enjoyed considerable popularity in the literature. A rather large number of papers on the photo-Fries rearrangement have best rationalized their findings by a radical cage recombination mechanism rather than by a concerted rearrangement.[13,23,33,37] In addition, a number of other photochemical rearrangements like the photo-anilide,[39-41] photo-Claisen[42,43] and photochemical ether[42,44,45] rearrangements are thought to involve radical cage recombination as a step in their mechanisms. Many experimental results have appeared which give added support to such a mechanistic scheme for the photo-Fries rearrangement.

The identification of acetaldehyde from the photolysis of p-t-butylphenyl esters in ethanol,[33] mentioned earlier, is consistent with a step involving hydrogen abstraction from the solvent by phenoxy radicals. Similarly, the isolation and identification of various other products, conceivably derived from free radicals, including the phenoxy radical coupling product 2,2'-dihydroxy-5,5'-di-t-butylbiphenyl is compatible with Kobsa's mechanism. Horspool and Pauson report finding some hydrocarbon gas production in the irradiation of phenyl acetate which they ascribe to acetyl radical decomposition. However, because this irradiation was done in ethanol which has been shown to yield acetaldehyde by hydrogen abstraction, it is impossible to rule out solvent derived acetaldehyde as the source of methane.

Bradshaw, et al. reported finding a small amount of benzaldehyde in addition to the usual products from the irradiation of 2-methoxy-4-methylphenyl benzoate in benzene.[20] This is the first report in the literature establishing the fate of a least some of the acyl radicals which have escaped the solvent cage recombination.

In addition to these reports of radical derived products, Finnegan and Mattice have also favored a solvent cage recombination mechanism to explain the photochemistry of phenyl esters.[13] They believe the radical mechanism best explains the loss of stereochemistry in the decarbonylation reaction mentioned earlier in addition to rationalizing formation of rearrangement products, phenol, and polymer. Finnegan and Mattice suggest that the decarbonylation product is formed by initial homolysis of the acyl oxygen bond, followed by rapid loss of CO and radical recombination to give the racemic ether.

Shizuka has recently reported the results of a study of the photochemistry of phenyl acetate.[37] Assuming, from the similarities to his study of the photo-anilide rearrangement, that the mechanism of the photo-Fries rearrangement also involves a radical cage recombination step, he has made some very interesting calculations. By comparing the quantum yields for o- rearrangement and phenol formation from phenyl acetate to those from p- cresyl acetate, and making the assumption that the quantum yields for photodissociation in both esters are about equal, he was able to estimate values for Φ_{diss}, the photodissociation of the ester into radical pairs, and Φ_B, the back reaction regenerating the starting ester. For phenyl acetate in cyclohexane these values were found to be $\Phi_{diss} = 0.61$ and $\Phi_B = 0.23$. Taken with the rearrangement quantum yields these values allowed calculation of the recombination ratio β, the ratio of rearrangement to dissociation. β for phenyl acetate was calculated to be 0.90. This high value of β indicates, that reactions between phenoxy and acetyl occur with high efficiency within the solvent cage. In addition, Shizuka has found excellent correlation between the ratios of the rate constants for the recombination reactions with the appropriate odd π electron densities calculated for the phenoxy radical. This result gives some support to a cage recombination of radicals causing rearrangement to the hydroxyphenones formed in the photo-Fries rearrangement.

These papers taken together underscore an alternative proposal to the molecular rearrangement explaining the photo-Fries rearrangement by a cage recombination mechanism. It is this parallel development of two conflicting hypotheses to explain the mechanism of the photo-Fries rearrangement which encouraged this investigation of the problem. As a result of our studies, we believe we have obtained results which contribute significantly toward resolving the mechanism of this rearrangement.

II. EXPERIMENTAL

Materials

n-Amyl Alcohol was obtained from J. T. Baker Chemical Company.

1-Butanethiol was received from Matheson, Coleman and Bell.

Cyclohexane (spectroquality) was obtained from Matheson, Coleman and Bell.

Diethyl Ether (anhydrous reagent) was obtained from Mallinkrodt Chemical Works.

Ethanol (absolute) was obtained from U. S. Industrial Chemical Company.

n-Heptane (reagent grade) was obtained from Matheson, Coleman and Bell.

n-Pentane (99% pure) was obtained from Phillips Petroleum Co.

o- and p-Hydroxyacetophenones were purchased from Aldrich Chemical Company.

o- and p-Hydroxybenzophenones were obtained from Aldrich Chemical Company.

o- and p-Hydroxybutyrophenones were received from Aldrich Chemical Company.

o-Hydroxydiphenyl Ether was purchased from Eastman Organic Chemical Company.

Phenol was obtained from Mallinkrodt Chemical Works.

Phenyl Acetate was either purchased from Aldrich Chemical Co. or synthesized according to the method of Chattaway.[46]

Triethylsilane was received from Pennisular Chemresearch Inc.

bis-(Trimethylsilyl)acetamide was obtained from Pierce Chemical Company.

1-Butanethiol, triethylsilane, and ethyl ether were used as received from the suppliers.

Purification of n-Pentane. Phillips 99% pentane was stirred over concentrated sulfuric acid for several weeks during which time the acid discolored and was replaced several times. Following separation from the sulfuric acid, the pentane layer was washed several times with sodium bicarbonate solution and then with water. The pentane was then dried and passed through a chromatographic column packed with alumina and finally distilled (Bp 36°). The UV cutoff (OD = 1.0) had improved to 213 nm from 216 nm.

Purification of n-Heptane. Phillips 99% heptane was purified in the manner described for the pentane purification, however, following the washing and drying procedure, it was refluxed for 24 hours over granular phosphorus pentoxide and then distilled. The fraction boiling in the range 97.5-97.7° was collected and stored under nitrogen.

Purification of Cyclohexane. Cyclohexane was passed through an alumina column and then refluxed for 24 hr over granular phosphorus pentoxide, followed by distillation over the range 79.5-79.7°.

Purification of n-Amyl Alcohol. n-Amyl alcohol was purified by stirring over calcium sulfate for several days, and distilling from a small amount of sodium (sodium pentoxide). The fraction boiling at 137° was collected.

Phenyl Acetate was purified by chromatography on silica gel (40 g/g ester) with benzene followed by distillation at reduced pressure: 92-94°/28 mm. This procedure reduced the phenol impurity to less than 0.1%.

Phenol used in calibration for quantum yields was purified by sublimation.

o-Hydroxybenzophenone was purified by recrystallization from pentane (mp 37-38°).

p-Hydroxybenzophenone was purified by recrystallization from ether-pentane, and then sublimed (mp 133-134°).

bis-(Trimethylsilyl)acetamide was purified by distillation at reduced pressure. The middle fraction, bp 69-72°/40 mm, was retained and stored under nitrogen.

Phenyl n-Butyrate. 40 g (0.29 moles) of phosphorus trichloride was added to 60 g (0.68 moles) of *n*-butyric acid; the mixture was stirred and heated for 1 hr after which the organic layer was decanted from the phosphoric acid. Distillation yielded the acid chloride boiling 99-102° at atmospheric pressure. A solution of 96 g (1.02 moles) of phenol in 70 ml of dry pyridine was added, the mixture refluxed for an hour, and then stirred overnight. The organic material was next taken up in ether and extracted several times, first with 10% aqueous hydrochloric acid and then with 10% aqueous sodium hydroxide. Following the extraction, the ether solution was dried over anhydrous sodium carbonate (crude yield ca. 94 g - 64%) and then distilled boiling 220-225°. The distillate was finally freed from the last traces of phenol by elution from a silica gel column (40 g silica gel/g ester) with benzene.

Phenyl Acetate was prepared by the method of Chattaway. 23.5 g (0.25 moles) of phenol were dissolved in 160 ml of 10% aqueous NaOH. The solution was cooled, placed in a separatory funnel, and 175 g of crushed ice was added. Next 32.5 g (0.32 moles) of acetic anhydride was introduced into the separatory funnel and the mixture was vigorously shaken for five minutes. Ether was then added and the aqueous layer was removed; the organic fraction was washed several times with dilute sodium hydroxide, and water. The organic phase was removed and dried over anhydrous magnesium sulfate, following which the ether was evaporated and the phenyl acetate distilled. Yield: ca. 29 g (85%).

Phenyl Benzoate was prepared by dissolving 10.4 g (0.11 moles) of phenol in ca. 100 ml pyridine and adding 14.1 g (0.10 moles) of benzoyl chloride dropwise. After refluxing the mixture for 1 hr, it was cooled, taken up in ether, and washed several times each with dilute hydrochloric acid, dilute sodium hydroxide, and water. The ether solution was dried over magnesium sulfate and then concentrated. Distillation from ether yielded needles 15.7 g (79%). The phenyl benzoate was purified by sublimation and recrystallization from ether producing material melting 67-69°.

Phenyl Caprylate was synthesized by reacting the acid chloride with phenol in pyridine. The chloride was prepared by refluxing 72.1 g (0.50 moles) of caprylic acid with 243 g (2.1 moles) of thionyl chloride for 30 min. The excess thionyl chloride was distilled off in the form of its benzene azeotrope and the remaining caprylyl chloride was dissolved in benzene. This solution was added dropwise with stirring to 52.3 g (0.50 moles) of phenol in 400 ml of pyridine. After the addition was complete the solution was refluxed for one hour, cooled, and then extracted in the usual way with dilute acid, base, and water. The purified ester distilled at 115°1.3 mm. Yield: 88.5 g (80%). Infrared and nmr spectra were consistent with the structure of phenyl caprylate.

Phenyl Adamantane-1-Carboxylate was prepared from the acid chloride in the following way. 15 g (0.083 moles) of adamantane-1-carboxylic acid were refluxed with 49.6 g (0.4 moles) of thionyl chloride for 30 min. Excess thionyl chloride was removed as an azeotrope with benzene. The resulting material was dissolved in benzene and added drop wise to a pyridine solution containing 5.9 g (0.063 moles) of phenol. The mixture was stirred at reflux temperature overnight and the ester was extracted from solution and washed in the usual manner. The material was dried over magnesium sulfate and the ether was evaporated. Yield: 19.9 g (93.5%). Recrystallization from ether followed by sublimation produced white crystals melting 45.5-47°. The infrared spectrum (CCl_4) showed the following absorptions: 2950 (s), 2905, 2847, 1755 (s), 1745, 1595, 1490, 1478 (s), 1450, 1215, 1190, 1180 (s), 1160, 1050 and 685 cm^{-1}. The nmr ($CDCl_3$-TMS) showed the following signals: $\delta = 1.77$ (6H, s (broad)); 2.06 (9H, s (broad)); 7.23 (5H, complex multiplet).

Anal. calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.63; H, 7.77.

p-Hydroxyphenyldimethyl Carbinol was prepared in accordance with Gilman's method[47] by reacting methylmagnesium iodide with p-hydroxyacetophenone. The methylmagnesium iodide was prepared by reacting 40.1 g (0.28 moles) of methyl iodide with 6.7 g (0.27 moles) of magnesium in anhydrous ether. Following completion of the Grignard reaction 16 g (0.12 moles) of p-hydroxyacetophenone in 200 ml of ether was added dropwise to the Grignard reagent. The mixture was stirred at reflux temperature for two hours and then cooled. The organo-magnesium salts were decomposed by stirring the reaction mixture with aqueous ammonium chloride. The organic material was extracted with ether, washed, dried over magnesium sulfate, and concentrated. Crystallization of the carbinol resulted from concentration; recrystallization from water-ethanol yielded 13.1 g (73%) mp 101-104°. The infrared spectrum (nujol) had the following absorptions: 1611, 1594, 1503, 1379, 1367, 1255 (s), 1240, 1180, 1162 1114, 1104, 951, 866, 842, 828 cm^{-1}. The nmr gave the following signals: δ = 1.48 (6H, s); 7.40 (4H, aa'bb').

p-Isopropenylphenyl acetate was prepared by reacting p-hydroxyphenyl dimethyl carbinol with acetic anhydride.[47] 13.1 g (0.086 moles) of the carbinol were refluxed for 8 hr with 32.7 g (0.32 moles) of acetic anhydride. Following distillation of excess acetic anhydride, 5.4 g (36%) of p-isopropenylphenyl acetate distilled 105-107°/2.5 mm. The following infrared absorptions were observed: 3090, 3045, 2975, 2945, 2922, 1765, 1630, 1602, 1510, 1457, 1440, 1372, 1210, 1172, 1020, 918, 902, 856 cm^{-1}. The nmr ($CDCl_3$-TMS) gave the following signals: δ = 2.04 (multiplet) and 2.10 (6H, s); 5.01 (1H, multiplet); 5.30 (1H, s(broad)) and 7.20 (4H, aa'bb').

o-Hydroxydiphenyl Ether was prepared by the method of Norris, et al.[48] Benzene diazonium chloride was prepared by dissolving 40 g (0.43 moles) of aniline in 200 ml of hydrochloric acid solution (50% H_2O - 50% HCl).[49] The aniline hydrochloride solution was cooled to 0° and 32 g of sodium nitrite in 80 ml of water was added with stirring. Addition of the sodium nitrite was at a rate sufficiently slow to maintain a temperature of 0-3°. Next, 50 g of catechol in 50 ml of water was heated to 60° and portions of the diazonium salt solution were added keeping the temperature of the catechol solution between 50-60° during the addition. The black suspension which resulted was steam distilled. The first liter of distillate contained a yellow oil, and the next three liters yielded 2.9 g (6.4%) of o-hydroxydiphenyl ether in the form of long needles which precipitated from the water. Sublimation followed by recrystallization gave white needles, mp 104.5-105° (lit. 105-106°).[48]

Irradiations

Irradiations of solutions were made following one of two general procedures depending upon the nature of the experiment. Most of the general work and quantum yields were done *via* a sealed tube technique. When large amounts of photoproducts were required, a reactor was employed. An example of each technique is given.

Irradiation of Phenyl Benzoate. Quartz tubes of 13 mm diameter were filled with 3 ml of 0.1 M ether solution of a phenyl benzoate. The tubes were degassed by three freeze (77°K)-pump-thaw cycles and sealed off at a final pressure of less than 5×10^{-4} mmHg with a torch. The upper portion of the tubes were taped with black vinyl tape down to the level of the solution to avoid irradiation of the vapor. Tubes were placed in a 254 nm "merry-go-round" housing a Hanovia low pressure mercury lamp and irradiated for varying periods of time.

Alternatively many other irradiations using the tube technique employed an unfiltered 450 watt Hanovia medium pressure lamp in a water-cooled immersion well as the light source.

Irradiation of p-Isopropenylphenyl Acetate. 2.0 g of the above compound was dissolved in 1500 ml of reagent grade benzene and placed in a 2 liter reactor fitted with a water-cooled immersion well, housing a 450 medium pressure Hanovia lamp. Nitrogen was introduced through a glass frit in the bottom of the reactor and the solution was stirred throughout the 26 hr irradiation.

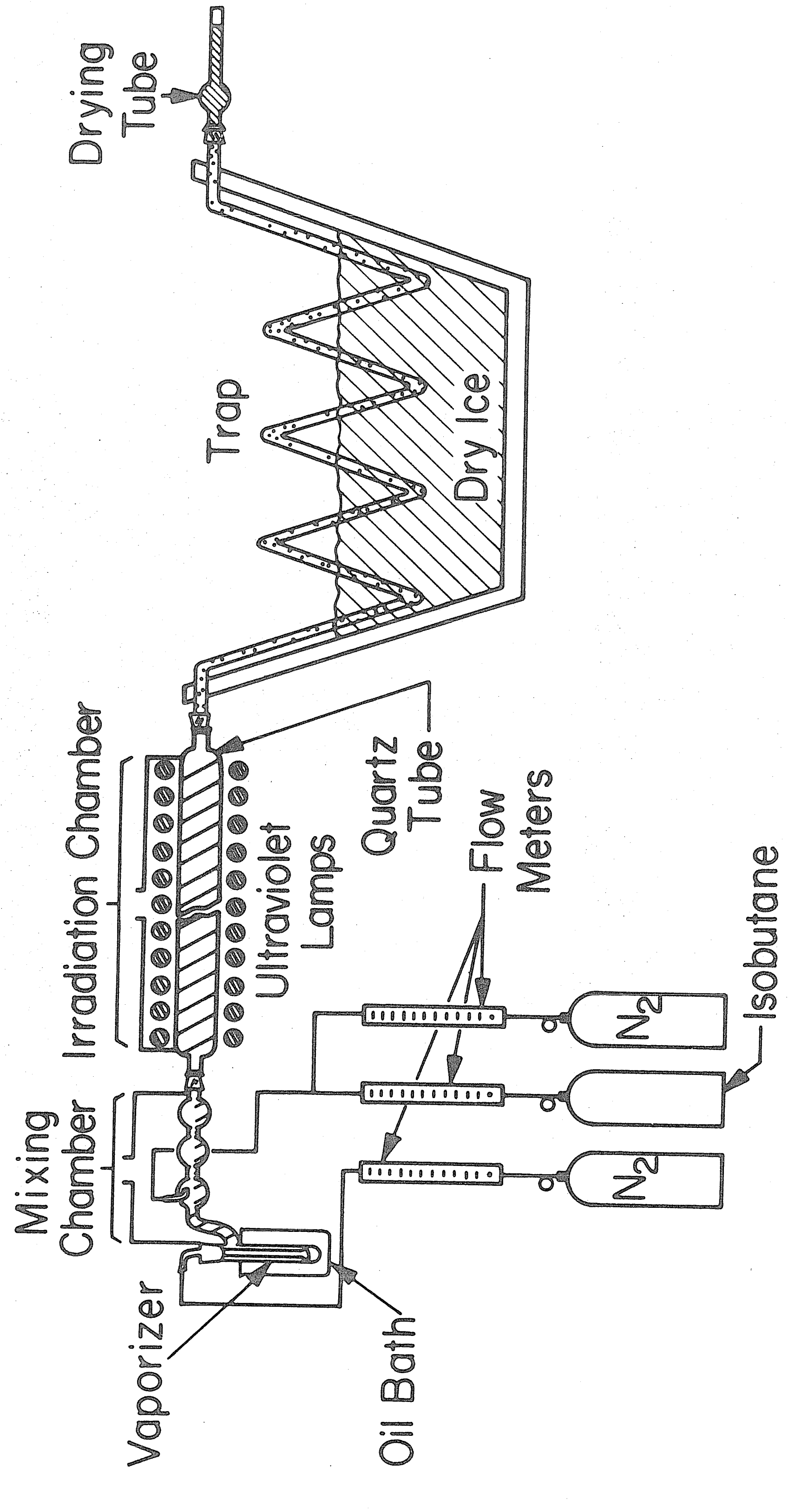
The techniques employed for the gas phase irradiations in this work utilized either a gas bulb or a flow system.

Photolysis of Phenyl Acetate (vapor). A sample containing 3.7 mg of phenyl acetate was injected, using a long needle, into the bottom of a 136 cc cylindrical quartz bulb (190 mm long x 35.5 mm diam) with a vacuum stopcock at one end. The bulb was degassed to 5 x 10^{-4} mmHg at 77°K with a mercury-free vacuum system. A predetermined amount of isobutane was added from the vacuum line to give a pressure of about 1000 mmHg during the irradiation, and the bulb was sealed off with the stopcock. The top and bottom ends of the bulb were taped leaving a 10 cm cylindrical window open in the center. The bulb was placed inside a quartz-walled lamp well which was maintained at 70° by means of a circulating constant-temperature bath. Ultraviolet light (253 nm) from an Ultraviolet Products PCQ-XI lamp[50] which surrounded the well caused partial conversion of the ester in about 2 hours. Following the irradiation, introduction of about 2 ml of dichloromethane into the bulb succeeded in extracting the products and unreacted ester for analysis by gas-liquid partition chromatography (glpc).

Vapor Phase Flow System. The flow system (Fig. 1) consists of three major subunits: a vaporizer-mixer, an irradiation chamber, and a trap. The vaporizer portion was a tubular vessel which held *ca.* 15 ml of the substrate through which nitrogen is passed by means of a glass frit on the end of an immersion tube. The nitrogen flow is carefully controlled and the rate is monitored by means of a flow meter. The vaporizer tube is kept at a constant elevated temperature by means of an oil bath. The vaporized substrate is carried out of the tube by the nitrogen flow into the first mixing bulb where isobutane and the major nitrogen carrier flow, which controls the residence time in the irradiation tube, are added. All gas flows are controlled and monitored by flow meters. This mixture of gasses and substrate vapor pass through two more mixing bulbs before entering the irradiation tube. The entire mixing bulb assembly and connecting tube from the vaporizer are wrapped with nichrome wire and heated to a temperature of *ca.* 90°. The gas mixture upon leaving the last mixing bulb enters one end of the 51 cm x 5.0 cm diam cylindrical quartz irradiation tube of 960 cc volume which is surrounded by a battery of three Ultraviolet Products PCQ-XI 253 nm lamp units. This quartz tube is similarily wrapped with nichrome wire and heated to about 80°. After a

Figure 1

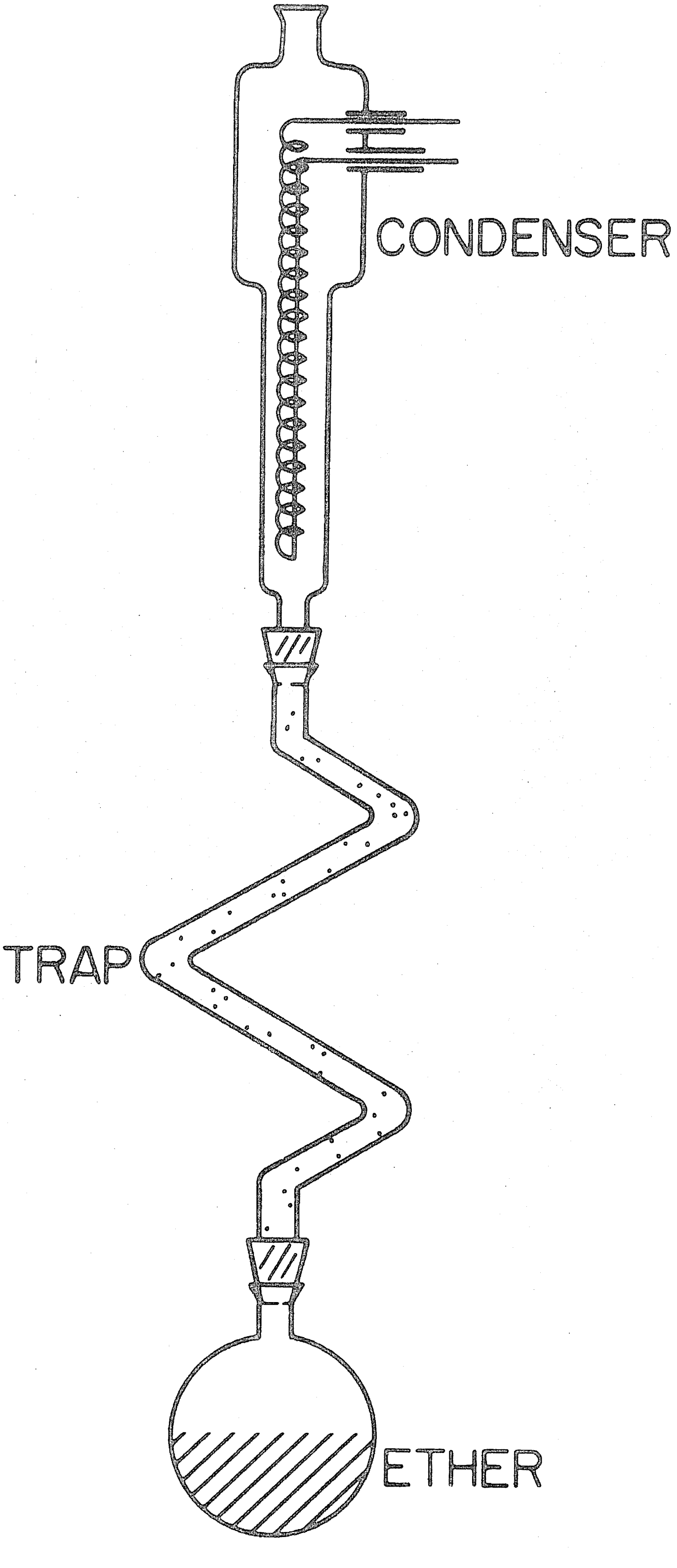
The Gas Phase Flow System


Mixing Chamber
Vaporizer
Oil Bath
Irradiation Chamber
Ultraviolet Lamps
Quartz Tube
Flow Meters
N_2
Isobutane
N_2
Trap
Dry Ice
Drying Tube

specified residence time in the irradiation chamber, the gas mixture exits at the opposite end and enters the trap. The trap is of special design and consists of a length of 14 mm diam pyrex tube bent in a "zig-zag" shape and packed with glass helices. The input end has a female ground glass joint and the first 10 cm is heated by means of a nichrome wire winding to about 80°; the output end is fitted with a male ground glass joint and accepts a drying tube. The entire "zig-zag" section of the trap is half-buried in powdered dry ice, with the upper loops of the zig-zag exposed to room temperature air. A styrofoam "beer cooler" with an added baffle was found to make an ideal container for the trap and dry ice. Such a configuration requires the vapors to be alternatively exposed to warm and cold sections as they proceed through the trap and thereby minimizes possible formation of aerosols. In practice, most of the material is trapped in the first cold loop and essentially no material passed beyond the second one. At the completion of the irradiation, the trap is removed, warmed to room temperature and, finally, the drying tube removed and exchanged for a 100 ml round bottom flask containing anhydrous ether. The zig-zag trap is clamped in a vertical position (Fig. 2) and a reflux condensor with drying tube is placed in the upper female joint. The trap contents are then quantitatively extracted by refluxing the ether through the trap. Generally a few hours of refluxing is sufficient for quantitative removal of the trapped compounds.

Figure 2

Reaction Mixture Extraction Technique


CONDENSER
TRAP
ETHER

Photolysis of Phenyl Acetate (vapor). 8.8 g of phenyl acetate were placed in the vaporizer of the flow system. The heating wire on the system was adjusted to give a temperature of *ca.* 80-90°, and the vaporizer oil bath was set at 40°. The flows were adjusted to give 100 cc/min of nitrogen through the vaporizer, 30 cc/min isobutane, and 900 cc/min main carrier nitrogen, giving a total flow rate of 1030 cc/min and an irradiation residence time of 56 sec. The trap's ice bath was filled with *ca.* 30 lb of dry ice and the baffle inserted. The lamps were turned on, and the irradiation was continued for 48 hr. In that time 3.08 g (7.9×10^{-6} moles/min) were collected in the trap.

Instruments

Infrared spectra were obtained from either a Perkin-Elmer 257 Grating Infrared Spectrometer or a Beckman IR-7 Infrared Spectrometer. A Varian A-60-A spectrometer was used to measure nmr spectra. Ultraviolet spectra were obtained from a Cary 14 Recording Spectrophotometer. Melting points were taken on a Thomas-Hoover Melting point apparatus or a hot plate microscope and are reported uncorrected. Emission spectra measurements were made on an Aminco Bowman Spectrophotofluorometer with a phosphorescence accessory.

Flash spectroscopy and double-flash spectroscopy was carried out with an instrument from this laboratory. The apparatus and general technique of making the measurements have been previously described.[51]

The electron paramagnetic resonance spectrum of phenyl-*n*-butyrate in benzene was obtained while being irradiated with ultraviolet light on an apparatus from this laboratory.[52]

Mass spectra of some of the products in the mixture resulting from the gas phase irradiations of phenyl acetate were obtained from a combination gas chromatograph-mass spectrometer. A Hewlett-Packard model 7620A Temperature Programming Research Gas Chromatograph, interfaced with an EAI Quad 300 quadrupole mass spectrometer, was employed for the determinations.

Gas Chromatography

Analysis of photoproducts from the scavenging experiments was made on a 6 ft x ¼ in, 5% Apiezon L on Chromosorb G-AW-HMDS at 80° and 220°. Two instruments were used in these experiments, a Loenco Model 15B gas chromatograph with thermal conductivity detection and a Loenco Model 160 with dual column compensation and flame ionization detection.

Analysis of the gaseous compounds resulting from decarbonylation in the scavenging experiments was obtained with a *ca*. 2 ft x 1/8 in column containing Grace 60-200 mesh activated silica gel. A Loenco Model 160 operating in the temperature range of ambient to 40° was employed for the determination.

Phenyl Benzoate Quantum Yields. The quantitative analyses for the quantum yield of dissappearance of phenyl benzoate and associated product formation were made on a

Loenco Model 70 gas chromatograph incorporating dual column compensation and flame ionization detectors. A 10 ft x ¼ in column of 4% Apiezon L on Chromosorb G operated at 20° was used to determine the benzene content of photolyzed samples. Dual columns of 10 ft x ¼ in, 5% SE-30 on Chromosorb W-HMDS were operated at 270° to determine quantities of phenyl benzoate and the TMS ethers of o- and p-hydroxybenzophenone. A temperature of about 120° was used to determine the amounts of the TMS (trimethylsilyl) ether of phenol.

Alternatively, a Hewlett Packard No. 5750 Research Gas Chromatograph with facility for temperature programming, dual column compensation, and flame ionization detection was used to determine the relative quantum yields of the o- and p-hydroxybenzophenones (TMS ethers). Dual columns 5 ft x 1/8 in of 5% SE-30 on Chromosorb W-HMDS were used in conjunction with a program consisting of a 3 min post-injection delay at 45°, followed by a 6 min programming rate to 215°, followed by a 3 min upper temperature delay.

Photoproducts from Irradiation of p-Isopropenylphenyl Acetate were determined as their TMS ethers by gas chromatography on a 10 ft x ¼ in 5% SE-30 column at 280°.

Analysis of starting material and photoproducts resulting from vapor phase bulb irradiations were made on the HP-5750 with a 5 ft x 1/8 in, 5% column on Chromosorb W-HMDS. Typical conditions employed a 40 cc/min carrier flow and the following temperature program: 5 min at 80°; 10°/min from 80° - 200°; 5 min at 200°.

Product analyses from the flow system irradiations of phenyl acetate vapor and related compounds were made on the HP-5750 with a 7 ft x 1/8 in column of 10% DC-LSX-3-0295 on Chromosorb W (acid washed). A flow rate of ca. 40 cc/min and a temperature program consisting of a post-injection delay of 8 min at 108°, a rate of 15°/min between 108 and 210°, and an upper limit delay of 3 min at 210°. Alternatively, a 5 ft x 1/8 in 5% SE-30 on Chromosorb W (acid washed DMCS) with a program consisting of a 5 min post-injection delay at 80°, 10°/min rate between 80° and 200°, and a 5 min upper limit delay at 200°. Similarly a 5 ft x 1/8 in column of 5% XE-60 on Chromosorb W (HMDS) at 160° was also used.

Quantum Yields

Samples of phenyl benzoate (ca. 0.1 molar) in various solvents were irradiated by means of the sealed tube technique with a 253 nm "merry-go-round" apparatus. Light intensities of ca. 6.1×10^{-8} E/min were monitored throughout the irradiation period with potassium ferric oxalate actinometry.[53a] Consumption of ester and conversions to non-phenolic products were measured directly by gas chromatography. Phenolic products resulting from the irradiation, were analyzed by first converting them quantitatively to their more volatile trimethylsilyl ethers by the action of bis-(trimethylsilyl)-acetamide, and then measuring them by gas chromatography. Measurement of peak areas from the chromatograms was made by means of either the cutting and weighing technique or by using a disk integrator. Triplicate data points were taken for each value.

The inclusion of an internal standard in the solutions provided accurate values of the amounts of conversion for measured volumes of solution. Comparison of these values with calibration curves for each compound gives the concentration of photoproducts in each sample. By plotting the mmoles of conversion _vs._ m Einsteins of light, extrapolating the curve to zero at zero time, and measuring the slope, one can obatin the quantum yield at low conversion.

Silylation of Phenols with bis-(Trimethylsilyl)acetamide (BSA).[53b] A 2 ml aliquot of the photolyzed solution (typically 0.1 M in phenyl benzoate) was placed in a 5 ml serum bottle fitted with a serum cap. To this sample ½ ml of purified BSA was introduced through the cap by means of a syringe and needle. (An additional 1 ml of BSA was added to those samples which contained acid.) The bottle was agitated a few seconds and allowed to react for 24 hrs. Independent experiments showed that this period was sufficient to assure quantitative conversion of the sample.

Detection of Gases Resulting from Photodecarbonylation. The hydrocarbon gases resulting from photodecarbonylation in phenyl _n_-butyrate solutions were qualitatively analyzed by coincident injection of authentic gas samples with injections of the solutions containing dissolved gases on a silica gel column. Enhanced peak heights without a change in the shape was taken as strong evidence toward establishing the identity of the gas.

Measurement of carbon monoxide resulting from the flow system irradiation of phenyl acetate vapor was made by channeling the effluent gas from the drying tube through a three neck flask. The center neck of the flask contained a punctured serum cap through which a carbon monoxide analyzer tube could be placed. A Bacharach Universial Gas Sampler No. 1907016 with potassium-pallado-sulfite type carbon monoxide sampling tubes No. 19-0195 permitted measurement of concentrations to 10 ppm CO. The unit is manufactured by the Bacharach Instrument Co., Pittsburgh, Pa.

Identification of Gas Phase Photoproducts

Phenol was isolated from the rest of the components in the product mixture resulting from the irradiation of phenyl acetate by a preliminary separation using preparative gas chromatography. A Varian Aerograph Autoprep 700 Chromatograph and a 19 ft x 3/8 in column of 20% DC-LSX-3-0295 on Chromosorb W-HMDS was used at 135^o to effect the separation. Phenol isolated in this fashion was still impure and a second preparative chromatography at 100^o succeeded in removing most of the contaminant. The Infrared spectrum was obtained (CCl_4) revealing the following strong absorptions: 3600, 3340 (broad), 1607, 1598, 1510, 1482, and 1225 cm^{-1} (broad). The nmr (CCl_4-TMS) gave the following absorptions: $\delta = 6.18$

(1H, s) and 7.0 (5H, complex multiplet). Both the infrared and nmr spectra are completely superimposable with the spectra of an authentic sample of phenol. Similarly glpc analysis on three different columns (1) 5 ft x 1/8 in 10% DC-LSX-3-0295, (2) 5 ft x 1/8 in 5% SE-30 on Chromosorb W (acid washed - DMCS), and (3) 5 ft x 1/8 in 5% XE-60 on Chromosorb G (acid washed - DMCS) revealed that coincident injection of the isolated material with an authentic sample of phenol gave only a single peak. Furthermore, identical retention times of the isolated sample and one of the peaks in the photoproduct mixture indicated no chemical changes had occured during isolation.

o-Cresol was obtained by extraction of many combined runs from the flow system with 5% aqueous KOH. Reacidification produced an extract consisting of acidic photoproducts which were subjected to a primary separation by preparative gas chromatography with the LSX column at 132°. A fraction was collected which consisted of crude o-cresol and was resubjected to chromatography at the same conditions. Collection of the effluent from the second preparative separation yielded a pure compound. The infrared spectrum (CCl_4) had the following strong absorptions: 3600, 1589, 1510, 1492, 1462, 1325, 1257, 1210, 1165 and 1102 cm^{-1}. The nmr (CCl_4-TMS) showed the following peaks: $\delta = 2.18$ (3H, s); 4.58 (1H, s); 6.80 (4H, complex multiplet). The above spectra are completely superimposable with the infrared and nmr spectra of an authentic sample of o-cresol. Glpc mass spectrum gives the following major peaks (in order of decreasing intensity): m/e 108, 107, 90, 77, 89, 79. Except for a higher than expected abundance of m/e 89 peak, these values are in good agreement with the major peaks in the fragmentation pattern of o-cresol.[54a] Coincident injection of authentic o-cresol and this sample gave a single peak in the gas chromatogram; comparison of retention time of it and the product mixture revealed no chemical changes had taken place during the work up.

p-Cresol was isolated from the acidic extract by two successive preparative separations by gas chromatography at 132° using the 19 ft LSX column. An infrared spectrum (CCl_4) of the isolated material showed the following strong absorptions: 3602, 3340, 1618, 1599, 1514, 1257, 1094, 1091 cm^{-1}. The nmr spectrum (CCl_4-TMS) contained the following peaks: $\delta = 2.20$ (3H, s); 5.60 (1H, s); 6.73 (4H, aa'bb'). GLPC-mass spectroscopy of the peak corresponding to this compound in the photoproduct mixture gave the following m/e ratios: 107, 108, 77 and 87 which are in good agreement with the published fragmentation pattern for p-cresol.[54a] The nmr and ir spectra of the isolated material are superimposable with those taken of p-cresol. In addition, a single peak in the glpc resulted from coincident injections of the isolated product and authentic p-cresol. As before, no chemical change had occured during the isolation procedure, since retention times of the isolated material and a peak in the product mixture were identical.

o-Hydroxydiphenyl Ether was isolated by preliminary extraction with 5% aqueous potassium hydroxide. Following the reacidification, the extract was separated into fractions by preparative gas chromatography. A 10 ft x 3/8 in 15% DC-LSX-3-0295 on 60/80 Chromosorb W-AW at 190° and a flow rate of ca. 110 cc/min was used to isolate the two peaks of highest retention time in a single fraction. A second chromatography under the same conditions separated the fraction into the two components. The one with the shortest retention time was collected as a light brown solid, sublimed, and recrystallized from hexane to give white crystals melting 103-104° (lit mp 103-104°).[48] The infrared spectrum (CCl_4) had the following strong absorptions: 3460, 1598, 1592, 1500, 1492, 1267 and 1216 cm^{-1}. The nmr (CCl_4-TMS) absorptions were $\delta = 5.21$ (1H, s); and 6.83 (9H, complex multiplet). The above spectra were superimposable with infrared and nmr spectra taken of o-hydroxydiphenyl ether which was synthesized by the method of Norris, et al.[48] A mixed melting point gave the following ranges: isolated sample 103-104°; authentic sample 104.5-105.5°; mixture 104-105.5°. Similarly coincident injections of isolated and authentic material into the gas chromatograph produced a single peak which was identical in retention time to a peak in the photoproduct mixture.

p-Hydroxydiphenyl Ether was similarly collected from the second preparative gas chromatography described above. The compound in its impure form was yellow and crystalline. Sublimation followed by solution in methanol and filtration eliminated the yellow color. Recrystallization from hexane gave white crystals melting 82-83° (lit mp 84-85°).[54b] The infrared spectrum (CCl_4) revealed the following strong absorptions: 3608, 3420, 1591, 1508, 1490, 1233 and 1188 cm^{-1}. The nmr spectrum (CCl_4-TMS) was taken: $\delta = 4.52$ (1H, s); 6.90 (9H, complex multiplet). Both spectra were superimposable with those of an authentic sample of p-hydroxydiphenyl ether. A mixed melting point gave the following results: isolated compound 82-83°; authentic material 83.5-84°; mixture 82-83°. Injection of a mixture of authentic and isolated material gave a single peak on the gas chromatograph. There was no chemical change during the isolation as evidenced by the identical glpc retention times before and after isolation.

p-Benzoquinone - Although isolation of a small amount of pure p-benzoquinone by preparative gas chromatography with the 10 ft LSX column at 132° was successful, the major amount of this compound was obtained by physically separating colored crystals from a fraction consisting of the codistillation of three compounds. Apparently under preparative conditions where overloading becomes a problem, p-benzoquinone formed in the irradiation readily co-distills with the o-hydroxydiphenyl ether. Because of these problems, isolation of amounts adequate for analysis was very difficult. However a small amount was made pure enough to obtain analytical data. The infrared spectrum (CCl_4) although weak, had the following absorptions: 1669, 1658, 1511 (imp.), 1420, 1304, 1271, 1253, 1070, 897 and 885 cm^{-1}. The 220-nmr ($CDCl_3$-TMS) spectrum gave two absorptions: $\delta = 6.79$ (s) and 6.71 (s) (imp.). All absorption peaks in the infrared spectrum of authentic p-benzoquinone were superimposable with the spectrum of the isolated material. Similarly the chemical shift of the authentic sample agreed with the larger peak ($\delta = 6.79$) in the isolated sample. A glpc-mass spectrum allowed the aquisition of accurate mass spectral data on the pure sample of isolated material and the following m/e ratios were obtained: (decreasing intensity) 108, 110, 82, 80, 100, 81, and 54. This fragment pattern is in good agreement with published ones for p-benzoquinone.[55] Coincident injection of the isolated material with an authentic sample gave the expected peak enhancement. Identical retention times for the isolated benzoquinone and a peak in the photoproduct mixture assured that the isolation procedure had not caused any chemical changes.

o-Hydroxyacetophenone - By means of preliminary alkaline extraction and preparative gas chromatography with the 19 ft

LSX column a small amount of o-hydroxyacetophenone was obtained from the combined yields of a large number of irradiations. The fraction contained ca. 15% of an impurity of nearly identical retention time making further purification by gas chromatography fruitless. The infrared spectrum (CCl_4) was run and the following strong absorptions noted: 1642, 1618, 1511 (imp.), 1488, 1450, 1369, 1323, 1304, 1248, 1220 and 1160 cm^{-1}. The nmr (CCl_4-TMS) gave the following signals: δ = 1.32 (s, impurity); 2.62 (3H, s); 7.26 (complex multiplet, integration ca. 5 due to impurity).

Products from the Irradiation of p-Isopropenylphenyl Acetate in Solution

The mixture resulting from the irradiation of the above compound in benzene for 25 hrs resulted in a conversion of about 0.62. The products were separated by preparative thin layer chromatography on a silica gel plate. Elution with benzene on analytical plates revealed four components in the mixture with the following R_f values: 0.70, 0.64, 0.33 and 0.08. Each fraction was analyzed by glpc and the infrared and nmr spectra were taken.

Fraction with R_f = 0.64 had the following major bands in the infrared (plates): 1760, 1640, 1629, 1508, 1372, 1202 (broad), 1171, 1020, 918 and 856 cm^{-1}. The nmr ($CDCl_3$-TMS) was taken: δ = 2.14 (3H, s); 2.27 (3H, s); 2.62 (imp.); 5.09 (1H, quartet); 5.32 (1H, s) and 7.28 (4H, aa'bb').

These data and the glpc retention time are superimposable with those from the starting material.

Fraction with R_f = 0.70 was the major product of the irradiation acounting for better than 80% of the three photoproducts. The following major absorptions in the infrared were recorded (plates); 1641, 1485, 1372, 1287 and 1219 cm^{-1}. Similarly the nmr ($CDCl_3$-TMS) gave the following absorptions: δ = 2.11 (3H, quartet); 2.26 (imp.); 2.61 (3H, s); 5.10 (1H, complex multiplet); 5.30 (1H, complex miltiplet); and 7.34 (4H, complex multiplet). The above spectral data are consistent with the structure of 2-acetyl-4-isopropenylphenol.

Fractions with R_f = 0.33 and 0.08 were isolated in considerably smaller amounts since each accounts for 10% or less of the photoproducts; their purity was also lower. The glpc retention times of both compounds were intermediate between those of the starting ester and the *o*-rearrangement product.

Fractions with R_f = 0.33 had the following major infrared absorptions (plates): 3400 (broad) (H_2O), 1670, 1610, 1600, 1588, 1515, 1270, 1205, 1170 and 843 cm^{-1}. The nmr ($CDCl_3$-TMS) had the following peaks: δ = 2.09, 2.30, 2.56, 4.97, 5.28 and 7.10 (*ca.* aa'bb') (spectral data were of poor quality). The fraction with the 0.08 R_f had the infrared absorptions: 3360, 1700, 1510, 1370, 1275, 1222, 1210, 1174, 914 and 738 cm^{-1} The nmr ($CDCl_3$-TMS): δ = 1.48, 1.82, 2.03, 2.12, 2.25 (s, large), 2.50 and 7.05 (comples multiplet).

III. RESULTS

Irradiations in the presence of hydrogen donors

A solution of 0.1 M phenyl *n*-butyrate in cyclohexane, heptane, benzene and *n*-amyl alcohol was made up containing large concentrations of compounds which are facile hydrogen donors. Both *n*-butyl mercaptan in concentrations of 1.0 and 9.5 M, and triethylsilane in 1.0 M concentrations provided a ready source of hydrogen to scavenge any free radicals formed in these experiments.[56] Many irradiations of these solutions in sealed tubes for periods of from 10 to 175 hr, causing from 15 to 95% disappearance of the phenyl *n*-butyrate produced the expected products: *o*-hydroxybutyrophenone, *p*-hydroxybutyrophenone and phenol (Table I). There was a trend in the relative disappearance quantum yields of phenyl *n*-butyrate in these solvents with the least amount of reaction occuring in the hydrocarbon solvents, cyclohexane and *n*-heptane. Reaction was markedly enhanced in benzene, and the highest relative yields resulted with *n*-amyl alcohol. Analysis of the reaction mixtures by thin-layer chromatography revealed that only the above mentioned photoproducts formed in the samples containing hydrocarbon solvents, while the tubes with *n*-amyl alcohol as the solvent gave two additional photoproducts. Although some phenol could be detected from every irradiation in this series, careful analysis by gas chromatography failed to provide a single case in which any n-butyraldehyde was found. The analytical technique was good enough to detect as little as 0.5% conversion of the phenyl n-butyrate into n-butyraldehyde.

TABLE I

Relative Rates of Phenyl n-butyrate

Solvent	% Conversion*	Relative conversion
Cyclohexane	21 - 25	1.1
Heptane	18 - 23	1
Benzene	52 - 65	2.8
n-Amyl alcohol	~95	4.5

*54.5 hr on unfiltered Hanovia 450 lamp

Based on these results, the photochemical stability of the sought-for compound, n-butyraldehyde, was determined by another set of experiments. Samples were prepared containing amounts of phenyl n-butyrate and scavenger identical to those used in the previous study plus an additional 1.0 M concentration of n-butyraldehyde. Again, the samples were exposed to an unfiltered Hanovia 450 W medium pressure lamp for 54.5 hr, and then the products were analyzed by gas chromatography. The results, tabulated in Table II, show that n-butyraldehyde decomposes under the conditions of the reaction. Although the extent of decomposition and therefore the rate (with

TABLE II

Relative* Rates of Decomposition of Phenyl n-Butyrate and n-Butyraldehyde

Solvent	Ester converted	Aldehyde decomposed
Cyclohexane	27%	17%
n-Heptane	24%	27%
Benzene	99%	82%
Alcohol	100%	100%

*54.5 hr on unfiltered Hanovia 450 lamp

appropriate assumptions) is dependent upon the solvent, in all but the cyclohexane solutions, the rate of decomposition of the aldehyde is comparable to or faster than the photolysis of phenyl n-butyrate. As a result, scavenging experiments designed to trap a butyryl radical as butyraldehyde would be expected to have a very low, if not zero probability for success.

During the course of this study, peaks with extremely short retention times were observed in the gas chromatograms of irradiated samples of phenyl n-butyrate. Comparison of these with the chromatograms of aldehyde-containing samples, suggested that the peaks might be the products of decarbonylation of the acyl fragment of the ester. Once again sample tubes containing 0.1 M phenyl n-butyrate in the four solvents were made up and exposed to ultraviolet light. In addition, two sets of control samples were prepared and irradiated;

one which contained only the solvent and scavenger, and another which contained 0.1 M n-butyraldehyde and solvent. Gas chromatograms of the samples again showed the short retention time peaks which upon further study were identified as hydrocarbon gases dissolved in solution. Table III gives the product distribution from each sample and a semi-quantitative indication of the total amount of hydrocarbon gas

Table III

Sample	Total Gaseous Product (semi-quantitative) (arbitrary units)	Relative Distribution Ethane	Ethylene	Propane	Propylene
0.1 M phenyl n-butyrate in cyclohexane	28.5	1	0.34	4.9	-
0.1 M phenyl n-butyrate in n-heptane	17.8	1	0.62	8.6	-
0.1 M phenyl n-butyrate in benzene	15.8	1	1.84	6.54	0.15
0.1 M phenyl n-butyrate in n-amyl alcohol	71.5	1	11.3	19.2	4.2
0.1 M n-butyraldehyde in cyclohexane	126.1	1	-	6.3	-
0.1 M n-butyraldehyde in benzene	169.1	1	39	32.9	-
1 M Et_3SiH in benzene	11.2	1	trace	trace	-

dissolved in solution. Since liquid samples were withdrawn by syringe and injected onto the vpc to obtain these data, the total amount of gas in each is subject to variations due to solubility and sample handling techniques. Therefore, the totals are at best, semi-quantitative indicators of the extent of decarbonylation accompanying ester photolysis, and probably only reliably indicate that considerably more decarbonylation takes place in n-amyl alcohol than in the other solvents. It is clear from the product distribution data that irradiation of phenyl n-butyrate in all four solvents favors the formation of propane relative to all other hydrocarbons. (Methane and butane have also been looked for in this study.) In the photolysis of n-butyraldehyde however, both propane and ethylene are major products, with ethylene formation favored by about 15%.

As a result of the irradiations run in the presence of large concentrations of n-butyl mercaptan, hydrogen sulfide was formed in pressures sufficient to burst thick-walled quartz tubes. Subsequent study revealed that high concentrations of mercaptan resulted in significant light absorption and direct photolysis of the sulfur compound. Hydrogen sulfide, butyl disulfide, and the previously unreported dibutyl sulfide were identified from the irradiations of 1-butanethiol.[57] As a result, triethylsilane, which does not have significant absorption in the region around 250 nm, was substituted for butyl mercaptan as a hydrogen donor.

Irradiation of p-Isopropenylphenyl Acetate

Irradiation of 0.005 M solution of p-isopropenylphenyl acetate in benzene gave one major photoproduct and two minor ones. Following separation of the components of the mixture by preparative thin layer chromatography, nmr and infrared spectra of each fraction were taken. Spectral data for the fraction corresponding to the compound which made up 81% of the photoproduct mixture were consistent with the structure of 2-acetyl-4-isopropenylphenol. Spectral data on the other two photoproducts, each amounting to about 10% of the product total, were of considerably poorer quality due to impurities. The nmr spectrum of one of the compounds showed no styrene proton absorptions similar to those present in the starting material and major photoproduct. However, study of these compounds was not pursued further because of their minor role in the photochemistry of the ester.

Emission Spectra

Phosphorescence and total emission spectra were recorded at 77° K in EPA glass from phenyl n-butyrate (Fig. 3), phenyl benzoate (Fig. 4), phenyl adamantane-1-carboxylate (Fig. 5) and phenyl caprylate (Fig. 6). Phenyl benzoate showed no emission at all, even at very sensitive settings of the spectrophotometer. In contrast, the other esters all displayed a relatively strong phosphorescence band with a λ_{max} at 380 nm and peak onset at 335 nm which corresponds to a triplet energy of 85 kcal. Phenyl caprylate and phenyl adamantane-1-carboxylate also showed a small fluorescent emission peak λ_{max} 280 and peak onset at 260 nm. A similar fluorescent emission could not be observed with phenyl n-butyrate because of the appearance of a large amount of

Figure 3

Absorption and Emission Spectra
of Phenyl _n_-Butyrate

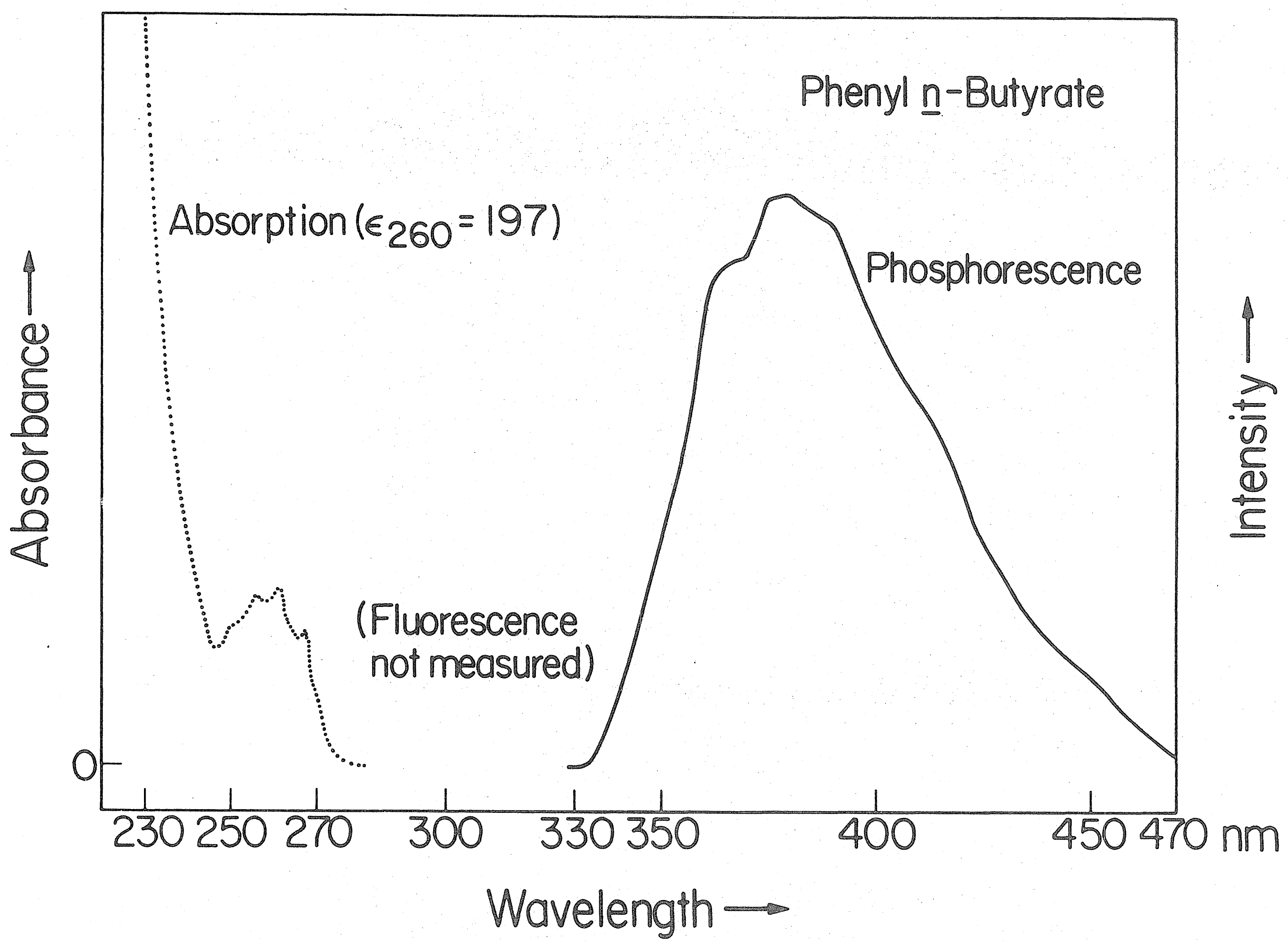

Phenyl n-Butyrate
Absorption ($\epsilon_{260} = 197$)
Phosphorescence
(Fluorescence not measured)
Absorbance ⟶
Intensity ⟶
0
230
250
270
300
330
350
400
450
470 nm
Wavelength ⟶

Figure 4

Absorption and Emission Spectra

of Phenyl Benzoate

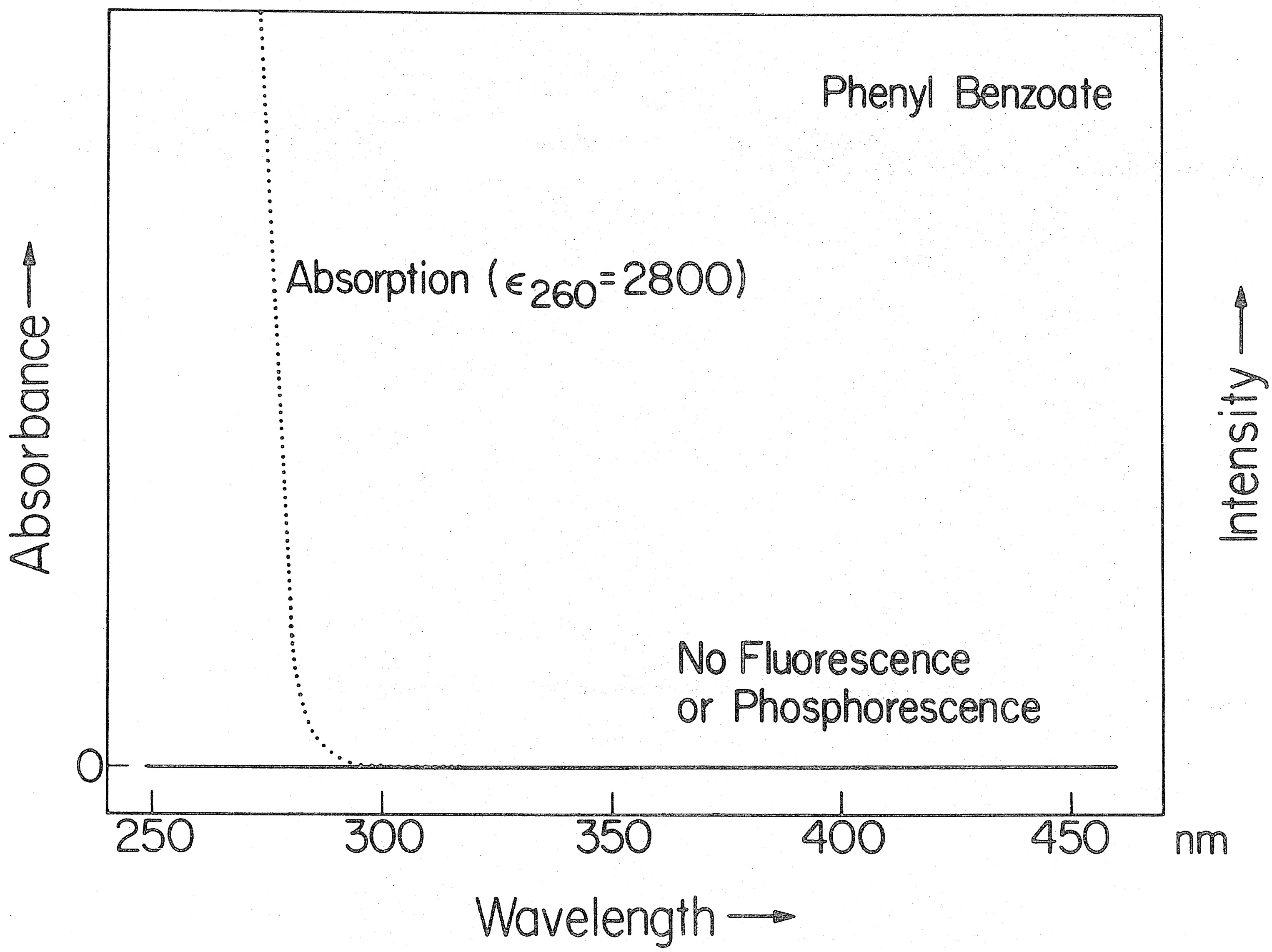

Phenyl Benzoate
Absorption (ϵ_{260}=2800)
No Fluorescence
or Phosphorescence
Absorbance ⟶
Intensity ⟶
0
250
300
350
400
450
nm
Wavelength ⟶

Figure 5

Absorption and Emission Spectra
of Phenyl Adamantane-1-carboxylate

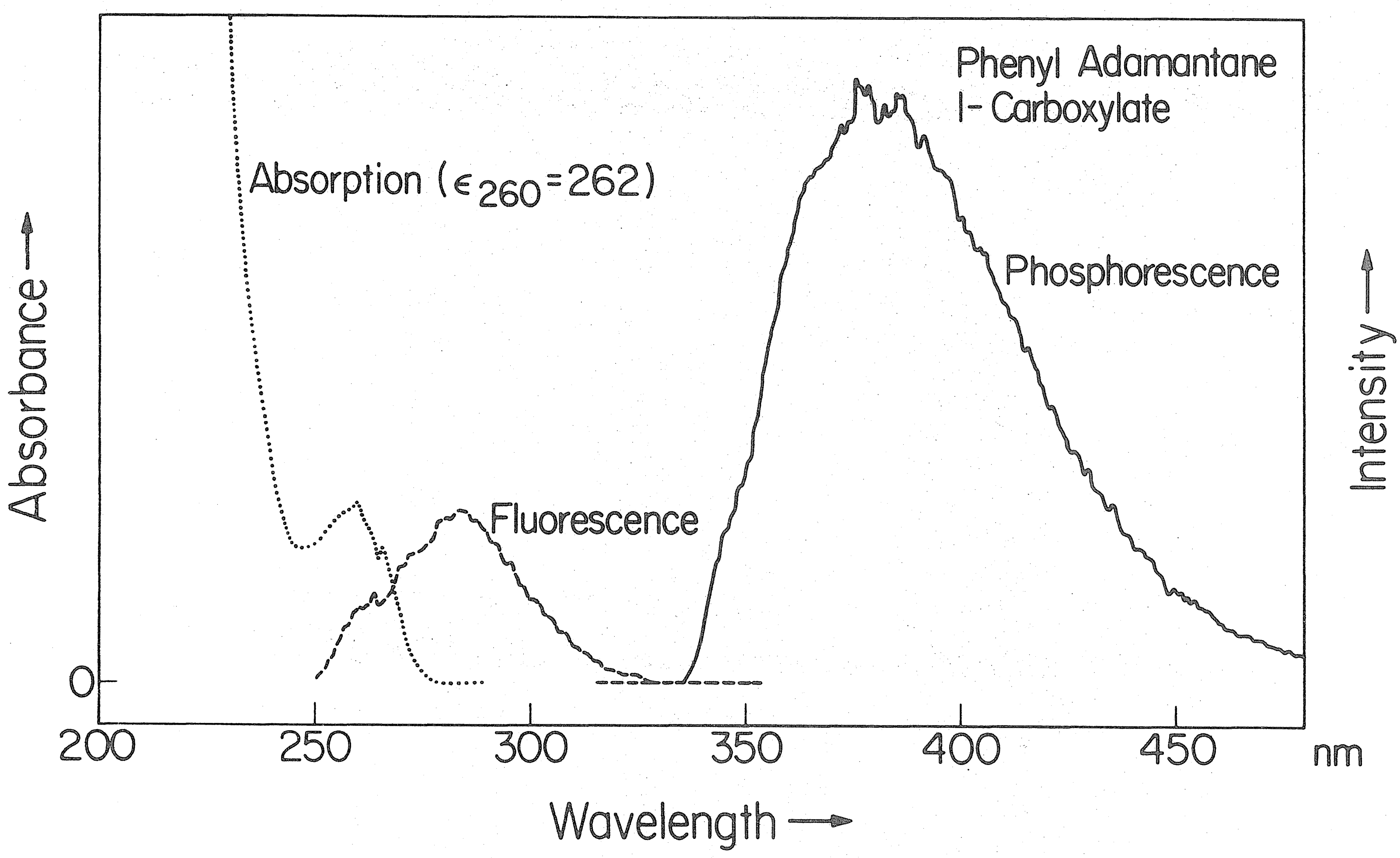
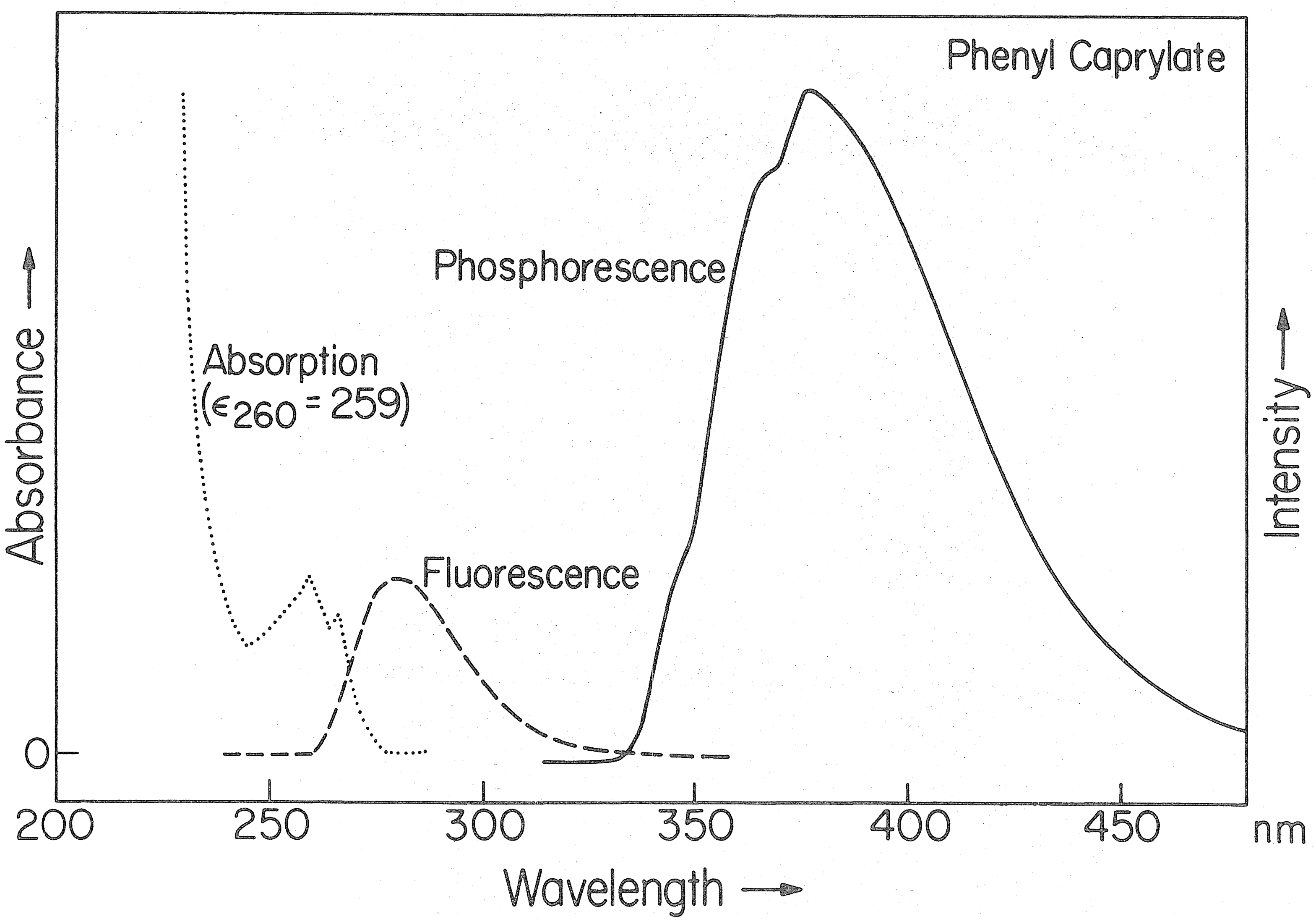

Phenyl Adamantane
I- Carboxylate
Absorption (ϵ_{260}=262)
Phosphorescence
Fluorescence
Absorbance ⟶
Intensity ⟶
0
200
250
300
350
400
450
nm
Wavelength ⟶

Figure 6

Absorption and Emission Spectra

of Phenyl Caprylate


Phenyl Caprylate
Phosphorescence
Absorption
($\epsilon_{260} = 259$)
Fluorescence
Absorbance →
Intensity →
0
200
250
300
350
400
450
nm
Wavelength →

scattered light from the excitation source in the spectrum. In all cases where emission was observed, excitation spectra were taken revealing a strong absorption in the region of 265 nm which overlaps the first peak of the absorption spectra of these esters. Absorption spectra, for comparison purposes, were obtained from ethanol solutions.

Electron Paramagnetic Resonance Studies

Irradiation of a benzene solution of phenyl *n*-butyrate with ultraviolet light in the cavity of an EPR spectrometer produced a weak light-dependent signal. The signal was a broad, structureless peak with a line width of 48 g and a g = 2.0.

Flash Lamp Spectroscopy

Several experiments were carried out involving kinetic spectroscopy of solutions of phenyl benzoate and phenyl caprylate. No transient absorptions were observed in the region of 400 nm from phenyl benzoate; the results of similar experiments with phenyl caprylate were inconclusive.

Quantum Yields

The quantum yields for disappearance of ester and the formations of *o*-hydroxybenzophenone, *p*-hydroxybenzophenone, and phenol were measured in ether solution. Because of competitive light absorption due to the intense absorption coefficients of the products, determinations were made at low ester conversions. Tubes containing solutions of 0.1 M phenyl benzoate in anhydrous ether were irradiated for varying lengths of time on a 254 nm "merry-go-round". Quantitative conversion of phenolic products to their more soluble trimethylsilyl ethers followed by gas chromatographic analysis established the product yields. Extrapolation of a plot of these values versus the integrated light intensity produces the quantum yields at zero percent conversion (Fig. 7). Quantum yield for ester disappearance was $\Phi = 0.85 \pm 0.04$. The quantum yields for formation of products were: *o*-hydroxybenzophenone $\Phi = 0.30 \pm 0.01$, *p*-hydroxybenzophenone $\Phi = 0.28 \pm 0.01$ and phenol $\Phi = 0.14 \pm 0.01$. In addition, attempts to measure a quantum yield for benzene, a possible decarbonylation product, indicated none was formed. Analytical procedures could have easily measured a conversion of 0.1%, or in terms of quantum yields, Φ 1.5×10^{-3}.

In a similar manner, the relative quantum yields of formation of *o*- and *p*-hydroxybenzophenones was determined as a function of solvent acidity. A set of samples of 0.1 M phenyl benzoate in ether and a second identical set containing an additional 0.1 M concentration of acetic acid were irradiated and analyzed. The results (Table V) indicate that, within experimental error, increased solvent acidity does not influence the rearrangement product distribution.

Figure 7

Quantum Yields Associated with the Irradiation of Phenyl Benzoate

(Loss of ester, and formation of *o*- and *p*-Hydroxybenzophenones and Phenol)

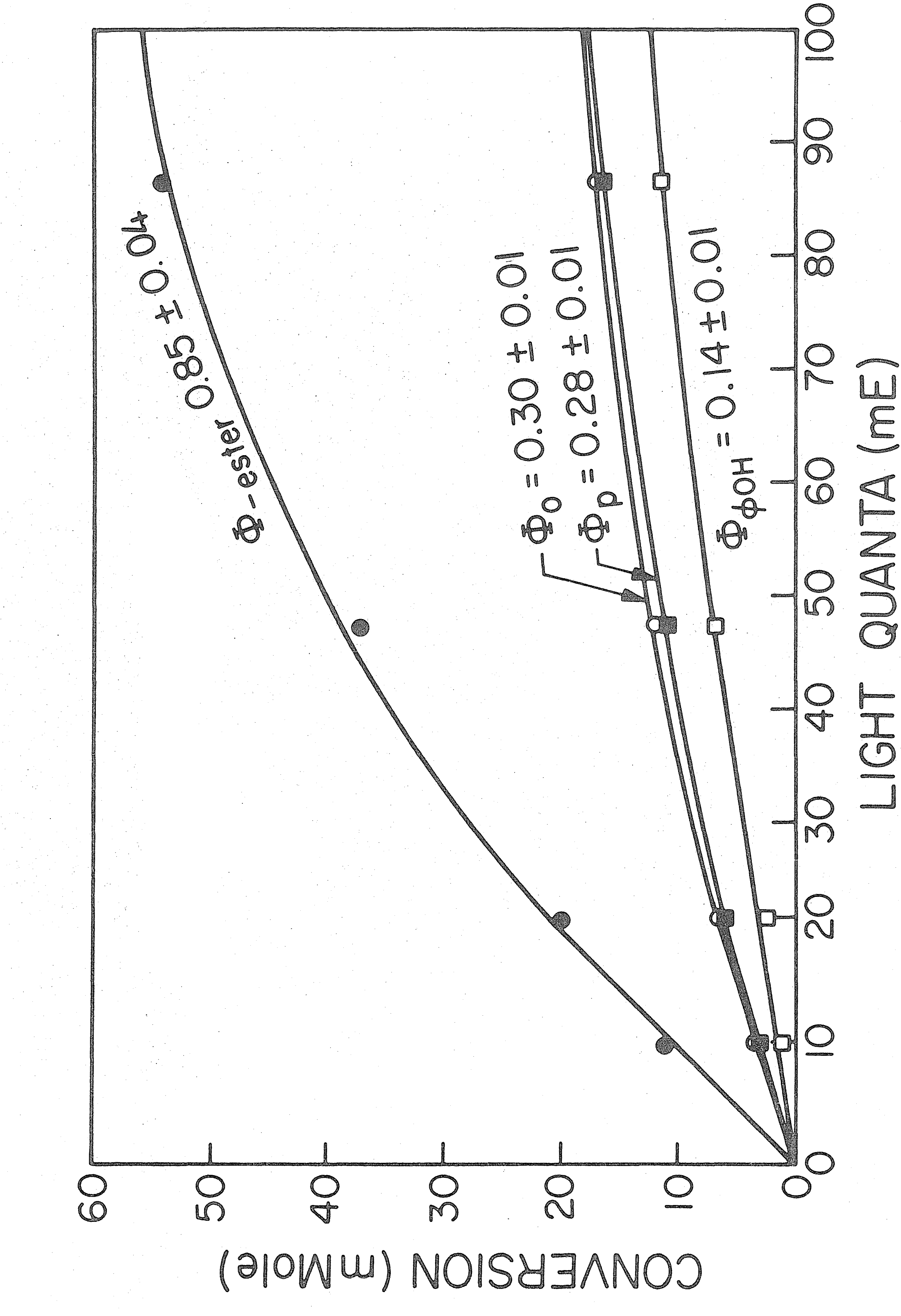

CONVERSION (mMole)
0
10
20
30
40
50
60
LIGHT QUANTA (mE)
0
10
20
30
40
50
60
70
80
90
100
Φ-ester 0.85 ± 0.04
Φ_o = 0.30 ± 0.01
Φ_p = 0.28 ± 0.01
$\Phi_{\phi OH}$ = 0.14 ± 0.01

Table IV

Quantum Yields Associated with the Irradiation of Phenyl Benzoate

	mE x 10^2	m moles x 10^2			
		Ester	o	p	φOH
	0	33.9	0	0	0
1.	1.09	31.4	.33	.31	.13
2.	2.16	30.4	.69	.63	.28
3.	4.71	27.8	1.20	1.07	.76
4.	8.68	26.1	1.70	1.61	1.15
5.	12.7	26.9	1.84	1.77	1.08
6.	17.5	20.7	2.99	2.81	1.84
7.	22.1	22.9	3.15	2.89	1.86
		± 5%	± 4%	± 4%	± 10%

Table V

Effect of Acidity on the Rearrangement of Phenyl Benzoate

Duration of UV exposure	o-/p- ratio* neutral sample	o-/p- ratio* sample 0.1 M acid
6 hr	1.00 ± .05	1.05 ± .01
12 hr	1.08 ± .07	0.98 ± .02
30 hr	0.92 ± .09	0.99 ± .01
Average	1.00 ± .07	1.01 ± .02

*Ratio of peak areas

Vapor Phase Irradiations

Preliminary experiments involving the irradiation of phenyl acetate in the gas phase were carried out in sealed quartz bulbs, over a wide variation of reaction parameters. Specifically, irradiations were conducted with partial pressures of phenyl acetate at 1 and 10 mmHg and at several total pressures within the range of 10 to 1000 mmHg for periods of from two to 25 hours. In addition, pentane, isopropanol, trimethylsilane or isobutane was added as a ready source of hydrogen for potential radical abstractions. Despite this wide variation of conditions the photochemistry in the vapor state displays some rather general traits. Gas chromatographic analysis of the reaction mixtures indicated a substantial difference in the product distribution when compared to those resulting from the solution irradiations of phenyl acetate. Chromatograms of the vapor phase mixtures showed several product peaks one of which was tentatively identified as phenol (by glpc retention time) to be the major product of reaction. Peaks corresponding to o- and p-hydroxyacetophenones, which are the major photoproducts in solution, were virtually nonexistent when purified phenyl acetate is irradiated in the vapor phase. Instead the chromatograms of the vapor phase irradiations indicated formation of a large number of unidentified photoproducts. The irradiation of phenyl acetate, for example, at a partial pressure of 10 mmHg in 1000 mmHg of isobutane for two hours at 70° gave 25 products (by glpc).

o-Hydroxyacetophenone. As a result of similar experiments, it was tentatively established that exposure of o-hydroxyacetophenone to 254 nm light results in photolysis which appears to be pressure dependent. Such behavior is in direct contrast to the results of solution photochemistry of this compound. Solutions of o-hydroxyacetophenone in both heptane and pentane were irradiated for 8 hr at 254 nm, with no detectable changes in the ultraviolet - visible spectra. In contrast, exposure of a bulb containing a few mmHg of the vapor in about 100 mmHg of pentane at 50° to 254 nm light results in phenol formation. Within two hours roughly 20% of the ester photolyzes to give phenol (detected by glpc retention time). When the total pressure in the bulbs is increased to ca. 1000 mmHg, the photochemical pathway leading to phenol ceases to be the preferred route.

Instead, phenol formation virtually drops to zero and is replaced by another photoproduct. Within 2 hr o-hydroxyacetophenone at 1000 mmHg total pressure photolyzes about 5% giving a compound whose retention time on an SE-30 column is identical to that of salicylaldehyde.

The photochemical stability of the second product of the photo-Fries rearrangement, p-hydroxyacetophenone, was also studied by these techniques. Relative to its ortho isomer, it was found to be considerably more stable, and only on prolonged exposure to ultraviolet light was a small amount of decomposition to phenol observed.

Irradiation of Phenyl Acetate Vapor by Flow Techniques. In order to irradiate phenyl acetate in quantities sufficient to permit identification of the photoproducts, a flow system was developed. The key component of the system consisted of a large-diameter, heated quartz tube surrounded by a battery of 254 nm mercury lamps. Through this tube was passed a mixture of vaporized phenyl acetate (99.9% pure), (0.15 mmHg), isobutane (ca. 25 mmHg) and nitrogen (735 mmHg). A total flow rate of 1030 cc/min was chosen to give a residence time of 56 sec for the irradiation. With flow rates adjusted in this manner about 1.5 g of phenyl acetate was vaporized and irradiated in about 24 hours. The mixture of photoproducts and unreacted starting material were trapped at -70^o and then extracted with ether. Gas chromatographic analysis showed the mixture contained six major photoproducts and phenyl acetate; conversions were typically 3-4%. Although there were a few other small peaks, the six products account for greater than 95% of the total photoproduct yield, with the remaining few percent distributed among about six other very small peaks. Irradiation of considerable quantities of phenyl acetate, coupled with extensive preparative gas chromatography, permitted successful isolation of all the major photoproducts. Identification was by comparison to authentic samples either purchased or synthesized by other routes. The following compounds were identified as the major products resulting from photolysis of purified phenyl acetate in the gas phase (numbers in parentheses indicate approximate fractions of the total product mixture): phenol (65%), o-cresol (7.5%), p-cresol (6.0%), p-benzoquinone (7.0%), o-hydroxydiphenyl ether (4.0%) and p-hydroxydiphenyl ether (9.0%). In addition, carbon monoxide was measured in the product flow in concentrations between 0.004 and 0.0025% during the irradiation. This value corresponds to about 2% conversion of ester going to carbon monoxide. During the course of the irradiation and product isolation, a seventh compound whose yield was less than 1% when purified phenyl acetate is irradiated, was recovered somewhat impure, and tentatively identified as o-hydroxyacetophenone, one of the two rearrangement products common to solution irradiations of phenylacetate.

Additional gas chromatographic studies were carried out during this study to determine the possible existance of anisole, toluene, benzene, t-butylphenols and a number of other compounds in the photoproduct mixture. Although the chromatograms had very small peaks with retention times which were close to those for anisole, toluene, benzene and p-t-butylphenol, the amounts of each of these peaks were well below 1% of the total product mixture and therefore judged not significant to this study.

After several hours irradiation of phenyl acetate, build-up of a brown polymer became noticeable on the quartz irradiation tube and in the first segment of the trap. By the end of 30 hours of exposure, darkening of the polymer became appreciable. However, a check showed that the total build up of polymer, which proved to be soluble in 10% aqueous potassium hydroxide, in the quartz tube accounted for less than 10 mg of material.

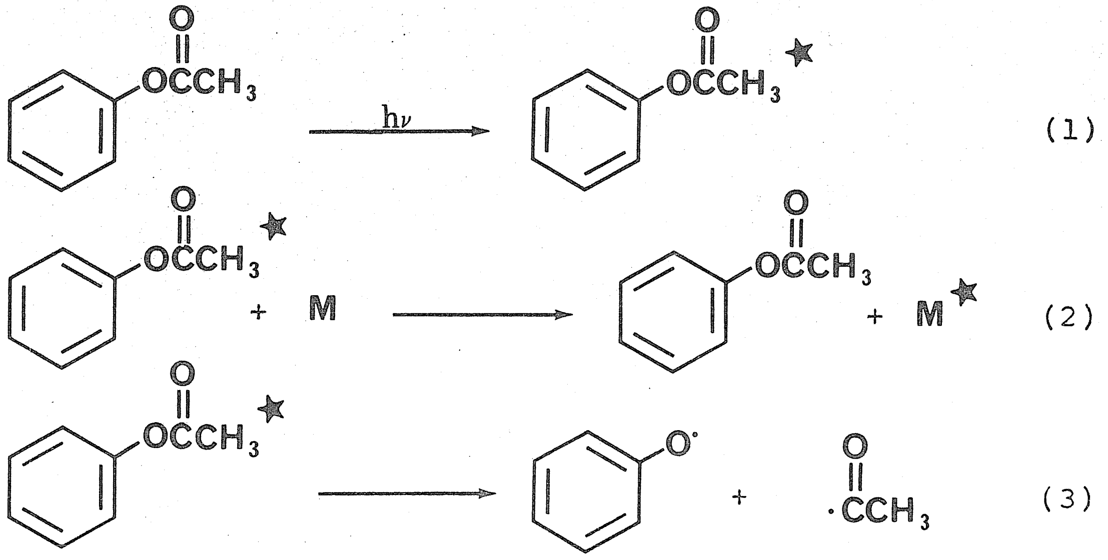
Another rather interesting observation was made during these photolyses. Inspection of trap contents at -70° after about 30 hrs of irradiation revealed the trapped material had a bright red color. As the trap and its contents were warmed to room temperature the color rapidly disappeared and only a yellow liquid remained. Such behavior could be characteristic of a reactive species which is stable at -70° but decomposes at room temperature.

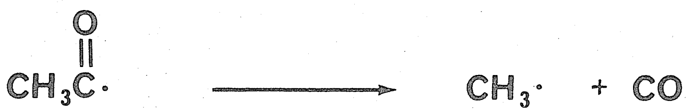
As was done with the vapor phase experiments conducted in bulbs, the stability of o-hydroxyacetophenone was checked under the conditions of the flow system irradiations of phenyl acetate. A 0.70 g sample of purified o-hydroxyacetophenone was passed through the system over a period of 18.3 hours. Relative to the phenyl acetate runs, the quartz tube remained considerably cleaner in this irradiation. Extraction of the trapped material with ether, followed by gas chromatographic analysis established that none of the major photoproducts observed in the irradiations of purified phenyl acetate were formed by photochemistry of o-hydroxyacetophenone.

IV. DISCUSSION

Discussion of Gas Phase Results

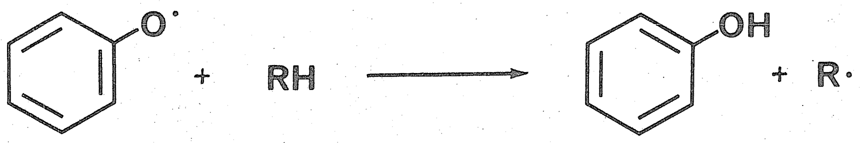
The results of our studies of the gas phase photolysis of phenyl acetate clearly indicate a radically different photoproduct composition than that obtained in solution. Most noteworthy is the fact that phenol makes up 65% of all the photoproducts. This suggests that C–O bond cleavage is the major reaction of phenyl acetate in the gas phase. Furthermore, the virtual absence of either o- or p-hydroxyacetophenone from the gas phase product mixture, despite their proven stability under the conditions, also suggests the photochemical pathways of phenyl acetate in solution and vapor are substantially different. The following scheme is proposed to explain formation of five of the six major photoproducts isolated in this study:





$$CH_3\overset{\overset{O}{\|}}{C}\cdot \longrightarrow CH_3\cdot + CO$$

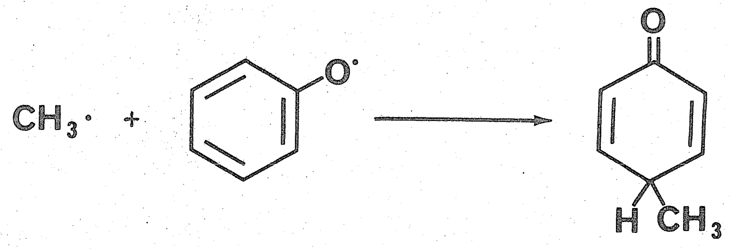
(4)



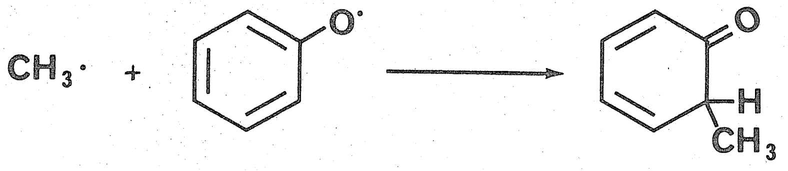
(5)

$$CH_3\cdot + RH \longrightarrow CH_4 + R\cdot \qquad (6)$$

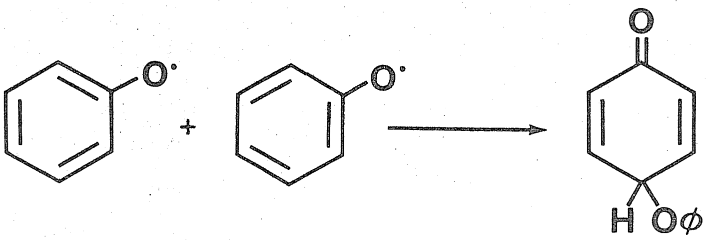
$$2CH_3\cdot \longrightarrow C_2H_6 \qquad (7)$$



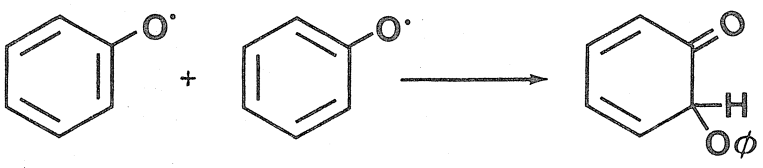
(8)



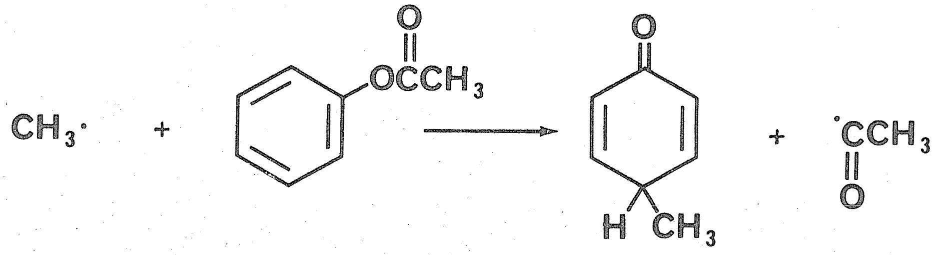
(9)



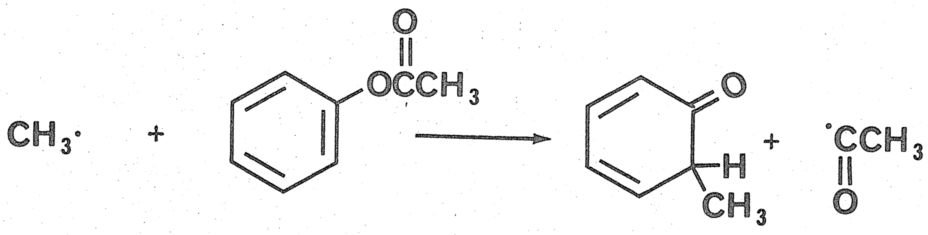
(10)



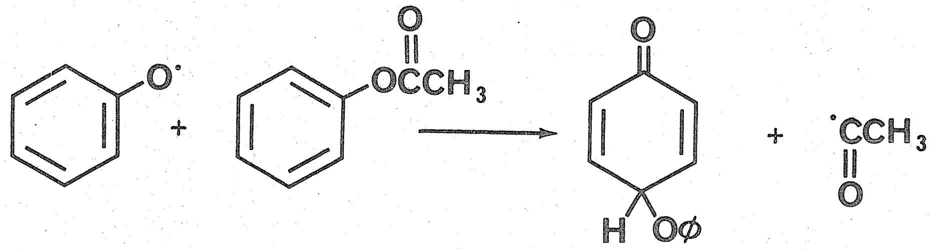
(11)



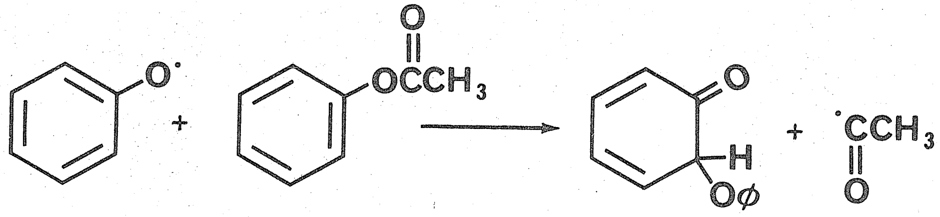
(12)



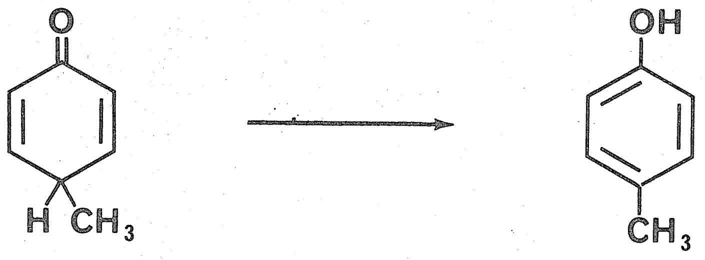
(13)



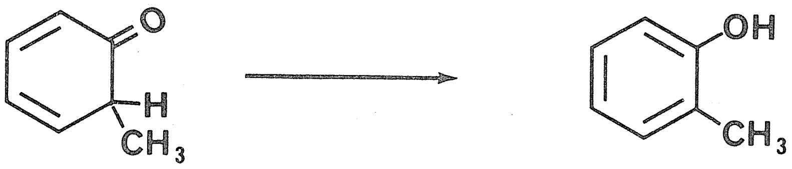
(14)



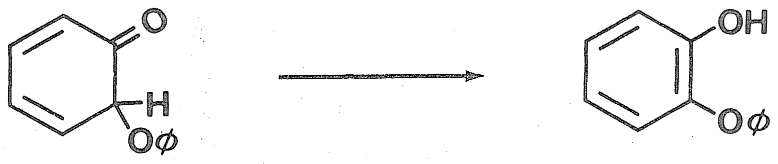
(15)



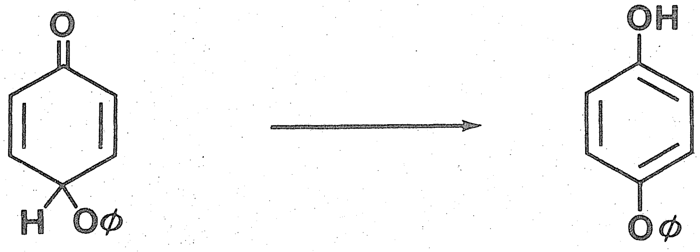
(16)



(17)



(18)



(19)

In the first step (1), absorption of a photon results in promotion of a phenyl acetate molecule to an excited state. Discussion of the nature of this excited state will be temporarily defered, and it suffices to say that PhOAc* is an ester molecule containing enough energy to break the C-O bond. This excited molecule may lose its energy through collision with another gas molecule and revert back to an unexcited state (2). Alternatively a significant number of the activated phenyl acetate molecules must escape collisional deactivation, and undergo C-O bond homolysis (3). The phenoxy radicals may abstract hydrogen from a suitable hydrogen donor such as isobutane and form phenol (5), or be involved in one of the numerous successive steps in the scheme which results in the other five minor photoproducts from the reaction. Based on the fact that phenol composes 65% of all the photoproducts formed, the majority of the phenoxy radicals follow step (5) to become phenol.

There is good reason to believe that the acetyl radicals formed with the phenoxy radicals in the homolysis step (3) rapidly decarbonylate giving methyl radicals and carbon monoxide.

The results of studies on the photochemistry of alkyl carbonyl compounds in the gas phase indicate facile decarbonylation of acetyl radicals should take place at these temperatures and pressures.[58,59] From these results, decarbonylation to give methyl radicals is proposed as the major chemical pathway of the acetyl radicals in the mechanism (4).

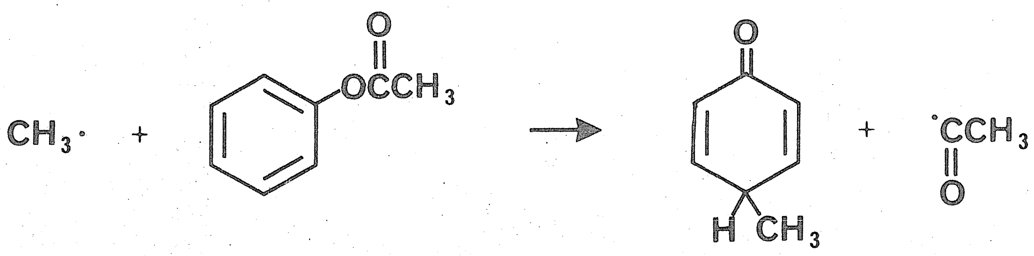
This hypothesis is backed up by the detection of considerable quantities of carbon monoxide from the phenyl acetate irradiations. In addition, two of the minor photoproducts, o- and p-cresol are considered to be derived from the reactions of methyl radicals (8,9 and 12,13). Attempts at detecting either ethane or methane, the expected products from hydrogen abstraction and coupling of methyl radicals were not made (6,7). Nevertheless, they are expected products in this scheme.

As an alternative to the hydrogen abstraction and coupling reactions, methyl radicals may react to form the o- or p-cresols which were isolated in this study and make up 7.5% and 6.0% of the total photoproduct yield respectively. Parallel reactions exist in the mechanistic scheme by which methyl radicals can form these products. One pair of pathways involves the coupling of methyl and phenoxy radicals (8,9), while the other forms the cresols by attack of methyl radicals on phenyl acetate (12,13). In a similar way the above scheme provides a mechanism for the formation of o- and p-hydroxydiphenyl ethers by reactions of phenoxy radicals with either other phenoxy radicals (10,11) or phenyl acetate (14,15). In both the reactions involving phenoxy and methyl radicals with a phenoxyl moiety, 2- and 4-substituted cyclohexadienones are formed as intermediates (8-15). Just as in the mechanisms of the solution rearrangement of this and other phenyl esters, a rapid enolization of these intermediates is proposed, giving the substituted phenols observed in this work (16-19). It is conceivable that this enolization may not take place in the gas phase (although some may occur on the wall of the reaction vessel), but instead during the work up when the trap is warmed. Behavior of this type would provide a possible explanation for the color change which accompanies the warm-up of the trap contents.

As outlined in this scheme, two parallel pathways exist for the reaction of methyl and phenoxy radicals to give the cresols and hydroxydiphenyl ethers respectively. In one route, the products result from the coupling of a phenoxy radical with either methyl radicals or other phenoxy radicals. The other pathway involves reaction of the radicals with a molecule of phenyl acetate. In this later route, radical attack is followed by expulsion of an acetyl radical which with step (4) constitutes a chain reaction with a methyl radical as the chain carrier. We have no evidence which would demand a distinction between the sequence of steps (1), (3), (4) and (8-11), or the sequence (1), (3), (4) and (12-15). Nevertheless, the factors favoring each pathway merit discussion.

The radical attack on phenyl acetate is postulated for several reasons. The concentrations of phenyl acetate are at least twenty times greater than any other possible reactant (with the exception of isobutane) in the vapor phase under the conditions of the experiment. On a statistical basis, the collisions of radicals with phenyl acetate molecules will occur with a much higher frequency than collisions with other radicals. Of course for increased collisional frequency to be effective in causing higher rates of reaction, the energetics of the reactions must be favorable.

The proposed chain reaction between methyl radicals and phenyl acetate can be shown to be nearly isoenergetic by the following calculation.



The heats of formation of phenyl acetate and 4-methyl-2,5-cyclohexadien-1-one were not found. However, roughly speaking, the transformation involves the breaking of two C-O single bonds and one C-C double bond, the formation of two C-C single bonds and one C-O double bond, and the difference in resonance energy between the two compounds.[60]

Broken		Formed		Total
2 C-O	77 = 154	2 C-C	-66 = -132	-294
1C=C	113	1 C=C	-162	267
	267		-294	- 27

The result of this calculation, taken with the additional requirement of 36 kcal/mole[61] for the resonance energy of the phenyl ring, gives a value of +9 kcal/mole for the reaction. This amount may easily be less than the resonance energy of the dienone, and the heat of reaction is probably slightly exothermic. Furthermore, a small activation energy for this reaction is expected on the grounds that the rate of addition of methyl radicals with benzene and other aromatic compounds is known to be fast.[62] Hence a chain reaction involving methyl radicals and phenyl acetate is plausible on thermodynamic grounds. However, a similar estimate of the energetics of a chain transfer step between phenoxy radicals and phenyl acetate predicts that the reaction is quite endothermic, and therefore unfavorable.

The failure to find significant quantities of anisole among the photoproducts, can likewise be interpreted by means of the chain mechanism. In this mechanism, methyl radical attack on a phenyl acetate molecule must necessarily give only ortho and para cresols. Attack at the oxygen atom, which would yield anisole, is blocked in the ester by the acetyl group which in this scheme functions as a homolytic leaving group. Products resulting from phenoxy radical attack are of course expected only in the o- and p-positions because oxygen attack results in the very stable diphenyl peroxide.

Alternatively, the cresols and hydroxydiphenyl ethers may result from the reactions of phenoxy radicals with methyl radicals or other phenoxy radicals respectively. The bimolecular reaction of two free radicals is expected to be very favorable on energetic grounds. One would expect that a relatively few collisions between such species would be required for reaction in contrast to reactions between radicals and phenyl acetate. This higher reactivity of a biradical reaction is however balanced by a much lower concentration of radicals with respect to phenyl acetate.

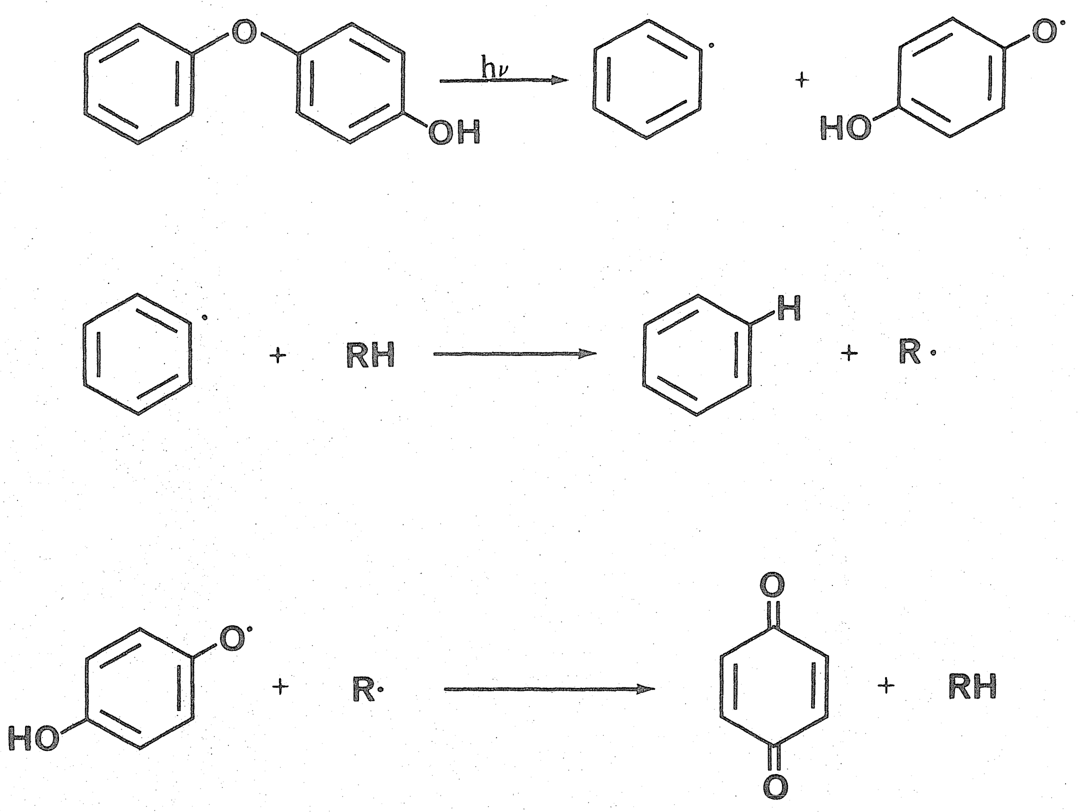
Since the rate of reaction to form the hydroxydiphenyl ethers and cresols will involve a term for both energy and concentration, it is difficult to predict which pathway provides the faster route. However, based on the well-established high reactivity of methyl radicals, one would expect that reactions with other molecules would probably pre-empt any build-up of significant concentrations of methyl radicals. As a result, the alternative step involving the reaction with phenyl acetate may be the predominate pathway in the formation of cresol. Phenoxy radicals, in contrast, are probably present in the gas phase in considerably higher concentrations than the methyl radicals because of their relatively lower reactivity. Higher concentrations will favor the biradical process, and in view of the unfavorable energetics for a reaction with phenyl acetate, it seems likely that the hydroxydiphenyl ethers result from the coupling of phenoxy radicals.

At first glance a reaction between methyl and phenoxy radicals would be expected to give not only o- and p-cresols but also a measurable amount of anisole, which as we have pointed out earlier was not observed. Based on the prediction that relative reactivity might correlate with the free electron densities in the o- and p- ring position and the oxygen, some anisole would be expected. The relative spin densities obtained from the EPR proton coupling constants[63] have been calculated to be o- = 0.63 ± .06, p- = 1.0 and oxygen = 0.26.[64] Our values for the relative amounts of o- and p-cresols isolated from the gas phase photolysis of phenyl acetate are 7.5% and 6% or a ratio of o- to p- of 1.25 ± .25 and the calculated spin densities predict a value of 1.26. The failure to isolate anisole (spin density calculations predict about 2%) and for that matter, other, more volatile, compounds may be the result of the experimental set up. The -70° dry ice trap may simply not be cold enough to lower the small partial pressure of these compounds sufficiently for collection. However, an alternative explanation may be that the relative reactivity of methyl radicals with phenoxy radicals is lower than expected at the phenoxy oxygen. The results of Mulcahy and Williams indicate that this is the case for thermally generated radicals.[64] Phenoxy and methyl radicals were generated in the gas phase at 445 - 547°K by the reaction of t-butyl peroxide on phenol in a stirred reactor. As in this study, the major products resulting from reaction between phenoxy and methyl radicals were o- and p-cresol which were isolated in the relative ratio of 1.1. The yield of anisole from this reaction was considerably smaller with a relative yield of 0.17 compared to p-cresol. The predicted value from the EPR data was 0.26.

The correlation between the predicted ortho/para ratio and measured values from the gas phase photolysis of phenyl acetate could indicate that a reaction between radicals is the predominate pathway to cresol formation. However, the alternate route in which radicals react with phenyl acetate molecules cannot be discarded for reasons outlined earlier. Until the time when evidence is available which clearly indicates a choice between the two, both pathways must be considered as plausible mechanistic alternatives for the formation of the cresols and perhaps the hydroxydiphenyl ethers. Of course there is good probability that both processes will contribute to product formation.

Irradiation of purified phenyl acetate in the gas phase failed to produce significant quantities of o- and p-hydroxyacetophenone, which would be expected if similar reactions occured with the acetyl radical. A small amount of o-hydroxyacetophenone has been isolated, however it was derived from the irradiation of impure samples of phenyl acetate. Although a step similar to (6) involving acetyl instead of methyl radicals, or a concerted formation cannot be rigorously ruled out, there is a far more plausible explanation. It is very likely that the small amount of o-hydroxyacetophenone results from the irradiation of phenyl acetate liquid in the vaporizer of the flow system. This section of the system is exposed to the UV light of the lamps, and although it is made of pyrex, it is probable that a small amount of solution photochemistry results on extended irradiations. Phenyl acetate which remains in the vaporizer after a several-day irradiation does have a slight yellow color characteristic of the o-rearrangement product. Furthermore, in those runs in which freshly purified phenyl acetate (and not exposed to room light for long periods) was irradiated, the yields of o-hydroxyacetophenone were essentially nil.

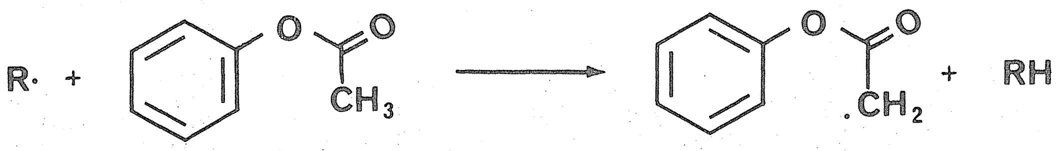
One of the products isolated from the vapor phase irradiations of phenyl acetate in 7% yield was p-benzoquinone. This compound, in contrast to all the other major photoproducts, is not seen as arising from the photolysis of starting material. Rather, p-benzoquinone must arise from a secondary photolysis of one of the primary gas phase photoproducts. The only attractive scheme that has occurred to us is the one in which p-hydroxydiphenyl ether, excited by light absorption, undergoes homolysis of the ether-phenyl bond to give a phenyl radical and a semiquinone radical. The alternative homolytic bond fission which is the reverse of step (7) would yield two phenoxy radicals. Excellent evidence from the literature on the aqueous solution photochemistry of p-hydroxydiphenyl ether

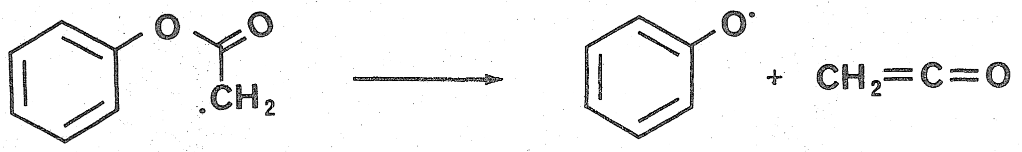


suggests the former method of cleavage to give the semiquinone radical is preferred.[45] The semiquinone radical, in the presence of other radicals, would be expected to act as an intensely reactive source of hydrogen. Abstraction of this hydrogen by collision with a radical (probably phenoxy) results in formation of the photoproduct, p-benzoquinone. Several observations from the phenyl acetate vapor photolysis support this scheme. First, fluctuations in the yields of p-hydroxydiphenyl ether and p-benzoquinone over a wide range of conditions appear to generally offset each other. In other words, higher yields of quinone are accompanied by generally lower yields of the diphenyl ether and *vice-versa*.

Gas chromatographic analysis of the product yields shows a peak which has a retention time equal to that of benzene, although it is present in relatively small yield. However, as noted earlier, isolation of volatile components with this equipment is subject to question and perhaps more benzene was formed but escaped the trap. Finally the brown polymer build-up in the quartz tube could be compatible with the secondary photolysis of p-hydroxydiphenyl ether. This compound is the least volative of all the photoproducts isolated in this work, and therefore it is not unreasonable to expect that it is the most likely to condense on the walls of the reactor. Secondary photolysis of p-hydroxydiphenyl ether could occur in the condensed phase, giving reactive intermediates similar to the solution photochemistry of the compound. In addition to causing the formation of benzene and p-quinone, a fraction of the radical intermediates may react with other molecules of p-hydroxydiphenyl ether resulting in formation of the brown phenolic polymer build-up on the walls of the reactor.

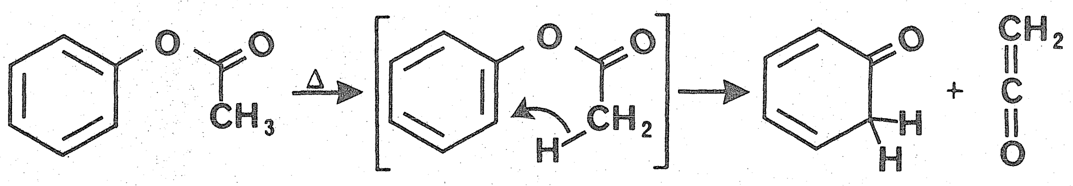
It is worthwhile to note that the gas phase pyrolysis of phenyl acetate has been studied at 625°.[65] The investigators reported finding phenol and ketene as the major products of reaction and the following radical chain reaction was proposed to explain these results.

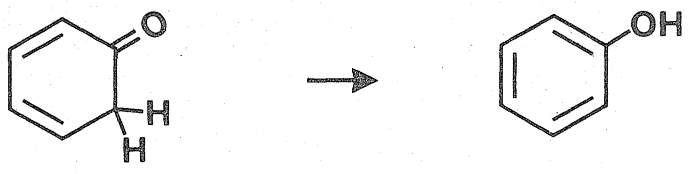




Comparison of Hurd's results with those obtained in this work suggests that the mode of excitation is important in determining the chemistry leading to products. Although it would be difficult to obtain, we have found no evidence in our studies that would cause us to postulate existence of ketene as an intermediate. If any ketene is formed in the gas phase irradiations, it must react only with phenol to regenerate phenyl acetate and not with any of the other phenolic products since no acetate esters other than phenyl acetate were isolated. With the flow rates used in our experiments, any ketene which might escape reaction in the irradiation chamber would not be collected in the trap. Furthermore, significant ketene formation from the irradiations is incompatible with the relatively high concentrations of carbon monoxide detected in this work.

It is difficult to explain why similar products are not isolated in both the pyrolysis and photolysis if they do in fact involve the same radicals (namely phenoxy). It is even harder to explain our results with anything but a mechanistic scheme involving radicals. However, the results of Hurd and Blunck from the gas phase pyrolysis of phenyl acetate seem to be equally compatible with a cyclic molecular rearrangement. In such a rearrangement ketene and phenoxy radicals could be formed by the transfer of hydrogen in a six-membered ring transition state.





It is interesting to note that Trecker, *et al.* have proposed that ketene formation may be involved in the solution photochemistry of *p*-tolyl acetate in ethanolic solvents.[35]

Our study of the vapor phase photolysis of phenyl acetate is, to our knowledge, the only detailed investigation of the gas phase photo reactions of phenyl esters. However several studies of a related problem, the photoanilide rearrangement, are relevant to this work.[39-41,66,67] Shizuka, et al. have extensively studied the photochemistry of acetanilide[40,41,66,67] which closely parallels the photochemistry of phenyl acetate. One of their publications reports that the vapor phase irradiation of acetanilide fails to give the rearrangement products formed in solution; in their place, ethane and carbon monoxide were detected from the gas sample.[41] Shizuka's interpretation of the vapor phase photochemistry of acetanilide is very similar to ours for phenyl acetate since the mechanism he proposes includes steps for homolysis of excited acetanilide into anilino and acetyl radicals, decarbonylation of the acetyl, and methyl radical coupling and hydrogen abstraction reactions. Our results have been explained with a mechanistic scheme involving identical steps. The close analogy between the results of the gas phase photochemistries of phenyl acetate and acetanilide provides additional evidence in support of the proposal that the photochemical mechanisms of the two compounds are identical.

Recently, Shizuka has reported results of a study of the solution photochemistry of n-acetylcarbazole.[68] In a footnote in this paper it is stated that the vapor phase irradiation of phenyl acetate gave no rearrangement products.

This finding is of course in agreement with our results which indicate substantial differences in the composition of the photoproduct mixtures resulting from solution and gas phase irradiation of this compound.

Relevance to the Liquid Phase Studies

As was indicated in the introductory section of this thesis, two different mechanistic schemes have been proposed to explain the solution photochemistry of phenyl esters, and both have gained considerable popularity among workers in this field. One scheme involves a molecular rearrangement to give *o*- and *p*-hydroxyphenones, the photo-Fries rearrangement products, and a separate, competitive reaction to give phenol. The alternate mechanism pictures both the phenol and the rearrangement products as resulting from the same reaction. The proponents of this hypothesis propose a solvent cage recombination of acetyl and phenoxy radicals to give the *o*- and *p*-hydroxyphenones, and cage escape followed by hydrogen abstraction steps to give phenol. The controversy over which mechanism represents a more valid explanation of the experimental results has gone on largely unsettled for nearly a decade. It is our belief that these results of the gas phase irradiation of phenyl acetate contribute valuable evidence in favor of the radical recombination mechanism proposed for solution.

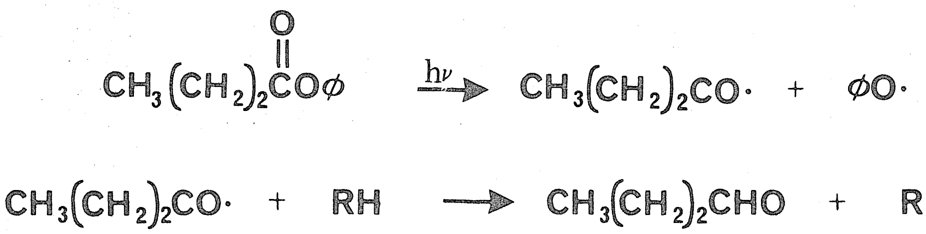
In this scheme, irradiation of a phenyl ester such as phenyl acetate results in homolysis of the acetyl-oxygen bond and yields a radical pair. Formation of significant quantities of the rearrangement products, _o_- and _p_-hydroxyacetophenones depends upon the coupling of the acetyl and phenoxy radicals while they are in close proximity to each other. Since, on the average, many collisions with each other are required for coupling, the confining influence of neighboring solvent molecules becomes very important in keeping the radical pair together. Thus, a greater confining force exerted by a solvent results in a higher yield of the rearrangement products. Our gas phase experiments represent the extreme opposite case. In the vapor phase, the confining force is very small, and in effect, a solvent cage does not exist. As a result, most of the acetyl and phenoxy radicals diffuse, with a relatively few of them coupling to give either _o_- or _p_-hydroxyacetophenones. This would explain the failure to isolate significant amounts of either of these compounds in this study, despite their proven stability under the conditions.

Furthermore, the isolation of phenol as the major photoproduct and phenoxy radical-derived products as minor photoproducts in our irradiations is consistent with predictions of gas phase reactivities made from the radical recombination mechanism proposed for solution. It follows that since the phenol formed in solution is the result of cage escape followed by hydrogen abstraction, phenol formation should be very important in the vapor phase irradiations. In parallel fashion, it is predicted that the reactions of free acetyl radicals will be of major importance in the gas phase, and this is born out by the detection of considerable amounts of carbon monoxide and methyl radical derived products.

Such results are, of course, in direct contrast to the predictions of a molecular rearrangement mechanism. Since the acetyl and phenoxy portions of the rearranging ester molecule never become free of each other in a molecular mechanism, formation of o- and p-hydroxyacetophenones from gaseous phenyl acetate might be expected to occur with about the same quantum yields as in solution. The 65% yield of phenol isolated from the photoproducts in the gas phase, coupled with a virtually zero yield of rearrangement products, constitutes at least a 300-fold change in the ratio of phenol to rearrangement products in going from solution to the gas phase. Such a large disparity between this value and the prediction clearly indicates our results are inconsistent with a molecular rearrangement mechanism for the photo-Fries rearrangement. Implicit in the above discussion is the assumption that the mechanism which explains gas phase results is valid in solution. Although we have no evidence which would exclude the possibility of an additional mechanism occurring in solution, we believe that such a view is unnecessary to explain the photochemistry of phenyl acetate.

Discussion of the Results of Experiments in Solution

A large fraction of the studies involving the irradiation of phenyl esters in solution were aimed at chemically trapping the acyl radicals which are proposed in this mechanism as the counterparts to the phenoxy radicals which undergo cage escape and become phenol. At the time this study was begun, there was no evidence establishing the fate of these radicals. To date, in fact, there has been only one unambiguous report in the literature of the formation of a compound derived from a free acyl radical.[20] (Bradshaw has found in only one of several photochemical runs a small amount of benzaldehyde which was derived from photolysis of a benzoate ester in benzene). In an attempt to chemically trap butytyl radicals by forming the stable *n*-butyraldehyde, phenyl *n*-butyrate was irradiated in the presence of high concentrations of reactive hydrogen donors.



$$CH_3(CH_2)_2\overset{O}{\overset{\|}{C}}O\phi \xrightarrow{h\nu} CH_3(CH_2)_2CO\cdot + \phi O\cdot$$

$$CH_3(CH_2)_2CO\cdot + RH \longrightarrow CH_3(CH_2)_2CHO + R\cdot$$

n-Butyl mercaptan and triethylsilane were chosen as reagents because of their well-established reputation as good hydrogen donors.[56] As a result of irradiations in several different solvents, a trend in the amount of product formation quickly became apparent: the highest yields of photoproducts were always from irradiations in alcoholic solvents. In addition, alcohols, unlike hydrocarbon solvents which gave only o- and p-hydroxybutyrophenone and phenol, caused formation of additional photoproducts. Similar findings by others suggest that the additional compounds may be the result of reactions of the solvent with the excited phenyl ester resulting in ester exchange and carboxylic acid formation.[8,13,35]

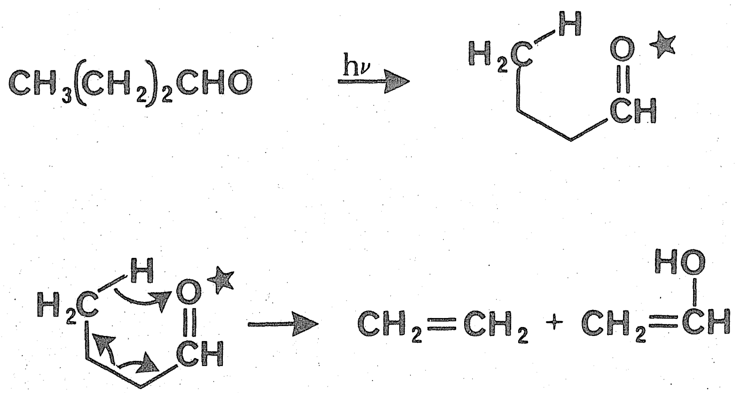
Despite a wide variation of solvents and conditions, none of the irradiations produced detectable amounts of the aldehyde. A check of the stability of n-butyraldehyde indicated that under conditions of the irradiations, photolysis was very fast, making detection of butyryl radical-derived aldehyde virtually impossible.

Nevertheless, it was clear from the analysis of hydrocarbon gases resulting from the irradiations of the phenyl-n-butyrate solutions, that decarbonylation of butyryl radicals accompanies the usual photo reactions of rearrangement and phenol formation. To our knowlege this is the first report which has unambiguously identified hydrocarbon gases as coming from the acyl radical. A careful analysis of the gases revealed that exposure of phenyl *n*-butyrate solutions to ultraviolet light produces mainly propane with lesser amounts of ethane and ethylene. In contrast, irradiation of similar solutions of *n*-butyraldehyde resulted in higher amounts of ethylene than propane. It has been well established that *n*-butyraldehyde displays two modes of decomposition which lead to different products.[69] The aldehyde may undergo a type I cleavage in which the bond connecting the alkyl chain to the carbonyl group is severed, resulting in the formation of a propyl radical and a formyl radical. Hydrogen abstraction by the propyl group results in propane formation.

$$CH_3(CH_2)_2CHO \xrightarrow{h\nu} CH_3(CH_2)_2\cdot + \cdot CHO$$

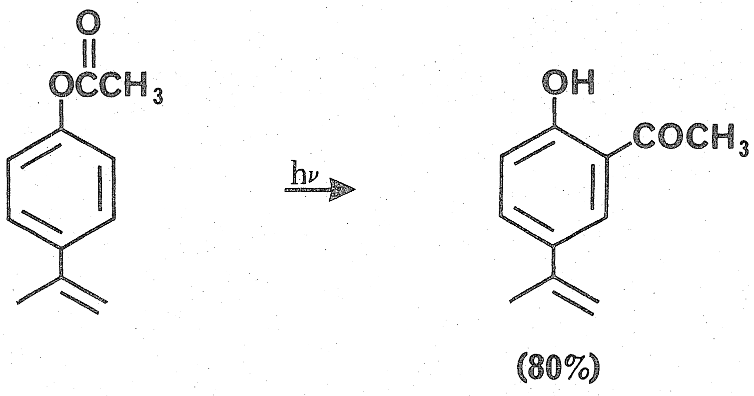
$$CH_3(CH_2)_2\cdot + RH \longrightarrow CH_3CH_2CH_3 + R\cdot$$

Alternatively the excited aldehyde molecule may decompose *via* a type II cleavage since it has a γ-hydrogen. This type of homolysis results in the formation of a molecule of ethylene. In contrast, the major mode of decarbonylation of a butyryl radical results in the formation of mainly propyl radicals,[58] which may also form propane by hydrogen abstraction.



Based on these results, the higher relative yields of propane from solutions of phenyl n-butyrate in comparison to those from n-butyraldehyde may mean that the majority of butyryl radicals which are formed from the photolysis of the ester decarbonylate faster than they abstract hydrogen and form the aldehyde. Furthermore, it is interesting to note that the decarbonylation reaction which is a major reaction pathway of excited phenyl acetate molecules in the gas phase, still occurs to some extent in solution. Such a finding supports the assumption that the gas phase mechanism, proposed earlier, is consistent with the solution photochemistry of phenyl esters.

Similar to the studies with phenyl n-butyrate, the irradiation of p-isopropenylphenyl acetate was designed to obtain evidence for the involvement of acetyl radicals in the rearrangement. The α-methyl styryl group on this molecule was expected to be especially vulnerable to attack by a free radical. In addition, by having this group on the same molecule undergoing reaction, attack at this position, it was hoped, would be extremely competitive with rearrangement. Unfortunately such was not the case because irradiation of the ester resulted in three products. The major one which accounts for 80% of the photoproducts has



spectral data compatible with the structure of the o-rearrangement product. One of the other photoproducts accounting for ca. 10% of the yield was the only one in which the nmr showed that loss of the double bond had occurred. Attempts to further identify it and the other product were not pursued because of the minor roles these compounds play in the photochemistry of the ester. It is somewhat surprising that this compound failed to trap acetyl or methyl radicals in view of our results with phenyl n-butyrate and the vapor phase studies of phenyl acetate. However, the only likely explanation which comes to mind is that the free electron density on the styryl group is lower in this compound than is expected.

During the course of our studies, the quantum yields for the photo reactions of phenyl benzoate in ether were determined: $\Phi_{-ester} = 0.85 \pm .04$, $\Phi_{\underline{o}} = 0.30 \pm .01$, $\Phi_{\underline{p}} = 0.28 \pm .01$ and $\Phi_{OH} = 0.14 \pm .01$. The value for o- rearrangement is in good agreement with Trecker's values for p-tolyl benzoate. No values for p- rearrangement of benzoate esters are available for comparison. Our value for the quantum yield of ester disappearance is slightly higher than other's (0.65),[1,35] however this difference could simply be due to the difference in solvents. Careful analysis indicated that benzene, which would result from the decarbonylation of benzoyl radicals, was not observed. However, this result is not surprising in view of the high energy required to break the carbonyl-phenyl bond. Furthermore, studies involving hydrogen abstraction reactions with benzaldehyde indicate that benzoyl radicals do not readily decarbonylate.[70] The fact that the quantum yield for p-rearrangement is almost as high as the value for o- rearrangement (o-/p- = 1.1) fits in rather well with a mechanism in which the rearrangement follows the observed free electron densities in the o- and p- positions for the phenoxy radical (o-/p- = 1.26). In contrast, due to the strained nature of the concerted intermediate proposed by Anderson and Reese, a molecular rearrangement mechanism of this sort would be expected to favor a greater ratio of o-/p- rearrangement.

While pursuing these quantum yield studies the possibility (although remote) occurred to us that rearrangement to give p-hydroxybenzophenone could result from a two step, two photon process with 2-benzoyl-3,5-cyclohexadien-1-one as an intermediate. The low quantum yield of 0.28 is, of course, low enough to permit a biphotonic mechanism for p- rearrangement. In this hypothetical mechanism, absorption of a photon by phenyl benzoate would be accompanied by rearrangement to the 2-substituted cyclohexadienone. However, before enolization converts this compound to a phenol, a significant fraction of 2-benzoyl-3,5-cyclohexadien-1-one molecules might absorb another photon and rearrange to the four position of the ring.

The lifetime of the 2-benzoyl-3,5-cyclohexadien-1-one is the crucial factor in this mechanism. It is clear that enolization must not be so fast that the probability of absorption of a second photon is negligible, or only o-hydroxybenzophenone will result from the dienone. The test of this mechanism was quite simple. Two sets of samples containing phenyl benzoate in ether were prepared, one of the sets contained only the ester while the other contained ester and a 1M concentration of acetic acid. Irradiation of both sets followed by analysis indicated identical values for the ratio of the o-/p- quantum yields. This result was taken as evidence against a biphotonic mechanism since if one were operative, the lifetime of 2-benzoyl-3,5-cyclohexadien-1-one would have to be relatively long in the ether solution to permit sufficient light absorption by this species. Addition of acid to some of the samples would accelerate the rate of enolization and thus significantly shorten the lifetime of this species causing higher relative quantum yields of the o-hydroxyacetophenone in the acidic samples. The unchanged value in ratio of quantum yields of o-/p- products in neutral and acidic media indicates that 2-benzoyl-3,5-cyclohexadien-1-one is probably not an intermediate in the formation of the p- rearrangement product of phenyl benzoate.

A number of attempts were made to observe spectroscopically any short-lived intermediates from the solution irradiations of phenyl esters. In particular it was hoped that direct evidence for presence of phenoxy and/or acyl radicals could be obtained through the techniques of flash lamp spectroscopy, and EPR spectrometry. The results of irradiations of phenyl acetate in the cavity of an EPR spectrometer produced a single, weak, structureless peak having line width of 48 gauss and a g value of 2.0. However because of the poor quality of the signal, it can only be stated that the signal is not inconsistent with the line widths reported for acetyl and phenoxy radicals.[63,71] Similarly the results of flash spectroscopy experiments on a number of solutions of phenyl esters were generally inconclusive, and therefore we were unable to obtain reliable data for the presence of phenoxy radicals as intermediates in these irradiations.

Emission Spectra and Excited States

The emission spectra of several different phenyl esters in these studies has provided important information relating to the excited states of these compounds. The most obvious result from this work was that alkyl phenyl esters of aliphatic carboxylic acids all displayed measurable emission while phenyl benzoate, the only phenyl ester of an aromatic acid studied, showed none. The failure to observe emission from phenyl benzoate is in accord with several other fragmentary reports which together indicate a general lack of either fluorescence of phosphorescence from phenyl esters of aromatic acids.[1,26] Furthermore, the general failure to sensitize or quench a triplet reaction is compatible with the results of emission studies. In view of the high values of the quantum yields for ester disappearance for these compounds, it is likely that the rate constant for reaction (from the singlet) is very high and therefore consumes excited states at a rate so fast that emission is pre-empted.

The emission spectra obtained from the three phenyl esters of aliphatic carboxylic acids all display strong phosphorescence bands at almost identical wavelengths. The onset of the phosphorescence which is taken as a rough indication of the 0-0 transition lies at about 335 nm or 85 kcal/einstein. Similarly a less intense fluorescence emission has been observed in these esters which is a reasonably good mirror image of the first absorption band. The 0-0 transition from comparison of emission and absorption spectra comes at about 270 nm or 106 kcal/einstein. These values are in excellent agreement with the reported emission spectra of phenyl acetate.[37] It is worth noting that the quantum yields for ester disappearance reported for phenyl acetate ($\Phi = 0.38$)[37] and p-cresyl acetate ($\Phi = 0.35$)[35] are considerably lower than those values reported for the benzoate esters ($\Phi = 0.65-0.85$).[1,35] These phenomena are all consistent with the proposal that the rate constant for reaction of phenyl esters of aliphatic acids (PhOCOR) is smaller than that for reaction of phenyl esters of aromatic carboxylic acids (PhOCOAr). In the case of PhOCOR the lower value of the rate constant for reaction places it in competition with those rate constants for emission and intersystem crossing. Consequently, a significant fraction of excited singlet states of PhOCOR emit and intersystem cross as well as react to give photoproducts.

We believe, as is evident from the above discussion, that the photo reactions of phenyl esters originate from an excited singlet state of the molecules. (This belief is based in part on the general failure by others to obtain any convincing evidence which would implicate an excited triplet state as the reactive electronic state.) The reaction itself is viewed as an exaggerated anharmonic vibration of the C-O bond in the electronically excited ester molecule which ultimately ends in bond homolysis. In this sense, the reaction may be considered as a form of radiationless decay from the singlet excited state. Whether this form of decay hypothetically involves intersystem crossing to a dissociative triplet σ^*state,[37] or crossing to a dissociative singlet state is in our opinion largely a matter of semantics, since both states provide the same end result, dissociation into acyl and phenoxy radicals.

Discussion of Peripheral Results

From the results of the irradiation of n-butyl mercaptan the following mechanistic scheme is proposed to explain the formation of the observed products:[72]

$$CH_3(CH)_3S\text{-}H \longrightarrow CH_3(CH_2)_3\cdot + \cdot SH \qquad (1)$$

$$\cdot SH + CH_3(CH_2)_3SH \longrightarrow CH_3(CH_2)_3S\cdot + H_2S \qquad (2)$$

$$2CH_3(CH_2)_3S\cdot \longrightarrow \left[CH_3(CH_2)_3S\right]_2 \qquad (3)$$

$$CH_3(CH_2)_3S\cdot + CH_3(CH_2)_3\cdot \longrightarrow \left[CH_3(CH_2)_3\right]_2S \qquad (4)$$

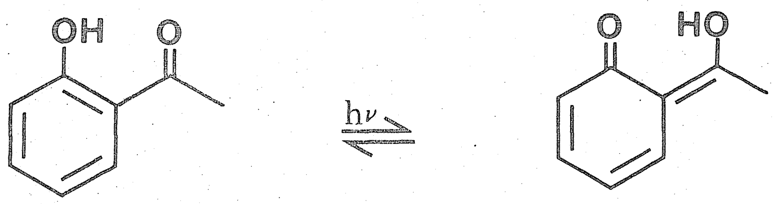
$$CH_3(CH_2)_3\cdot + \left[CH_3(CH_2)_3S\right]_2 \longrightarrow \left[CH_3(CH_2)_3\right]_2S + CH_3(CH_2)_3S\cdot \qquad (5)$$

$$CH_3(CH_2)_3S\cdot + CH_3(CH_2)_3SH \longrightarrow \left[CH_3(CH_2)_3\right]_2S + \cdot SH \qquad (6)$$

$$CH_3(CH_2)\cdot + CH_3(CH_2)_3SH \longrightarrow CH_3(CH_2)_3H + CH_3(CH_2)_3S\cdot \qquad (7)$$

The steps leading to the formation of hydrogen sulfide and the dibutyl disulfide have been proposed before.[73,74] The dibutyl sulfide which has not been previously reported may arise from reactions (4-6). Step (4), the coupling of butyl and thiyl radicals has a large negative value for the heat of reaction, however the high reactivity of butyl radicals and relatively low concentrations of thiyl radicals makes this step unlikely. The reactions of butyl radicals with dibutyl disulfide (5) or thiyl radicals with butanethiol (6) are far more likely on the basis of reactant concentrations. The work of Pearson in establishing quantum yields for the formation of dibutyl disulfide and dibutyl sulfide indicate that step (5) is not occurring to any great extent, since the quantum yields of dibutyl sulfide does not increase with time. In conclusion, attack of a thiyl radical on butanethiol maybe the major pathway for the production of dibutyl sulfide.

Photochemistry of o-Hydroxyacetophenone (vapor). The gas phase irradiations of *o*-hydroxyacetophenone produced the rather surprising result that this compound photolyzes. In solution the *o*-hydroxyketone is essentially photo-inert by virtue of a reversible intramolecular enolization.[75,76] Although photolysis is known to take place for a number of



aromatic ketones in the gas phase, these compounds do not have the option of expending the excitation energy in the form of a reversible, non-degrading step such as enolization.[77-79] It was therefore rather striking to find that the photochemistry of this compound changes in going from solution to the gas phase. Furthermore, the photochemistry of o-hydroxyacetophenone in the gas phase appears to be pressure sensitive. At low pressures the major photo reaction is cleavage of the carbonyl-phenyl bond to give phenol, and at higher pressures the carbonyl-methyl bond is apparently severed giving salicylaldehyde. These results are interpretable with a model in which the electronic excitation is quickly converted to excess vibrational energy by the reversible enolization step. However, at low pressures the number of collisions are relatively few and the excess vibrational energy is removed from the molecule by molecular collision at a slow rate. As a result, a significant fraction of these "hot" molecules retain sufficient excess vibrational energy long enough to sever the strong C-C bond to the phenyl ring. An increase in the pressure of an inert gas increases the collisional frequency with these hot molecules, lowering their average energy content to the point where homolysis of the phenyl-carbonyl bond is no longer a favorable process. However, the energy content of a significant fraction of these molecules is sufficient to sever the methyl-carbonyl bond and formation of salicylaldehyde results.

The solution results maybe rationalized as the extreme example of the "cooling-off" process. Molecular collisions in solution will occur with a much higher frequency than they do at the pressures studied in the gas phase. As a result, the hot molecules are quenched so quickly that the average energy content of the molecules is lowered to a level insufficient for bond homolysis at a rate much faster than the rate of photolysis.

Conclusions

We believe that the results of this work make a valuable contribution toward the understanding of the photochemistry of phenyl esters. Our results are most compatible with the hypothesis that electronic excitation populates a singlet energy level from which reaction occurs. Homolysis of the C-O bond is regarded as a form of radiationless decay of the excited singlet to form acyl and phenoxy radicals.

In the gas phase, all the products isolated from the photolysis of phenyl acetate are explainable on the basis of the established modes of reaction of these radicals. In support of this conclusion, the evidence gathered from the gas phase studies is completely incompatible with a molecular rearrangement mechanism which has been postulated for solution. Furthermore, the gas phase results strongly support the alternative solution mechanism which regards all photoproducts as arising from the reactions of acyl and phenoxy radicals. Although, as noted earlier, dual mechanisms might be operative in solution, we believe that a radical recombination mechanism is all that is necessary to explain the known photochemistry of phenyl esters.

REFERENCES

1. H. Kobsa, J. Org. Chem., 27, 2293 (1961).
2. J. C. Anderson and C. B. Reese, Proc. Chem. Soc., 217 (1960).
3. A. Davis and J. H. Golden, J. Chem. Soc., B, 425 (1968).
4. D. Bellus, K. Schaffner and J. Hoigne, Helv. Chim. Acta, 51, 1980 (1968).
5. Y. Noro, M. Ochiai, T. Miyazaki, A. Torikai, K. Fueki and Z. Kuri, J. Phys. Chem., 74, 63 (1970).
6. D. Bellus and P. Hrdlovic, Chem. Rev., 67, 599 (1967).
7. V. I. Stenberg, "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., M. Decker Co., New York, 1967, p. 127.
8. J. C. Anderson and C. B. Reese, J. Chem. Soc., 1781 (1963).
9. D. A. Plank, Tetrahedron Lett., 5423 (1968).
10. A. H. Blatt, "Organic Reactions," Vol. I, R. Adams, Ed., John Wiley & Sons, Co., New Yor, 1942 p. 342.
11. A. H. Blatt, Chem. Rev., 27, 429 (1940).
12. K. W. Rosenmund and W. Schnurr, Justus Liebigs Ann. Chem., 460, 56 (1928).
13. R. A. Finnegan and J. J. Mattice, Tetrahedron, 1015 (1965).
14. T. Rechstein, Helv. Chim. Acta, 10, 392 (1927).
15. F. Mauthner, J. Prakt. Chem., 2 118, 314 (1928).
16. K. Auwers, H. Bundesmann and F. Wieners, Justus Liebigs Ann. Chem., 447, 162 (1926).
17. K. Auwers and W. Mauss, Annalen, 460, 240 (1928).
18. K. Auwers and E. Janssen, Justus Liebigs Ann. Chem., 483, 44 (1930).

19. R. A. Finnegan, *Abstracts*, 145th Meeting American Chemical Society, New York, Sept. 1963, p. 30.

20. J. S. Bradshaw, E. I. Loveridge and L. White, *J. Org. Chem.*, *33*, 4127 (1968).

21. H. J. Hageman, *Tetrahedron*, *25*, 6015 (1969).

22. R. A. Finnegan and D. Knutson, *Chem. Ind.* (London), 1837 (1965).

23. P. Slama, D. Bellus and P. Hrdlovic, *Collect. Czech. Chem. Commun.*, *33*, 3752 (1968).

24. H. J. Hageman, *Chem. Commun.*, 401 (1968).

25. C. D. Pande, *Indian J. Chem.*, *6*, 543 (1968).

26. G. M. Coppinger and E. R. Bell, *J. Phys. Chem.*, *70*, 3479 (1966).

27. L. Schutte and E. Havinga, *Tetrahedron*, *23*, 2281 (1967).

28. R. A. Finnegan and D. Knutson, *Tetrahedron Lett.*, 3429 (1968).

29. R. A. Finnegan and D. Knutson, *Chem. Commun.*, 172 (1966).

30. R. A. Finnegan and D. Knutson, *J. Amer. Chem. Soc.*, *89*, 1970 (1967).

31. D. H. R. Barton, Y. L. Chow, A. Cox and G. W. Kirby, *Tetrahedron Lett.*, 1055 (1962).

32. D. N. R. Barton, Y. L. Chow, A. Cox and G. W. Kirby, *J. Chem. Soc.*, 3571 (1965).

33. W. M. Horspool and P. L. Pauson, *ibid.*, 5162 (1965).

34. M. R. Sandner and D. J. Trecker, *J. Amer. Chem. Soc.*, *89*, 5725 (1967).

35. M. R. Sandner, E. Hedaya and D. J. Trecker, *ibid.*, *90* 7249, 1968).

36. D. A. Plank, *Tetrahedron Lett.*, 4365 (1969).

37. H. Shizuka, T. Morita, Y. Mori and I. Tanaka, Bull. Chem. Soc. Jap., 42, 1831 (1969).

38. I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, 1965, p. 62.

39. D. Elad, D. V. Rao and V. I. Stenberg, J. Org. Chem., 30, 3252 (1965).

40. H. Shizuka, Bull. Chem. Soc. Jap., 42, 57 (1969).

41. H. Shizuka and I. Tanaka, ibid., 42, 909 (1969).

42. D. P. Kelly, J. T. Pinhey and R. D. G. Rigby, Aust. J. Chem., 22, 977 (1969).

43. G. Koga, N. Kibuch and N. Koga, Bull. Chem. Soc. Jap., 41, 745 (1968).

44. F. L. Bach and J. C. Barclay, Abstracts, 150th Meeting American Chemical Society, Altantic City, N. J., Sept. 1965, p. 9s.

45. H. I. Joscheck and S. I. Miller, J. Amer. Chem. Soc., 88, 3269 (1966).

46. F. D. Chattaway, J. Chem. Soc., 2495 (1931).

47. H. Gilman, S. Avakian, R. A. Benkeser, H. S. Broadbent, R. M. Clark, G. Karmas, F. J. Marshall, S. M. Massie, D. A. Shirley and L. A. Woods, J. Org. Chem., 19, 1067 (1957).

48. J. F. Norris, B. G. MacIntire and W. M. Corse, J. Amer. Chem. Soc., 29, 120 (1903).

49. G. A. Reynolds and J. A. Van Allan, "Organic Syntheses," Collective vol. IV, N. Ragjohn, Ed., John Wiley & Sons, Co., New York, 1963, p. 634.

50. PCQ-XI Lamps are manufactured by Ultraviolet Products, Inc., San Gabriel, Calif.

51. C. C. Wamser, Ph. D. Thesis, California Institute of Technology, 1970.

52. S. A. Weiner and G. S. Hammond, J. Amer. Chem. Soc., 90, 1659 (1968); 91, 986 (1969).

53. (a) H. L. Hyndman, Ph. D. Thesis, California Institute of Technology (1968).

    (b) E. M. Chambaz and E. C. Horning, Analytical Letters, 1, 201 (1968).

54. (a) T. Aczel and H. E. Lumpkin, Anal. Chem., 32, 1819 (1960).

    (b) C. Hausermann and E. Bauer, Chem. Ber., 29, 2083 (1896).

55. H. Budzikiewicz, C. Djerassi and D. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden Day, Inc., San Francisco, 1964, p. 203.

56. J. A. Kerr and A. F. Trotman-Dickenson, J. Chem. Soc., 3322 (1957).
    J. A. Kerr, D. H. Slater and J. C. Young, J. Chem. Soc., A, 134 (1967).

57. P. K. Pearson, Senior Thesis (Chemistry), California Institute of Technology, 1970.

58. C. H. Nicol and J. G. Calvert, J. Amer. Chem. Soc., 89, 1790 (1967).

59. J. A. Kerr and J. G. Calvert, J. Phys. Chem., 69, 1022 (1965).

60. T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press, Inc., New York, 1954, p. 275.

61. D. J. Cram and G. S. Hammond, "Organic Chemistry," McGraw-Hill Book Co., New York, 1959, p. 109.

62. C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc. New York, 1957, p. 496.

63. T. J. Stone and W. A. Waters, Proc. Chem. Soc., 253 (1962).

64. M. F. R. Mulcahy and D. J. Williams, Nature, 199, 761 (1963).

65. C. D. Hurd and F. H. Blunck, J. Amer. Chem. Soc., 60, 2419 (1938).

66. H. Shizuka and I. Tanaka, Bull. Chem. Soc. Jap., 41, 2343 (1968).

67. H. Shizuka, ibid., 42, 52 (1969).

68. H. Shizuka, M. Kato, T. Ochiai, K. Matsui and T. Morita, ibid., 43, 67 (1970).

69. J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley & Sons, Inc., New York, 1966, p. 372.

70. F. F. Rust F. H. Seubold and W. E. Vaughan, J. Amer. Chem. Soc., 70, 3258 (1948).

71. J. R. Morton and W. E. Falconer, Nature, 197, 1103 (1963).

72. This work and ref. 57.

73. M. Meissner and H. Thompson, Trans. Faraday Soc., 34, 1238 (1938).

74. W. Haines, G. Cook and J. Ball, J. Amer. Chem. Soc., 78, 5213 (1956).

75. J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley & Sons, Inc. New York, 1966, pp. 534, 589.

76. N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, 1967, p. 150.

77. H. H. Glazebrook and T. G. Pearson, J. Chem. Soc., 589 (1939).

78. R. G. Sowden and N. Davidson, J. Amer. Chem. Soc., 78, 1291 (1956).

79. F. J. Duncan and A. F. Trotman-Dickenson, J. Chem. Soc., 4672 (1962).

PROPOSITION 1

This proposal outlines a study of electronic energy transfer between organic sensitizers and transition metal-containing compounds. Specifically, I wish to assess the basic importance of, and determine the critical parameters involved in the transfer of electronic excitation energy from a number of organic photosensitizers to group VI transition metal carbonyls and substituted carbonyl complexes.

Thermally induced ligand substitution of transition metal carbonyls is a general reaction for electron rich ligands and has been the subject of extensive investigation.[1-3] A large variety of ligands have been shown to replace the carbonyl groups of the transition metals in groups V - VII.

$$L + M(CO)_n \xrightarrow{\Delta} M(CO)_{n-1}L + CO$$

In an analogous fashion, photochemical excitation has been shown to also cause similar ligand substitutions:[1,4,5,6,16-22]

$$M(CO)_n + L \xrightarrow{h\nu} M(CO)_{n-1}L + CO$$

Irradiation of these complexes with light in the wavelength range of 350-500 nm causes reaction with a quantum yield $\Phi = 1.0$ for all transition metal carbonyls.[4,6] This photochemical reaction is particularly useful in causing reaction (with unity quantum yield) of the group VI complexes which do not undergo thermal ligand substitution.[1,4] The mechanism of this photochemical reaction has been the subject of considerable study, and it has been shown for several carbonyl complexes that the first step involves the S_n1 elimination of carbon monoxide to give a chemically reactive imtermediate:[4,24,25]

$$M(CO)_n \xrightarrow{h\nu} M(CO)_{n-1} + CO$$

In a second step this intermediate attacks either another ligand in solution:

$$M(CO)_{n-1} + L \longrightarrow M(CO)_{n-1}L$$

or recombines with carbon monoxide in solution to give starting material.

$$M(CO)_{n-1} + CO \longrightarrow M(CO)_n$$

This intermediate has been characterized by both chemical and spectral techniques and shown to have a half-life of a few minutes.[7,8,24,25]

Despite the rather large number of papers that have appeared concerning the photochemical reactions of these compounds, the emphasis has been toward determining the scope and mechanisms of the ligand addition reaction. In contrast, it appears as though very little is known about the excited states capable of producing ligand expulsion.

In particular, studies of the sensitization of the photochemical reactions of transition metal carbonyls are non-existent. In fact, there have been only a very few papers concerned with electronic energy transfer in all of transition metal photochemistry.[9-12,23] Because experiments involving intermolecular energy transfer can provide very important information about the characteristics of the excited states giving rise to reaction, such studies are critical to the understanding of the mechanism of the photochemistry of transition metal carbonyls and transition metal phtochemistry in general.

For this reason, the experiments outlined in this proposal are intended to probe the excited states of transition metal carbonyls to determine the nature of the excited states which lead to reaction. Specifically they are designed to answer the following questions: 1. Can the ligand substitution in group VI carbonyls be sensitized by organic triplet sensitizers? 2. What is the energy of the triplet electronic state causing photochemical reaction? 3. Do physical differences exist in the excited states of substituted metal carbonyls which can be manipulated so as to control their chemistry? Each of these questions will now be considered in terms of the actual proposal.

Selection of an approporiate inorganic system is a major factor in determining the feasibility of a study of energy transfer processes between organic and inorganic molecules. For this reason a number of considerations have gone into the choice of the compounds to be studied.

The generally high quantum yields and relatively well understood mechanism of ligand substitution makes transition metal carbonyls excellent candidates for a study of energy transfer in metal-organic molecules. In addition, the good thermal stability, and large number of well-characterized derivatives of group VI metal carbonyls makes such a study experimentally feasible.[3,6] No details of the synthesis of either the substrates or expected products is discussed since they have all be synthesized and characterized elsewhere.[3,4]

The existence of a triplet pathway for ligand substitution can be determined by measuring the efficiency of photochemical sensitization of ligand exchange in $Cr(CO)_6$. The ground state configeration of the diamagnetic $Cr(CO)_6$ is singlet. It is reasonable to expect then, that direct light absorption by the complex would cause singlet excitation while energy transfer from the excited triplet state of an organic sensitizer would produce an excited triplet state in the metal carbonyl. If a mechanism exists by which this triplet energy can be turned into chemistry, ejection of carbon monoxide is likely to occur, followed by the second step, ligand incorporation. If no such pathway exists, the triplet excitation energy will be lost through radiationless decay or phosphorescence from the complex. It is my belief that the triplet energy will find a pathway by which the carbon monoxide will be expelled. My feelings are based to a large extent on the observation that within the same groups, $W(CO)_6$ does in fact, labilize CO upon irradiation.[13] The important difference between the two compounds is that tungsten is a much heavier atom than chromium, with many more electrons, and therefore considerably more spin-orbit coupling.[14] Increased spin-orbit coupling results in a much increased intersystem crossing ratio for the tungsten atom. This means that the direct excitation of $W(CO)_6$, unlike $Cr(CO)_6$, would be expected to cause considerable population of the triplet state. Since the quantum yield for ligand substitution of $W(CO)_6$ is unity, one would expect the triplet state to expel CO with very high efficiency.

In this determination, the experimental techniques involved are rather straight forward, however, I will describe them briefly since this type of experiment is common to the entire study. Solutions of $Cr(CO)_6$ will be prepared in hexane, THF or some other appropriate solvent, containing an organic triplet sensitizer such as benzophenone or acetophenone. Concentrations of $Cr(CO)_6$ and sensitizer will be adjusted so that 99% or more of the incident light (monochromatic) is abosrbed by the sensitizer. (This can be achieved even for very strongly absorbing complexes.)

The solutions will be degassed by standard freeze-pump-thaw techniques and irradiated at the appropriate wavelength. Under these conditions one can be certain that any excitation of the metal complex must come via the triplet sensitizer, and thus if ligand exchange is observed, it must be due to intermolecular triplet energy transfer.

The ligand exchange process could be monitored in a number of ways. A rather sophisticated and very sensitive technique involves carrying out the photo-sensitization in a solution saturated with ^{14}C carbon monoxide. Following the irradiation, the chromium Lexacarbonyl is isolated and its activity measured by standard β-scintillation techniques. The amount of activity in the isolated complex would provide a direct measure of the amount of ligand substitution which has taken place.

A somewhat less complicated procedure for determining the extent of ligand substitution involves replacement of a carbon monoxide ligand by a non-absorbing photochemically inert ligand like acetonitrile. By carrying out the sensitization of $Cr(CO)_6$ in the presence of high concentrations of acetonitrile (or even in neat acetonitrile) one could observe the formation of the substituted complex $Cr(CO)_5CH_3CN$ which is known to form and has been characterized.[15] The usual spectral techniques of ir and nmr would be employed to monitor formation of such a complex. By combining these techniques with ferrioxalate actinometery it will be possible to obtain a quantum yield for the sensitized ligand substitution in $Cr(CO)_6$. This quantum yield is a direct indication of the importance of a triplet pathway for ligand substitution in $Cr(CO)_6$.

Having outlined the experimental details of obtaining quantum yields of reaction, the second major goal of this study can be considered; namely, the determination of the energy of this triplet state. This value can be obtained in a straight forward manner. One simply correlates the value of the quantum yield for the sensitized ligand exchange as a function sensitizer triplet energies. As the energy of the sensitizer falls below that of the triplet state of the complex, energy transfer becomes endothermic and the efficiency of sensitization falls to zero. A plot of quantum yields as a function of sensitizer energy will show a sharp drop-off at that energy corresponding to the triplet state of the substrate.[16] Since there are a large number of organic molecules with triplet energies corresponding to electronic transitions in UV and visible range, it will be a relatively simple procedure to determine the energy of this triplet excited state of $Cr(CO)_6$.

The final phase of this proposal involves the study of the sensitized photochemistry of substituted metal carbonyls of group VI, in particular the reactions of $Cr(CO)_4$ diene. Direct photolysis of these olefine-metal carbonyl complexes has been shown to cause ligand substitution of not only the carbon monoxide ligands, but exchange of the hydrocarbon ligand was observed as well.[17,18] These observations suggest to me that the photochemistry of such compounds may have great potential. It is particularly exciting to consider the differences existing between the excited states leading to elimination of the diene ligand and the states causing expulsion of the carbon monoxide. A careful choice of sensitizer might succeed in preferentially removing only one ligand. For example, differences in the reactivity of the singlet and triplet excited states of the complex could give rise to very different product ratios for the direct and sensitized irradiation of $Cr(CO)_4$ diene. Similarly, the two ligand elimination reactions could arise from separate excited states of different energies, and in such a situation a sensitizer with a triplet energy intermediate between these levels would provide a means of controlling the photochemistry of the complex. Other factors such as a variation of the quenching rates due to structural changes in sensitizer might likewise prove to be important in understanding the characteristics of the excited states responsible for the photochemistry. Although, as yet, no precedence exists for such effects in the photochemistry of transition metals, there are numerous examples in which the photochemistry of organic compounds can be controlled by manipulation of sensitizer parameters.[16] The potential value of these studies lies in the ability to draw important conclusions about the nature of the excited states responsible for chemical reactions.

REFERENCES

1. F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions," New York, 1967 Chapter 7.
2. I. Wender and P. Pino, "Organic Synthesis Via Metal Carbonyls," Interscience, New York, 1968 Chapter 1.
3. G. Coates, M. Green and K. Wade, "Organometallic Compounds," Vol. 2, Methuen, London, 1968.
4. W. Strohmeier, *Angew. Chem. Intern*. Ed. *3*, 730 (1964).
5. D. Valentine, Jr., "Annual Survey of Photochemistry," Vol 1, Wiley, New York, 1969, pp 490-506.
6. A. W. Adamson, *et al*., *Chemical Review* *68*, 542 (1968).
7. W. Strohmeier and K. Gerlach, *Chem. Ber*. *94*, 398 (1961).
8. I. W. Stolz, G. R. Dobson and R. K. Sheline, *J. Amer. Chem. Soc*. *84*, 3589 (1952), *85*, 1031 (1963).
9. H. Gaussman and H. L. Schlafer, *J. Chem. Phys*. *48*, 4056 (1968).
10. D. Binet, E. Goldberg and L. Forster, *J. Phys. Chem*., *72*, 3017 (1968).
11. A. Vogler and A. W. Adamson, *J. Amer. Chem. Soc*., *90*, 5943 (1968).
12. G. Porter, *J. Amer. Chem. Soc*., *91*, 3980 (1969).
13. W. Strohmeier and D. Von Hobe, *Z. Physik. Chem*. (Frankfurt), *34*, 393 (1962).
14. S. McGlynn, F. Smith and G. Cliento, *Photochem. and Photobiology*, *3*, 269 (1964).
15. W. Strohmeier and K. Gerlach, *Z. Natureforsch*, *15B*, 622 (1960).
16. H. Schumann, O. Stelzer and W. Glick, *Angew. Chem. Int*., *8*, 271 (1969).
17. H. Brunner, *J. Orgmet. Chem*., *16*, 119 (1969).
18. M. Herberhold and C. R. Jablonski, *Chem. Ber*., *102*, 767 (1969).

19. W. Strohmeier and F. Muller, *Chem. Ber.*, *102*, 3608 (1969).

20. *Ibid.* 3613.

21. W. Jennings and B. Hill, *J. Amer. Chem. Soc.*, *92*, 3199 (1970).

22. M. Wrighton, G. S. Hammond and H. G. Gray, submitted for publication in *J. Amer. Chem. Soc.*

23. C. Parkanyi, M. Hofler and J. H. Richards *J. Paint Tech.*, *41*, 363 (1969).

24. J. A. McIntyre, *J. Phys. Chem.*, *74*, 2403 (1970).

25. A. J. Rest and J. J. Turner, J. *Chem. Soc.* *D*, 375 (1969).

PROPOSITION 2

Proposed: A direct method to determine the importance of the d_π-p_π interaction in back-bonding between mercury and cyanide is suggested.

Introduction

Back-bonding is a fairly common phenomenon observed in metal-ligand systems in which pi bonding exists between the atoms of the ligand (eg. $M(CO)_n$, $M(CN)_n$). The process is thought to occur through the donation of electrons from the d orbitals of the metal into the empty antibonding orbitals of the ligands. Despite the generality of the phenomenon, no example exists which does not also involve sigma bonding between metal and ligand. Therefore a distinction between d_π-p_π donation and inductive effects through the sigma structure is by no means clear, and most attempts to separate these effects involve rather elaborate explanations of the experimental results.[1,2]

Since this back-bonding process involves donation of d electrons into the ligand antibonding pi orbitals, the bond between the two ligand atoms is weakened, or in other words, the force constant for the bond is smaller. As a result, the absorption in the infrared region corresponding to the ligand diatomic stretching frequency occurs at longer wavelengths for the complexed ligand relative to an an uncomplexed one. As an example, in Hg(CN)$_2$ the CN stretching absorption appears at 2180 cm^{-1} [3] while in HCN and other organic nitriles in which back-bonding is not possible, the CN absorption occurs at _ca_. 2250 cm^{-1}.[4,10] Thus the weakening of the CN bond in Hg(CN)$_2$ could be explained by invoking a d_π-p_π type of interaction between the mercury d electrons and the cyanide π^* orbitals.

In an effort to evaluate the importance of d_π-p_π donation between mercury and cyanide the following model compound (1a) has been conceived in which no sigma bond exists between metal and ligand (Fig. 1). Measurements from molecular models indicate that the 2.7 Å separation of the cyanide and mercury in this compound places the d and π^* orbitals well within the van der Waals contact distance between the two groups. In fact, the 2.7 Å distance is precisely that measured for Hg--NC-bonding in solid Hg(CN)$_2$.[11] Hence one would expect that on the basis of overlap, d_π-p_π

Figure 1

(1a)

(1b)

interactions should readily occur in this compound if they are important in the bonding of $Hg(CN)_2$ (Fig. 2).

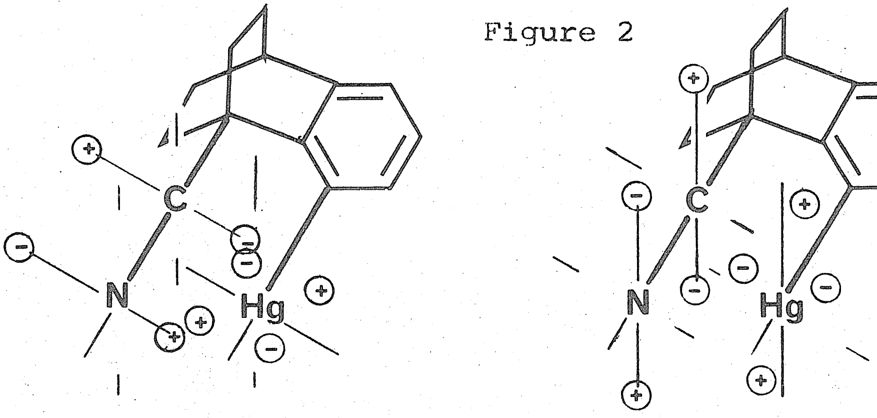


Figure 2

The results of recent studies have placed a new importance on pi bonding in metal nitrile complexes. The complexes of short carbon chain dinitriles with manganese and rhenium are believed to involve d_{π}-p_{π} bonding.[12,13] In these complexes, the nitrile appear to be bonded via C-N π-coordination rather than through the lone pair of electrons on the terminal nitrogen as is the case with most organonitrile complexes.[4] In addition, there is some precedence that mercury is capable of intramolecular coordination from work with bromoaromatic mercury compounds.[15]

The proposed synthesis of compound (1a) is elaborated in Fig. 3. Measurement of the infrared CN absorption frequency of (1a) would establish the importance of the d_{π}-p_{π} interaction. A suitable reference compound (1b) is also obtained from the synthesis of (1a) thus providing a convenient C-N stretch reference frequency. The difference between the infrared absorptions around 2200 cm^{-1} of (1a) and (1b) would provide a direct indication of the extent of $d_{\pi}-p_{\pi}$ interaction between mercury and the cyano group. If the type of interactions proposed in Fig. 2 are important, a decreased ir stretching frequency for (1a) is expected relative to (1b). Based on the value of $Hg(CN)_2$, a reduction on the order of 80 cm^{-1} might be expected, although the π-bonded nitrile complexes exhibit much lower shifts (ca. 200 cm^{-1}). If instead an interaction occurs primarily through the carbon atom of the nitrile group, the frequency would be shifted considerably lower due to the rehybridization to a sp^2 geometry. In this case absorptions of (1a) would be expected at 1600 - 1700 cm^{-1}.[13] Alternatively, bonding between mercury and cyanide could occur primarily through the nitrile nitrogen. In this case the C-N stretching frequency in (1a) should be similar to the acetonitrile complex of Hg(II) which bonds via the lone pair of electrons on the terminal nitrogen. Hence terminal nitrogen bonding would be indicated by an increase of ca. 24 cm^{-1} for the C-N stretching frequency of (1a) relative to (1b).[16] Of course, one other possiblity exists in which the C-N stretching frequencies for (1a) and (1b) would be identical and hence indicate no interaction at all. However, based on the work of Farona, et al.[12,13] the first possibility is probably the most likely.

It would be exceedingly interesting to synthesize similar derivatives of metals such as platinum, palladium and osmium to assess the importance of various atomic parameters such as the number of d electrons, the oxidation, and the coordination states with regard to d_{π}-p_{π} interactions. However, the synthetic problems of obtaining metal carbon bond formation in these compounds would be tremendous.

SYNTHESIS

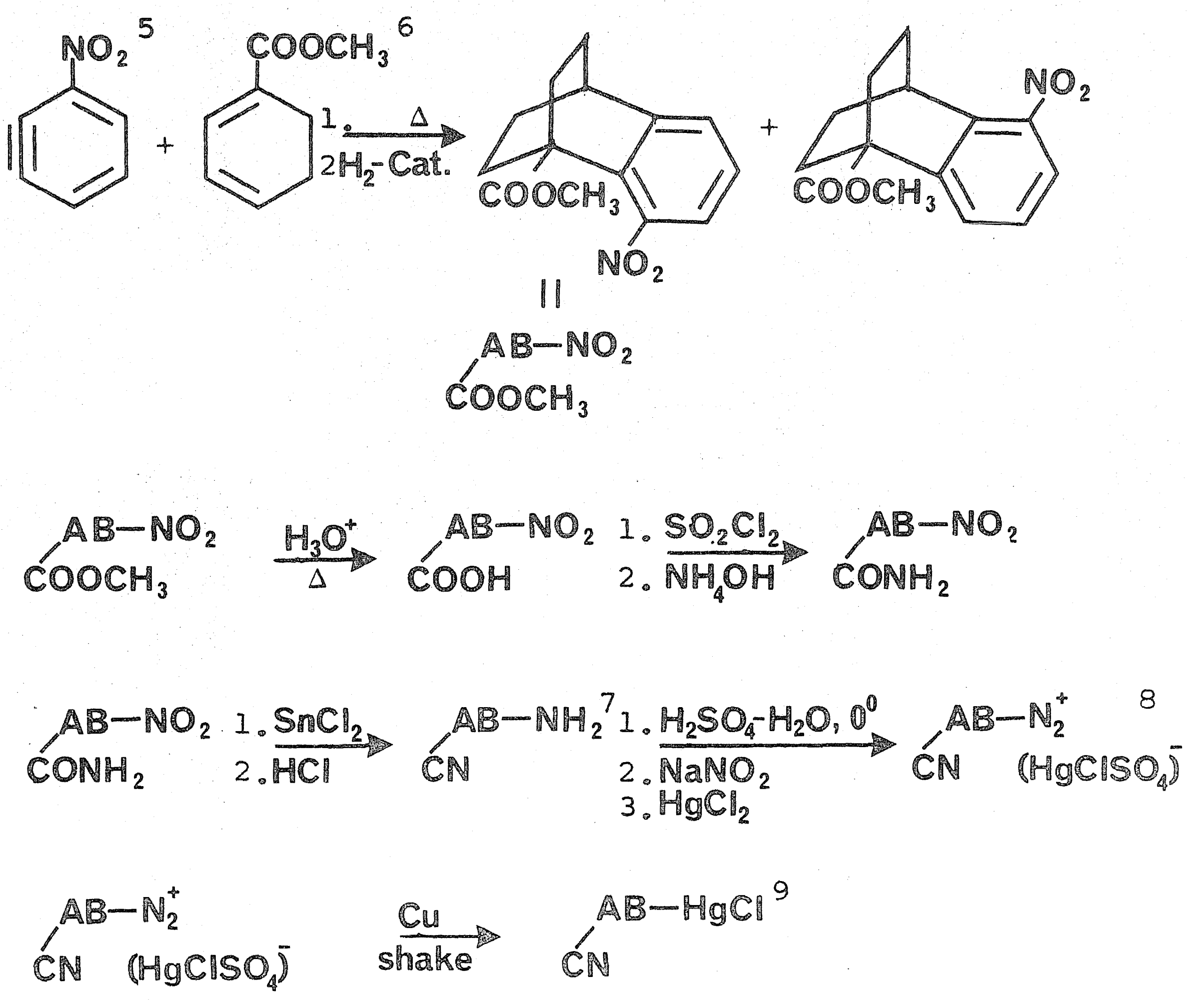


Figure 3

REFERENCES

1. M. F. A. El-Sayed and R. K. Sheline, J. Inorg. Nuc. Chem., 6, 187 (1958).

2. L. H. Jones, Inorg. Chem., 2, 777 (1963).

3. Kazuo Nakamoto, "Infrared Spectra of Inorganic Coordination Compounds," John Wiley & Sons, Inc., New York, 1964, pp. 166-173.
   J. R. Hall and J. C. Mills, J. Organometal. Chem., 445 (1966).

4. C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, 1963, pp. 343-344.

5. F. M. Logullo, Ph.D. Dissertation, Case Institute of Technology, 47 (1965).

6. Leon M. Stock, J. Am. Chem. Soc., 86, 5183 (1964).

7. Lewis J. Sargent, J. Org. Chem., 19, 599-607 (1954).
   E. A. Braude, R. P. Linstead, K. R. H. Woodridge, J. Amer. Chem. Soc., 3586-95 (1954).

8. Lewis J. Sargent, J. Org. Chem., 19, 599-607 (1954).
   A. N. Nesmeyanov, "Selected Workd in Organic Chemistry," Pergamon Press, New York, 1963, p. 19.

9. Ibid., pp. 20-21.

10. C. C. Addison, D. W. Amos and D. Sutton, J. Chem. Soc. A, 2285 (1968).

11. J. Hvoskef, Acta. Chem. Scand., 12, 1568 (1958).

12. M. F. Farona and K. F. Kraus, Inorg. Chem., 9, 1700 (1970).

13. M. F. Farona and N. J. Bremer, J. Amer. Chem. Soc., 88, 3735 (1966).

14. K. F. Purcell and R. S. Drago, J. Amer. Chem. Soc., 88, 919 (1966).

15. A. N. Nesmeyanov, D. N. Krautsov, E. I. Fedin, B. A. Kvasov, B. M. Pachevskaya, L. S. Golovchenko, Dokl. Akad. Nauk SSSR, 1079 (1968).

16. C. C. Addison, D. W. Amos and D. Sutton, J. Chem. Soc., A, 2285 (1968).

PROPOSITION 3

Prospsed: A direct chemical probe is presented to determine the nature of energy transfer in singlet quenching.

Despite considerable study, the mechanism of fluorescence quenching of aromatic hydrocarbons by dienes and other compounds is still not well understood. In addition to cyclic and acyclic dienes,[1-4,12-14] alkyl aryl sulfoxides,[8,9] multicyclic hydrocarbons,[5-7] azo compounds[10] and alkyl azides[11] have been shown to quench the fluorescence of napthalene and other aromatic hydrocarbons. Because the details of this process are still unclear several interpretations of the mechanism have been advanced.

From the results of quenching with dienes, quadricyclenes and sulfoxides, Hammond and coworkers have proposed a mechanistic scheme in which the quenching step involves exciplex formation (Fig. 1). This exciplex catalyzes radiationless decay of the excited singlet, and the electronic energy of the aromatic hydrocarbon is transformed into excess vibrational energy in the quencher, resulting in the isomerization of sulfoxides[8,9] or the conversion of quadricyclene into norbornadiene.[5-7] Recently Solomon, _et al_. have reported that they believe the results of experiments with

$A^{s0} \xrightarrow{h\nu} A^{s1}$	absorption
$A^{s1} + Q \xrightarrow{k_q} (AQ)^*$	singlet quenching
$(AQ)^* \xrightarrow{\quad} A + Q$	exciplex decomposition
$A^{s1} \xrightarrow{k_f} A^{s0} + h\nu'$	fluorescence
$A^{s1} \xrightarrow{k_d} A^{s0}$	internal conversion
$A^{s1} \xrightarrow{k_{ic}} A^{t1}$	intersystem crossing

Where A^{s0} and A^{s1} are the ground and first excited singlet states of the aromatic hydrocarbon, respectively and A^{t1} is the first excited triplet. Q is the quencher (either a diene or a triene), $(AQ)^*$ is the excited complex, the nature of which could be either electronic or vibrational excitation.

Figure 1

strained multicyclic hydrocarbons are better interpreted with an exciplex which is purely an excited charge transfer complex.

Still another interpretation postulates that fluorescence quenching occurs *via* endothermic electronic energy transfer. Lewis and Dalton[11] explain their results of the singlet sensitized decomposition of *n*-hexyl azide with a mechanism in which the azide is electronically excited by collisional energy transfer from excited aromatic hydrocarbons (Fig. 2).

$$A^{s1} + Q \xrightarrow{k_q'} Q^1 + A^{s0}$$

$$Q^1 \xrightarrow{\qquad} \text{products}$$

$$Q^1 \xrightarrow{\qquad} Q$$

Figure 2

It is apparent from these varying interpretations of the mechanism of fluorescence quenching that more information about the nature of the energy transfer step is necessary. It would be particularly valuable to determine the character of the energy transferred in the quenching processes, that is whether electronic or vibrational energy is specifically involved. Despite the fact that several studies have indicated that singlet quenching results in chemical reactions of the quencher,[5-11] in none of the systems studied was the reaction sensitive to the kind of energy transferred. It is proposed that the nature of the energy transfer step in singlet quenching can be probed chemically by examining the products from the electrocyclic reactions of diene and triene quenchers.

Woodward and Hoffman have demonstrated that the stereospecific nature of the electrocyclic interconversions of conjugated trienes and 1,3-cyclohexadienes can be predicted by considering the overlap of the highest filled molecular orbitals.[15,16] Thus the electronic excitation of trans-cis-trans-2,4,6-octatriene is predicted to give trans-5,6-dimethyl-1,3-cyclohexadiene, while the thermal activation should give cis-5,6-dimethyl-1,3-cyclohexadiene and vice-versa. Both the thermal and photochemical cyclizations of the octatriene to give the dimethyl-1,3-cyclohexadienes are well documented[17,18] (Fig. 3). By applying this reasoning in reverse order, the

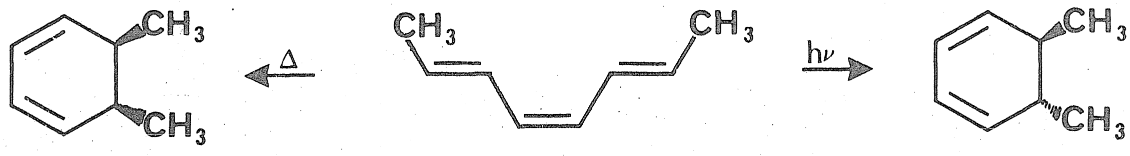


Figure 3

stereochemistry of the dimethyl cyclohexadiene formed in the singlet quenching of aromatic hydrocarbons with trans-cis-trans-2,4,6-octatriene would indicate the form of energy transfer.

Although the postulated fluorescence quenching by this triene is unprecedented, it is quite likely such compounds will prove to be efficient singlet quenchers.[19] In comparison with the isomerization of quadricyclene the energy required for the cyclization of the triene (~30 kcal/mole)[20] is less than that required to form norbornadiene (38.3 kcal/mole).[21] On this basis, one would predict that cyclization of the triene should accompany quenching of fluorescence in aromatic hydrocarbons (Fig. 4).

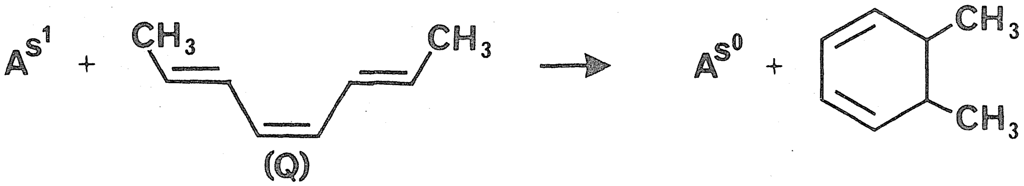


Figure 4

It is suggested that a series of aromatic sensitizers of various singlet energies be used in conjunction with this quencher. By investigating such a series in which the sensitizer singlet energies span a range extending well above and below the spectroscopic singlet of the triene (which by analogy to the trienes common to Vitamin D chemistry, probably lies at a wavelength slightly greater than 320 m (~89 kcal/mole)) any trend in the energy transfer process with regard to the relative energies would be revealed. For example, with aromatic sensitizers having singlet energies greater than that of the quencher, it will probably be necessary to include an additional step for classical quenching in the Hammond mechanism (Fig. 5).

$$A^{s1} + Q \xrightarrow{k_{cq}} A^{s0} + Q^{s1} \quad \text{Classical quenching}$$

Figure 5

In contrast, such a step seems unlikely (although Lewis and Dalton propose exactly this) when sensitizer energies drop below the level of the quencher singlet, and it is at this point that trends may become apparent. In short, the question is whether electronic energy transfer will continue in the exciplex, or whether a vibrational energy transfer process will take over, and by investigating the product stereochemistry of the proposed triene cyclization reaction, a simple and direct answer would be provided.

The following aromatic hydrocarbons along with their singlet energies comprise the series of sensitizers:[1,22]

Benzene	(S^1 = 108 kcal/mole)
Naphthalene	(S^1 = 89 kcal/mole)
2,3-Benzfluorene	(S^1 = 83.8 kcal/mole)
1,2-Benzanthracene	(S^1 = 74.3 kcal/mole)

Experimentally, the procedures involved in singlet quenching with the above compounds are essentially the same as those used by others.[1] One point of particular importance is that the concentration of the quenching 2,4,6-octatriene be adjusted so as to quench all the aromatic fluorescence, and in this way eliminate problems of triplet reactions. The method of product analysis is by VPC and has been established.[6]

Thus by combining the studies of electrocyclic reactions of trienes with techniques of singlet quenching, one can construct a simple method of probing the energy transfer step in the fluorescence quenching of aromatic hydrocarbons. This, it is hoped, will provide valuable information about the mechanism of singlet quenching.

REFERENCES

1. L. M. Stephenson, D. G. Whitten, G. F. Vesley and G. S. Hammond, J. Am. Chem. Soc., 88, 3665, 3893 (1966).

2. L. M. Stephenson and G. S. Hammond, Pure Appl. Chem., 16, 125 (1968).

3. L. M. Stephenson, D. G. Whitten and G. S. Hammond, " Chemistry of Ionization and Excitation," Taylor and Francis, Ltd., London, 1967, pp. 35-42.

4. A. Morikawa and R. J. Cvetanovic, J. Chem. Phys. 49, 1214 (1968).

5. S. L. Murov, R. F. Cole and G. S. Hammond, J. Amer. Chem. Soc., 90, 2957 (1968).

6. S. L. Murov and G. S. Hammond, J. Phys. Chem., 72, 3797 (1968).

7. B. S. Solomon, C. Steel and A. Weller, Chem. Commun., 927 (1969).

8. R. S. Cooke and G. S. Hammond, J. Amer. Chem. Soc. 90, 2958 (1968).

9. Ibid. 92, 2739 (1970).

10. P. S. Engel, J. Amer. Chem. Soc., 91, 6903 (1969).

11. F. D. Lewis and J. C. Dalton, J. Amer. Chem. Soc., 91, 5260 (1969).

12. G. N. Taylor and G. S. Hammond submitted for publication in J. Amer. Chem. Soc.

13. Ibid.

14. D. A. Labianca, G. N. Taylor and G. S. Hammond, J. Amer. Chem. Soc., in press.

15. R. B. Woodward and R. Hoffman, J. Amer. Chem. Soc., 87, 2045 (1965).

16. H. C. Longuet-Higgins and E. W. Abrahamson, J. Amer. Chem. Soc., 87, 2045 (1965).

17. G. J. Fonken, *Tetrahedron Lett.*, 549 (1962).

18. E. N. Marvell, G. Caple and B. Schatz, *Tetrahedron Lett.*, 385 (1965).

19. Preliminary work in this laboratory.

20. K. E. Lewis and H. Steiner, *J. Chem. Soc.*, 3080 (1964). This reference gives the activation energy for 1,3,5-hexatriene cyclization to be 29 kcal/mole.

21. J. R. Edman, *J. Org. Chem.*, *32*, 2970 (1970).

22. R. N. Nurmukhametov, *Russ. Chem. Rev.*, *35*, 469 (1966). I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, 1965. H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, 1962.

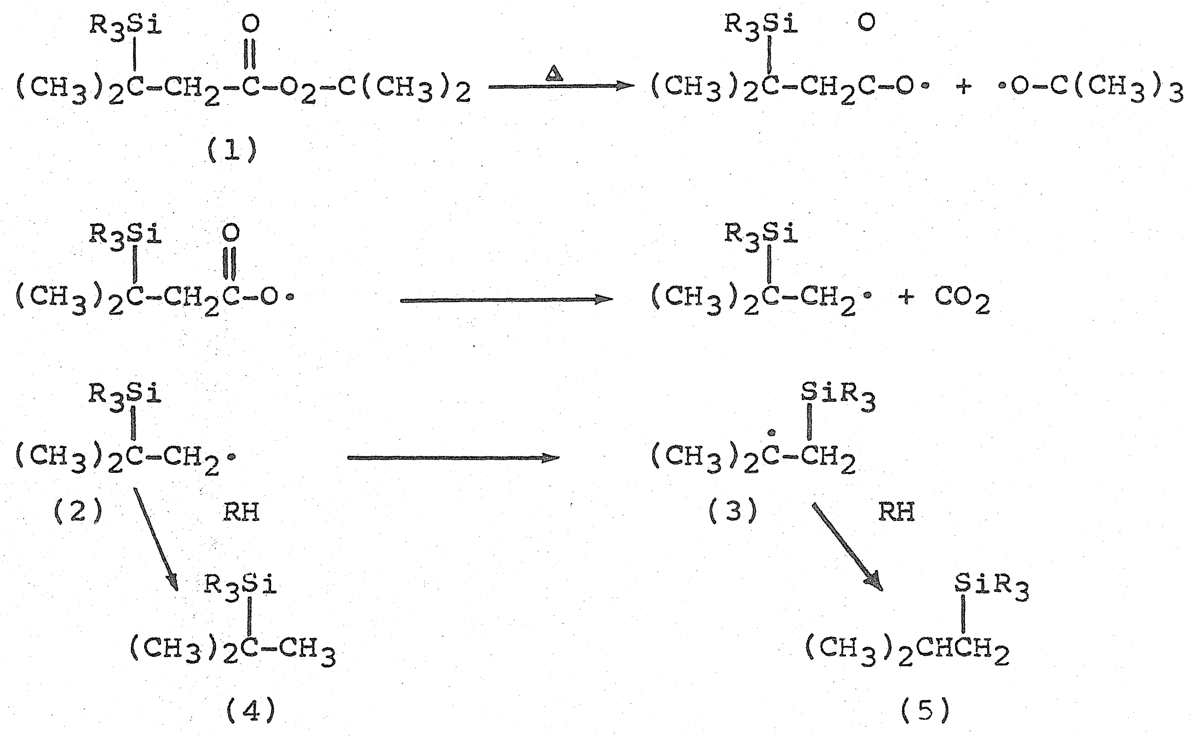
PROPOSITION 4

Proposed: A system in which to observe the 1,2-free radical shift of silicon in solution is suggested.

1,2-Free radical shifts of alkyl groups across carbon-carbon bonds have not been observed to take place even in the gas phase. However, 1,2-shifts in solution have been observed when the migrating group is phenyl,[1] Cl,[2] RS,[3] or Br.[4] To date, literature includes no mention of a free radical 1,2-shift of silicon across carbon-carbon bonds. It is therefore proposed to study a system in which a 1,2-silicon shift might be expected, and assess the importance of the d-orbital expansion of the valence shell in this rearrangement.

As stated above, no systems have been studied in which the 1,2-radical shift of silicon could be detected. However, there are cases in which a radical has been generated adjacent to a carbon-silicon bond, but because of the geometry of the starting material, the products corresponding to a silicon 1,2-shift would be identical to those formed from the initial radical. Thus no information could be obtained about silicon migrations from their studies.[5,6]

The proposed system (Fig. 1) suffers from neither of the shortcomings of those in the literature. Since no symmetrical relationship exists between the initially formed radical (2) and the proposed rearranged radical (3), the products arising from a 1,2-silicon shift will be different from those coming from the initially formed radical.



$$\underset{(1)}{(CH_3)_2\overset{R_3Si}{\overset{|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O_2-C(CH_3)_2} \xrightarrow{\Delta} (CH_3)_2\overset{R_3Si}{\overset{|}{C}}-CH_2\overset{O}{C}-O\cdot + \cdot O-C(CH_3)_3$$

$$(CH_3)_2\overset{R_3Si}{\overset{|}{C}}-CH_2\overset{O}{\overset{\|}{C}}-O\cdot \longrightarrow (CH_3)_2\overset{R_3Si}{\overset{|}{C}}-CH_2\cdot + CO_2$$

$$\underset{(2)}{(CH_3)_2\overset{R_3Si}{\overset{|}{C}}-CH_2\cdot} \longrightarrow \underset{(3)}{(CH_3)_2\dot{C}-\overset{SiR_3}{\overset{|}{CH_2}}}$$

$$(2) \xrightarrow{RH} \underset{(4)}{(CH_3)_2\overset{R_3Si}{\overset{|}{C}}-CH_3} \qquad (3) \xrightarrow{RH} \underset{(5)}{(CH_3)_2CH\overset{SiR_3}{\overset{|}{CH_2}}}$$

($R = CH_3$, CH_2F, CF_2H)

Figure 1

Not only would the rearrangement products from (3) be discernable, but there would also be a significant driving force in forming the more stable tertiary carbon radical.[7] Generation of a free radical of the form (2) is therefore proposed to provide information about the migratory aptitude of silicon in a 1,2-free radical shift.

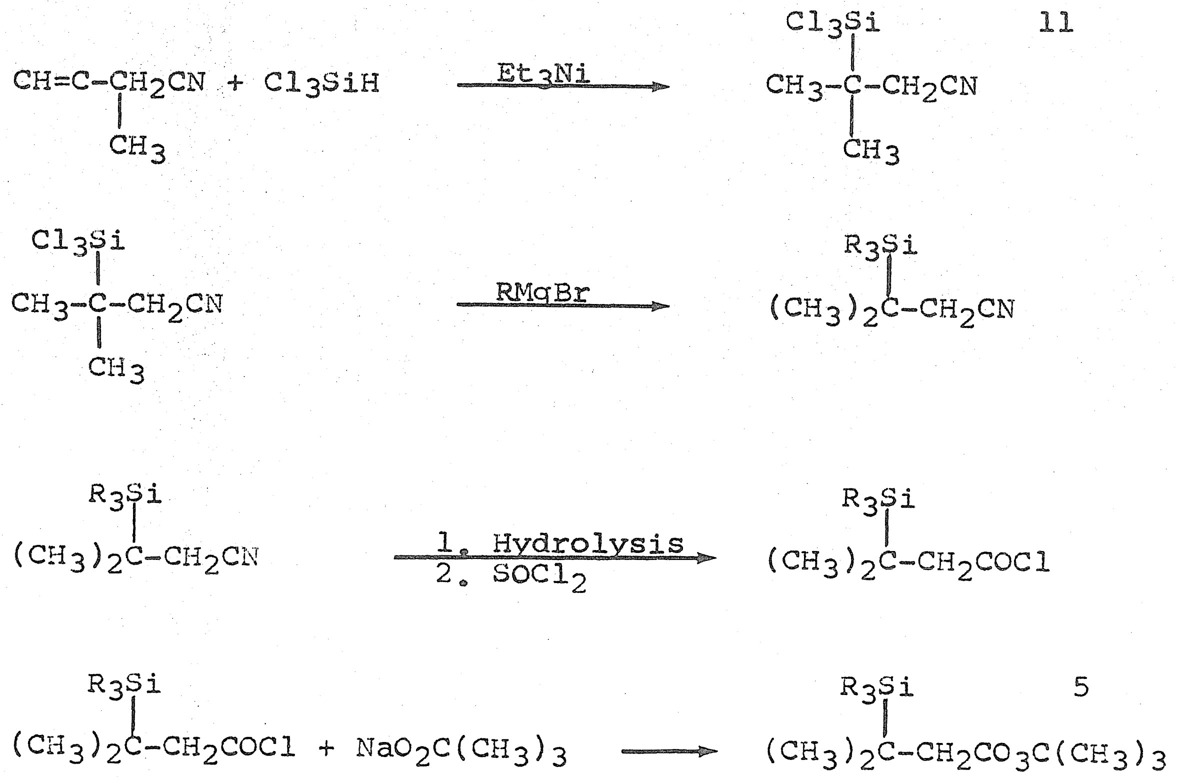
Jaffe has demonstrated that increasing the electron affinity of the central atom in compounds of the form BA_4 caused increased values of the overlap integrals for the BA bond due to greater 3d orbital interactions with the electrons of the A atoms.[9]

Thus if the nature of the R groups on radical (2) is such that they increase the silicon electron affinity but cannot increase the overlap integral through back-bonding, there should be enhanced interactions between the adjacent free electron and the silicon d orbitals. The greater the interaction between silicon d orbitals and the adjacent free electron, the more stable the transition state intermediate. This lower transition state is then, in turn, reflected by a higher migratory aptitude. It is suggested that fluoromethyl groups would cause such interactions due to their electron withdrawing ability. The importance of the d orbital interaction and therefore the migratory aptitude, would be expected to grow as R was successively changed from CH_3- to CHF_2-. Since the relative steric bulk of these groups increases only slightly with increased fluorine content, the steric effect would probably provide little driving force for rearrangement.

Thus by investigating the series of compounds just elaborated, one would have a clear indication of the importance of d orbital interactions of silicon for 1,2-free radical rearrangements.

The experimental methods required to investigate the proposed 1,2-shift would involve the thermal decomposition of (1) in dilute chlorobenzene solutions containing small quantities of a hydrogen donor. Analysis by nmr of the product mixture would provide an adequate means of monitoring the formation of (5), the product of the proposed rearrangement. An alternate means of analysis is offered by vpc since the silane (5) can be easily synthesized by an independent method.[10]

Synthesis:



$$CH{=}C-\underset{CH_3}{C}H_2CN + Cl_3SiH \xrightarrow{Et_3Ni} CH_3-\overset{Cl_3Si}{\underset{CH_3}{C}}-CH_2CN \qquad 11$$

$$CH_3-\overset{Cl_3Si}{\underset{CH_3}{C}}-CH_2CN \xrightarrow{RMgBr} (CH_3)_2\overset{R_3Si}{C}-CH_2CN$$

$$(CH_3)_2\overset{R_3Si}{C}-CH_2CN \xrightarrow[2.\ SOCl_2]{1.\ Hydrolysis} (CH_3)_2\overset{R_3Si}{C}-CH_2COCl$$

$$(CH_3)_2\overset{R_3Si}{C}-CH_2COCl + NaO_2C(CH_3)_3 \longrightarrow (CH_3)_2\overset{R_3Si}{C}-CH_2CO_3C(CH_3)_3 \qquad 5$$

(1)

($R = CH_3, CH_2F, CHF_2$)

REFERENCES

1. S. Winstein and F. H. Seubold, J. Amer. Chem. Soc., 69, 2916 (1947).

2. A. N. Nesmeyanov, A. N. Freidlina and V. I. Firstov, Izv. Akad. Nauk SSSR, Otdel Khim Nauk, 505 (1951).

3. R. K. Freidlina, A. B. Terentiev and R. G. Petrova, Dokl. Akad. Nauk SSSR, 149, 860 (1963).

4. P. S. Skell, R. G. Allen and N. D. Gilmor, J. Amer. Chem. Soc., 83, 504 (1966).

5. N. S. Vyazankin, G. A. Razuvaev and T. N. Brevmova, Dokl. Akad. Nauk SSSR, 163, 1389 (1965).

6. H. G. Kuivila and P. L. Maxfield, J. Organometal. Chem., 10, 41 (1967).

7. W. A. Pryor, "Free Radicals," McGraw-Hill, New York, 1966, p. 11.

8. C. Walling, "Molecular Rearrangements," Vol. 1, Interscience Publishers, New York, 1963, p. 427.

9. H. H. Jaffe, J. Chem. Phys., 58, 185 (1954).

10. C. Earborn, "Organosilicon Compounds," Academic Press, New York, 1960, p. 48.

11. Shun'ichi Nozakura, Bull. Chem. Soc. Jap., 29, 784 (1956).

Proposition 5

Proposed: An experimental method is proposed which would permit the direct detection of free radicals and other unstable species resulting from photochemical processes in the gas phase.

Classically, studies of the mechanisms of chemical reactions have, out of necessity, involved the clever manipulation of experimental parameters or molecular architecture in order to distinguish between hypothetical molecular pathways. The study of photochemical processes is a typical example in which kinetic rates of product formation, scavenging, sensitization and many other indirect tests have been used to elucidate mechanisms. Although these studies are valuable, too often they fail to distinguish between a number of possible molecular pathways. This problem is clearly delineated in Hoare and Pearson's review of gas phase photo-oxidations.[1] A far more desirable method is, of course, to observe the reactive intermediates responsible for the chemistry by some direct means. This is usually very difficult on an experimental basis mainly because their very nature insures that they will have short lifetimes and low concentrations. Nevertheless, the value of such techniques in photochemistry is amply demonstrated by the widespread use of emission spectrophotometers, flash lamp spectroscopes and spectrographs, and electron paramagnetic resonance spectrometers. Although these methods have been extremely valuable to study solution photochemical problems, their application to gas phase studies, although possible, are very difficult. The difficulties arise to a large extent from sensitivity problems, however other limitations also exist.

The mass spectrometer provides a potentially very useful technique for studying free radical formation from photodissociation, and is ideally suited for studying gas phase reactions since it has the potential for measuring extremely small concentrations and can easily handle the molecular weight range encountered in almost any gas phase experiment. For this reason it is proposed that an instrument be constructed to study the radicals resulting from gas phase photodissociation reactions directly.

Mass spectrometry of free radicals is a well-established technique,[2] and others have used this technique to study gas phase photochemical reactions.[3-6] However, because of limitations in the experimental apparatus, generally only mercury sensitized reactions can be observed.[3,7-10] It is of interest to construct an instrument which would study fragmentation reactions resulting from the direct irradiations of molecules. Until recently, the experimental requirements of such an apparatus have been prohibitively complex. Although the construction of the instrument in this proposal constitutes a major commitment of time and funds, recent advances in mass spectrometry and molecular beam technology make the operation of such an instrument by a photochemist on a "semi-routine" basis feasible.

The proposed experiment is quite simple. A high density molecular beam of substrate molecules is intercepted by a second beam of photons of a wavelength which is known to cause chemical reaction. The interaction of the light with these molecules causes a small fraction of them to become excited and dissociate into radicals. These radical fragments recoil out of the beam and drift without collision into the ionizer section of a quadrupole mass spectrometer where they are ionized by electron bombardment and discriminated by the mass analyzer on a mass/e basis. In this way, free radicals and other unstable intermediates resulting from the photodissociation of the substrate molecules in the gas phase can be detected directly. As pointed out earlier, there is ample precedence in the literature on the successful mass spectrometry of free radicals to insure that their detection by this method is possible.

The major obstacle in carrying out experiments of this type is machine design. Careful consideration of all the parameters involved in the experiment is necessary to insure sufficient detection sensitivity to make the experiment workable. The following description of the apparatus is an attempt to briefly layout its design and point out the critical factors of its construction, and in this sense, represents a feasibility study. A large portion of this design is the result of critical discussion with several people considerably more knowledgeable than myself in the areas of mass spectrometry and molecular beam design; their suggestions are gratefully acknowledged.[11]

The instrument consists of basically three vacuum chambers in which the molecular beam is formed, bombarded with light, and the fragments from photodissociation detected (Fig. 1). The three chamber system has the inherent advantage over other designs by permitting three stages of differential pumping. Since each chamber has its own separate vacuum system, a much higher vacuum is attainable in the final detection chamber. This is desirable because a higher vacuum at the detector means a lower background noise level for the experiment. All three chambers of the vacuum system would be fabricated from stainless steel with metal seals at the major flanges. The entire system would be wrapped with heater tape making it bakeable to *ca.* 300°C for efficient outgassing.

A high density molecular beam of substrate molecules is formed within the source chamber (Fig. 2). A heated inlet system supplies vaporized substrate molecules in a pressure range of about 0.1 - 5 Torr to the beam-forming nozzle. The nozzle suggested for this apparatus is an effusive type made up of a mosaic of fine capillary tubes of 10-25 μ diameter.[10] This capillary array, as it is called, has the desirable property of producing a high density molecular beam which is necessary for this experiment. Beams with densities of $\sim 10^{13}$ molecules/cm^3 have been obtained with this device.[4,13,14] Calculations indicate that a 25μ pore capillary array $\sim$ 4 mm in diameter will produce a beam of density of about 10^{13} molecules/cm^3 in the experimental chamber. A collimator, which removes all molecules with angular trajectories greater than a small angle from the beam, is placed close to the source nozzle (ca. 1 cm). To keep molecular scattering of the beam to a minimum, this chamber must be kept in a pressure range of 10^{-4} - 10^{-5} Torr. Because 99% of the molecular flux from the effuser will probably be trimmed before entering the experimental chamber, a calculated minimum pumping capacity of 3300 l/s is necessary in the sample chamber. The entire sample inlet system and capillary array is enclosed within the sample oven which allows wide variation of the source temperature.

Transmission of the beam through the collimator places it in the second vacuum chamber, the experimental chamber.

The intersection with the photon beam should be as close as possible to the entrance from the sample chamber (~2-3cm) so that a beam density of about 5 x 10^{13} molecules/cm^3 is attained.[4] At this point a collimated beam of ultraviolet light intersects the beam causing photochemical excitation of a fraction of the molecules in the beam. Based on the absorption cross section and quantum yield for photodissociation, a certain number of the molecules (10^{12}, see calculations) will dissociate and the fragments will recoil out of the beam.[5] Because the density of these fragments will fall off as the square of the distance from the point of intersection, it is crucial that the orifice into the detection chamber be placed very close to the molecular beam. With careful design, and a reasonably wide aperature (~1 cm) perhaps 10% of the recoiling fragments will enter the detection chamber, and the ionizer of the mass spectrometer. Although certainly higher numbers of fragments would enter the ionizer of the mass spectrometer if it were positioned on the axis of the molecular beam, just behind the point of intersection, the configuration with the mass spectrometer perpendicular to the plane of the two intersecting beams is preferred for several reasons. Since the ionizer voltage will be at a relatively high level (70-100 ev), electron bombardment of the parent molecules will produce the same fragments as photodissociation in most cases. Although phase sensitive detection will be used to discriminate the photo-fragments, a component of those fragments produced by electron bombarbment of parent molecules can be expected to have the same periodicity, and therefore it is necessary to exclude as much of the parent beam from the mass spectrometer as possible. Furthermore, the perpendicular configuration results in a minimum of scattered light entering the mass spectrometer and striking the electron multiplier.

Because the detection of fragments depends on their free recoil out of the molecular beam into the mass spectrometer pressures in this second chamber should be maintained around 10^{-6} - 10^{-7} Torr. A pumping speed of ~5000 l/sec is calculated to be sufficient to hold this pressure.[16]

Using a 2.5 kw mercury-xenon high pressure lamp with a suitable quartz lens system as the light source, assuming an optical density of about 200 l/moles cm, and a quantum yield for dissociation of about 0.5, a value of 1×10^{11} radicals/sec is calculated for the number of fragments entering the ionizer.

The vacuum chamber which contains the mass spectrometer is maintained at the lowest pressure of the entire system, 10^{-8} - 10^{-9} Torr by means of both conventional and cryoscopic pumping. The ionizer should be placed as close to the orifice of the third chamber as possible to obtain the maximum flux of fragments. High ionizer efficiency is also a very important factor in producing enough ions to insure an adequate signal in the detector. About the maximum attainable levels of efficiency at this time are 10^{-3}.[17] Calculating this final factor produces a predicted ion current of 1×10^8 ions/sec or 1.7×10^{-11} amps. Since the limit of sensitivity of a typical commercially available quadrupole mass spectrometer is about 10^{-13} amps,[18] this calculation suggests that the signal would be detectable. Considerably weaker signals could be detected if the standard 14 stage multiplier detector with a gain of *ca.* 5×10^5 were replaced by a newly developed 22 stage electron multiplier with a gain of 10^9.[19]

Because of the weak nature of the signal and the need for discrimination of those ions coming from photodissociation from the background, special techniques must be employed to extract the signal.[20] Following preamplification and preliminary filtering, the signal is fed to a phase sensitive amplifier. Synchronization of this device with the light source rejects all other signals coming from the electron multiplier except those having the same phase and frequency of the chopped light source. As a result, a very large increase in the signal to noise ratio can be obtained. By connecting a computer of average transients to the output of the phase sensitive amplifier, the light induced signal can be accumulated and stored for a large number of pulses. The connection between the X base of the CAT and the mass analyzer control permits scanning of the mass range of interest to obtain the appropriate mass spectrum of the photo-fragments.

On the basis of these preliminary calculations the construction of a molecular beam apparatus of this type to study photochemical fragmentation and related reactions is feasible. Because of the complexity of the instrument, it is worthwhile to review the critical factors in the design.

1. A high density molecular beam is required to assure the maximum absorption of light. Presently beams from capillary arrays produce molecular flows on the order of 10^{18} molecules/$cm^3 \cdot s$. In order to maintain a high density the design should be such that the point of intersection with the light beam is as close as possible to the molecular beam source.

2. Light sources are probably the least adequate component in the instrument. The calculated value of 10^{16} photons/sec from the mercury lamp may be too low for many molecules. High power lasers with intensities three orders of magnitude higher than this value already exist. Certainly present indications suggest that sources of this kind of power in the ultraviolet region will become

available in the next few years. A laser light source in this instrument would greatly increase the signal to noise ratio, and therefore, if financially possible, one should be added.

3. The positioning of the orifice leading to the ionizer over the mass beam is critical to obtaining the highest possible signal. The 10% value used in these calculations is only an estimate based on reasonable geometry. Actual component selection and position will determine the real value.

4. A high ionizer efficiency must also be included to insure an adequate signal to noise ratio. The value of 10^{-3} is a maximum at this time for ionizer efficiencies. Depending on the selection of other components in the system, a lower efficiency ionizer could be used.

5. Of course, the type of molecules selected for study will also influence the signal strength. The selection of a relatively small absorption coefficient ($\epsilon = 200$) for the calculation was done to provide a conservative estimate. There are many organic molecules with values of ϵ one and two orders of magnitude higher. This parameter is the least desirable one to have to vary.

Before ending the discussion of the instrument design, it should be noted that the inclusion of a laser light source opens up the possiblity of measuring the time of flight, and hence, the velocity of the fragments. Such information would provide a means of determing the occurence of secondary fragmentations of the radicals while on route to the detector. At the present time, at least one such apparatus of this type is in existence.[4]

In conclusion, the need for an instrument of this type which could be used on a "semi-routine" basis is very great. The number of photochemical systems in which it would be of value to directly detect the intermediacy of free radicals is practically limitless. A very few of the types of organic compounds which would be amenable to this type of study are listed below:

ketones
nitrite esters
azo compounds
hypohalites
nitroso compounds
phenyl esters
phenyl amides
phenyl ethers
mercaptans and other sulfur compounds

As stated earlier, the construction of this instrument represents a major commitment of time and funds. The following is a rough estimate of both the present day cost and time required to fabricate and debug the instrument.

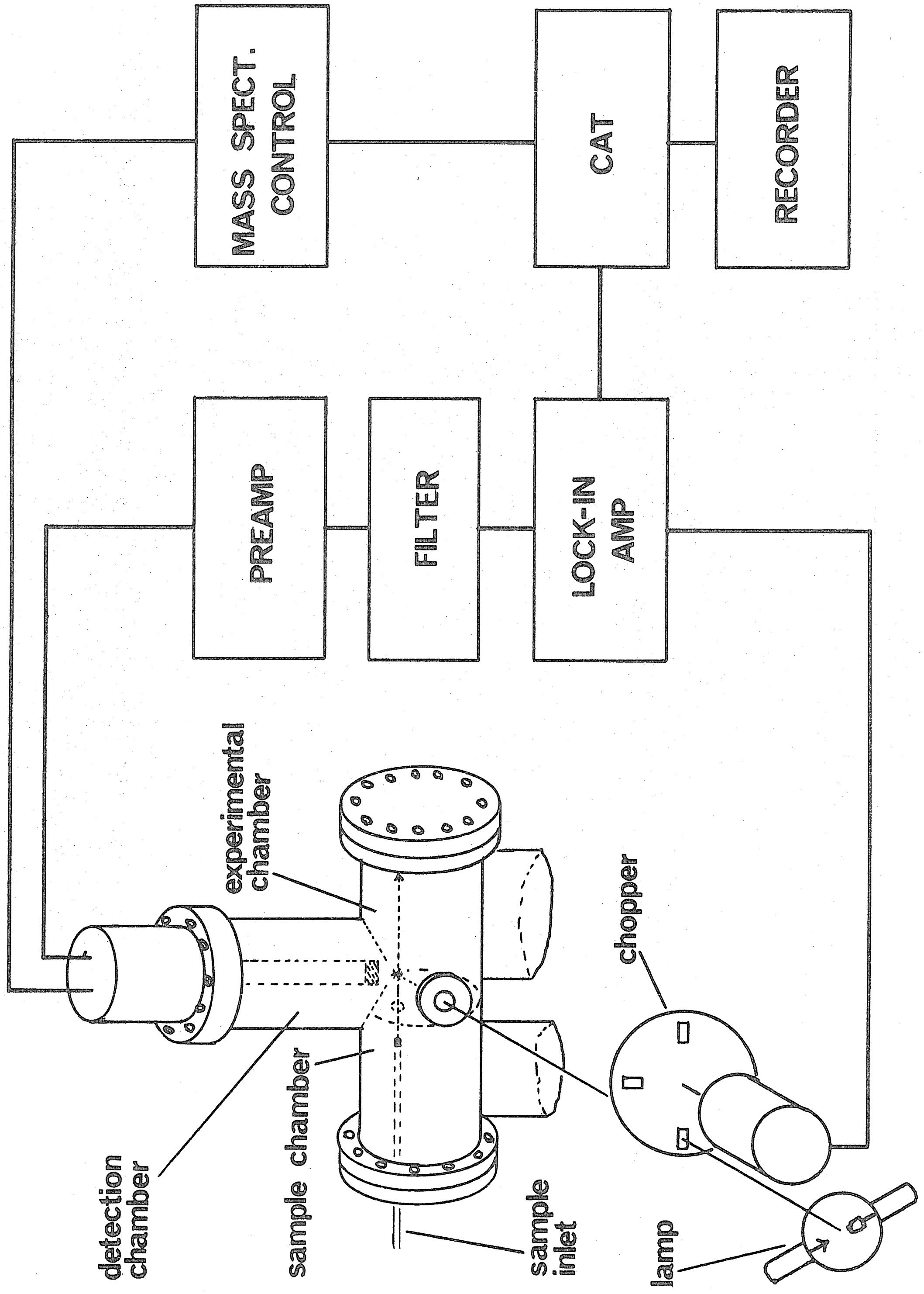

MASS SPECT. CONTROL
CAT
RECORDER
PREAMP
FILTER
LOCK-IN AMP
experimental chamber
chopper
detection chamber
sample chamber
sample inlet
lamp

Figure 1

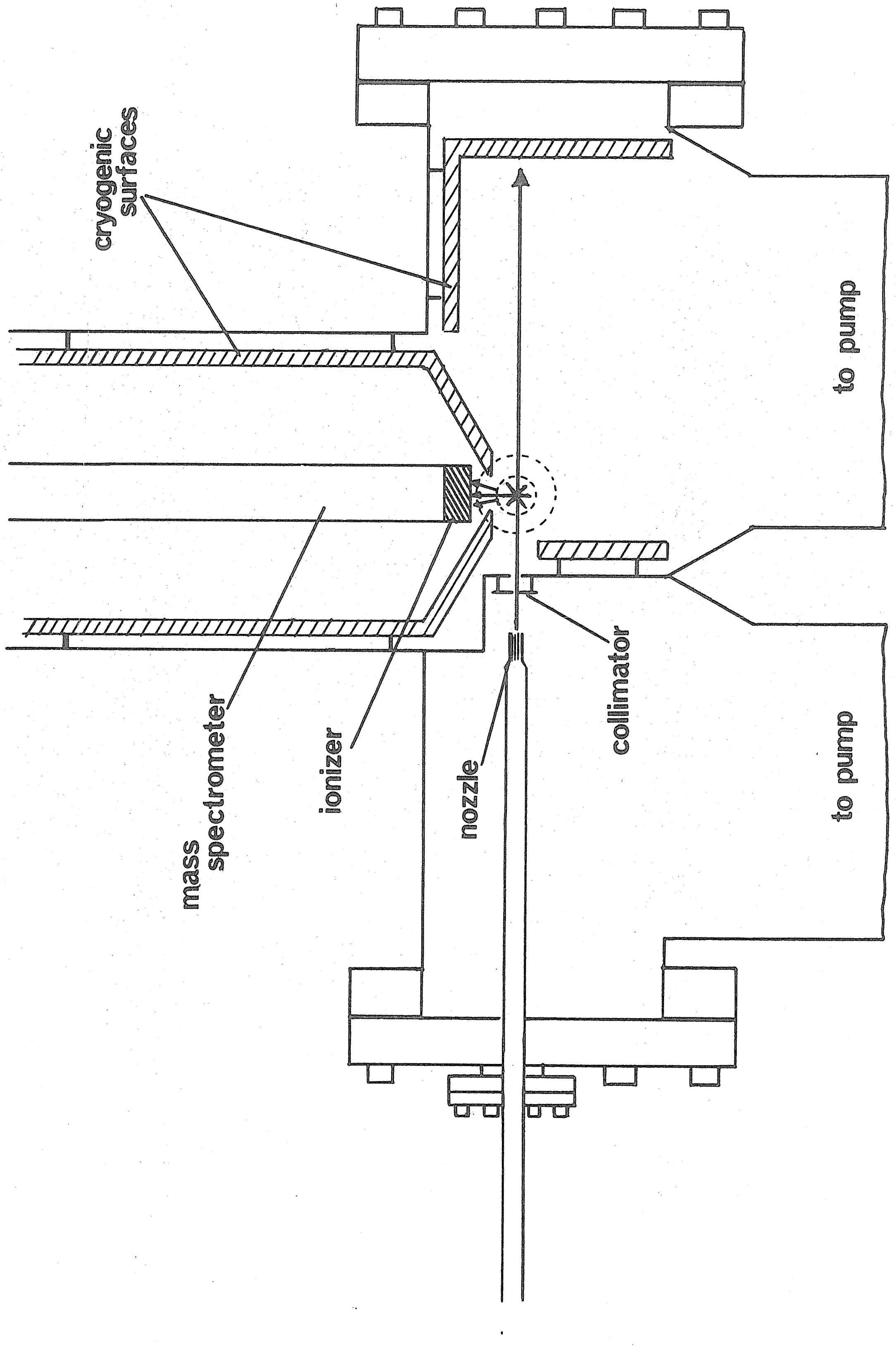

cryogenic surfaces
mass spectrometer
ionizer
nozzle
collimator
to pump
to pump

Figure 2

Quadrupole Mass Spectrometer**	$15,000
Vacuum Chamber	10 to 15,000
Pumping System	10,000
Light Source* **	5,000
Electronics	10 to 20,000
Estimated total cost	$65,000 ± 15,000

*Based on a high pressure mercury source

**These components have been offered to the Hammond group by JPL.

Time estimate: 6 - 10 man years

The lower limit may be the most valid if a photochemist and a research fellow with previous experience in the construction of molecular beam instruments are teamed for the project. In view of this fact, it would be desirable to undertake the project in this manner. The chemistry department has long advocated joint research projects between two groups. This project is natural for such a joint effort and collaboration between the Hammond and Kuppermann or Beauchamp groups is viewed as a very attractive means of reaching the goal.

Again, because of the complexity of such an undertaking, a partial list of possible consultants has been prepared:

Prof. J. Beauchamp, Chem. Dept. Caltech.

Prof. A. Kuppermann, Chem. Dept. Caltech.

Dr. D. Winocur, Research fellow, Chem. Dept. Caltech.

Prof. K. Wilson, Chem. Dept. University of California at San Diego.

Prof. Yuan Lee, Chem. Dept. University of Chicago.

Prof. Eldon Knuth, Dept. of Engineering & Kinetics, School of Engineering & Applied Science, University of California, Los Angeles.

Prof. D. R. Olander, Lawrence Radiation Laboratory, University of California, Berkeley.

Calculations

Assuming a calculated molecular beam of 5 x 10^{13} molecules/cm^3.

Calculation of molecular cross section to light for typical compound with an $\epsilon = 200$, $\Phi = 0.5$

In solution:

$A = \epsilon Cl$ where ϵ = molar extinction coefficient in solution (l/mole cm)

C = concentration (moles/l)

l = path length (cm)

and:

$A = \log \frac{I_o}{I}$ where I_o and I are light intensities

For a gas phase absorption cross section the following relation exists:

$\frac{I}{I_o} = e^{-N\sigma_a X}$ where σ_a = molecular cross section

N = density of molecules

X = path length of light attenuation

Combining these equations:

$$2.3\ (\epsilon Cl) = N\sigma_a X$$

or:

$$\sigma_a = \frac{2.3\ \epsilon \cdot C \cdot l}{N\ X}$$

$$\frac{C}{N} = \frac{10^3}{6.02 \times 10^{23}} \qquad \frac{\text{moles}}{\text{molecule}}$$

$$\sigma_a = \frac{(2.3)\ (2 \times 10^2)\ (10^3)}{6.02 \times 10^{23}}$$

$$\sigma_a = 7.7 \times 10^{-19}\ \text{cm}^2$$

To make this a reaction cross section, multiply by the probability of a photon-causing reaction:

$$\sigma_r = \sigma_a \cdot \Phi$$

$$\sigma_r = 0.5 \cdot 7.7 \times 10^{-19}\ \text{cm}^2$$

$$\sigma_r = 3.8 \times 10^{-19}\ \text{cm}^2$$

From this value the fraction of molecules in the beam which will fragment can be calculated:

Assuming that attenuation of the light is negligible and the usable intensity from the lamp is 1 x 10^{-7} E/m or 5 x 10^{16} photons/sec:

The number of photons absorbed which lead to reaction is:

$I = I_o N\sigma_r X$ where $I_o = 5 \times 10^{16}$ photon/sec

$N = 5 \times 10^{13}$ molecules/cm^3

$\sigma_r = 4 \times 10^{-19}$ cm^2

$X = 1$ cm

$$I = (5 \times 10^{16})(5 \times 10^{13})(4 \times 10^{-19})(1)$$

$$= 100 \times 10^{10}$$

$$I = 1 \times 10^{12}\ \text{fragmentations/sec}$$

Assuming as much as 10% of the fragments reach the ionizer, and an ionizer efficiency of roughly 10^{-3}, the following value is calculated:

$(0.1)(10^{-3})(10^{12}) = 1 \times 10^{8}$ ions/sec

Since 1A = 1C/S = 6×10^{18} electrons/sec

This ion current corresponds to:

$$\frac{1 \times 10^{8}}{6 \times 10^{18}} = 1.7 \times 10^{-11} \text{ Amps}$$

References

1. D. E. Hoare and G, S, pearson, "Advances in Photochemistry," Vol. 3, Noyes, Hammond and Pitts, Ed's., Interscience Publishing Co., New York, 1964, p.83.

2. The reader is referred to the forty-odd papers by F. Plossing and his coworkers published on the mass spectroscopy of free radicals. F. P. Lossing, Div. of Pure Chemistry, National Research Council of Canada, Ottawa, Canada.

3. F. P. Lossing, Can. J. Chem., 35, 305 (1957).

4. G. E. Busch, J. F. Cornelius, R. T. Mahoney, R. I. Morse, D. W. Schlosser and K. Wilson accepted for publication in Review of Sci. Instrum., July issue (1970).

5. K. Wilson, to be published in "Symposium on Excited State Chemistry," J. N. Pitts, Jr., ed., Gordon & Breach, New York, 1970.

6. G. B. Kistiakowsky and P. H. Kydd, J. Amer. Chem. Soc., 79, 4825 (1957).

7. J. B. Farmer, F. P. Lossing, D. G. H. Marsde, and E. W. R. Steacie, J. Chem. Phys., 23, 1169 (1955).

8. A. Jones and F. P. Lossing, Can. J. Chem., 47, 1391 (1969).

9. S. Yamashita and F. P. Lossing, ibid., 46, 2925 (1968).

10. A number of other papers on the mercury sensitized photolysis of organic compounds have been published by Lossing (see footnote 2).

11. The lengthy discussions with Prof. J. L. Beauchamp, Dr. Daniel Winocur of the California Institute of Technology and Prof. Kent Wilson of the University of California, San Diego were most helpful and are gratefully acknowledged.

12. Mosaic Fabrications Division of Bendix Corp., Galileo Park, Sturbridge, Mass.

13. A. T. Stair, Jr., and J. L. Pritchard, J. Appl. Phys., 37, 1551 (1966).

14. R. H. Jones, D. R. Olander and V. R. Kruger, *J. Appl. Phys.*, *40*, 4641 (1969).

15. $V/S = \frac{\frac{N}{S}\,kT}{P}$ where V = volume (cm^3)

S = time (sec.)

diam. 0.4 cm $\frac{N}{S}$ = molecules/sec

area 0.12 cm^2 $kT = \sim 2.8 \times 10^{-17}$ $\frac{\text{Torr cm}^3}{\text{molecule}}$

With a flux of about 10^{20} molecules/cm^2 S from the nozzle about 1% of the beam will be transmitted through the collimator. Hence, 99% of the beam flux remains in the sample chamber or:

$$(1.2 \times 10^{-1}\ cm^2)(1 \times 10^{20}\ \text{molecules}/cm^2\ S)$$

$$= 1.2 \times 10^{19}\ \text{molecules/sec.}$$

$$\frac{V}{S} = \frac{N}{S}\,kT$$

$$= \frac{(1.2 \times 10^{19}\text{molecules/sec})(2.8 \times 10^{-17}\ \text{Torr cm}^3/\text{molec.})}{10^{-4}\ \text{Torr}}$$

$$= 3.3 \times 10^{3}\ \text{l/sec in sample chamber}$$

16. $$\frac{V}{S} = \frac{(1.2 \times 10^{17}\ \text{molecules/sec})(2.8 \times 10^{-17}\ \text{Torr cm}^3/\text{molec.})}{10^{-6}\ \text{Torr}}$$

$= 3.3 \times 10^{3}$ l/sec would be a minimum not including diffusion from the sample chamber which will depend on the orifice of the collimator chosen.

Auxillary cryoscopic cooling is suggested because of its efficiency at pumping the kinds of molecules to be studied.

17. This value is an estimate resulting from discussions with other people (reference 11). An ionizer of high efficiency is manufactured by the Extranuclear Corporation Inc., Pittsburgh, Pa.

18. EAI Quad-250 specifications give a sensitivity of 100 A/Torr and 10^{-15} Torr as the limit of detection. This value was also confirmed by Prof. J. Beauchamp.

19. Model number SPM 00-402 DuMont Electron Tube Division Fairchild Camera and Instruments Co., Clifton, New Jersey.

20. D. R. Olander and W. W. Waddel, *Anal. Chem.*, *40*, 1687 (1968).