THE INITIAL DECOMPOSITION RATE OF NITROGEN PENTOXIDE

Thesis

by

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Recent developments in chemistry afford few problems more interesting than that of reaction rates. The science of thermodynamics has become a most valuable tool in that it enables the chemist to distinguish between reactions that are possible and those that are impossible, as well as to determine in advance the optimum conditions under which will operate any process involving a system at equilibrium. Unfortunately it does not explain why certain theoretically possible reactions actually show little or no tendency to take place, nor can it predict how fast a reaction will proceed. The solution of these problems of reaction velocity cannot be accomplished by the methods of thermodynamics, but will necessitate the deeper insight provided by the methods of statistical mechanics, and it is hoped that the work on the initial rate of decomposition of nitrogen pentoxide, described in this article, may be of use in furnishing experimental material which will contribute to the ultimate solution of the problem.

The decomposition of N_2O_5 is a reaction which is peculiarly well adapted for study in connection with theories as to reaction velocities and their temperature coefficients. It is perhaps the only known unimolecular gas reaction which is not appreciably catalyzed by the walls of the containing vessel and it proceeds at moderate temperature very conveniently for measurement. The chief disadvantage, its corrosive action on mercury, rubber and other materials ordinarily used in handling gases, was obviated by means of an all-glass pressure measuring device employed by Daniels and Johnston,(1) who demonstrated the true unimolecular character of the reaction over the temperature range from 0° to 65°. They further(2) found that the decomposition was accelerated by blue light, but only in the presence of the dioxide, NO_2.

In the course of some later work by Daniels, Wulf and Karrer(3) on the oxidation of nitrogen tetroxide, a phenomenon was observed which raised some question as to the behavior of the pentoxide when entirely free from its decomposition products. After a quantity of $NO_2 + N_2O_4$ had been oxidized by a quantity of ozone just sufficient to give a colorless mixture, it was expected that the brown color of NO_2 would reappear in a very short time due to the decomposition of the N_2O_5 thus formed. From a yet unknown cause the mixture remained colorless for a great length of time even after being raised to temperatures where the ordinary decomposition is extremely rapid. Attempts to explain this curious fact brought forth the suggestion that the decomposition was retarded by the complete absence of NO_2 which might be a catalyst whose presence was necessary. No evidence to support this hypothesis had been adduced in the previous measurements of the reaction velocity, for in every case the rate appeared

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(1) Daniels and Johnston, J. A. C. S. <u>43</u>, 53 (1921).

(2) Daniels and Johnston, J. A. C. S. <u>43</u>, 72 (1921).

(3) Daniels, Wulf and Karrer, J.A.C.S. <u>44</u>, 2402 (1922).

to be independent of the concentration of the dioxide. Nevertheless the photochemical acceleration, already mentioned, and in addition some results obtained by Lueck(4) in a study of the reaction in carbon tetrachloride solution offered support to the argument for autocatalysis.

The present investigation was undertaken for the purpose of testing the possibility that nitrogen dioxide may act as a catalyst in the initial stages of the gaseous reaction

$$\begin{array}{c} N_2O_5 \longrightarrow N_2O_4 + \tfrac{1}{2} O_2 \\ \downarrow\uparrow \\ 2\ NO_2 \end{array}$$

As will be seen in the sequel, this study has shown that the reaction retains its unimolecular character even at the lowest concentrations of dioxide that it has been possible to measure. It is felt that this discovery considerably increases the theoretical interest and importance of this reaction.

Apparatus and Methods.

Although the glass manometer used in the previous investigations by Daniels and Johnston(1) is capable of measuring moderate pressures with considerable accuracy, it was necessary for the purposes of this experiment to devise a more sensitive method which would give a measure of the NO_2 independently of the total pressure. The colorimetric principle offered a very simple means of estimating concentrations of this reddish brown gas, and accordingly there was

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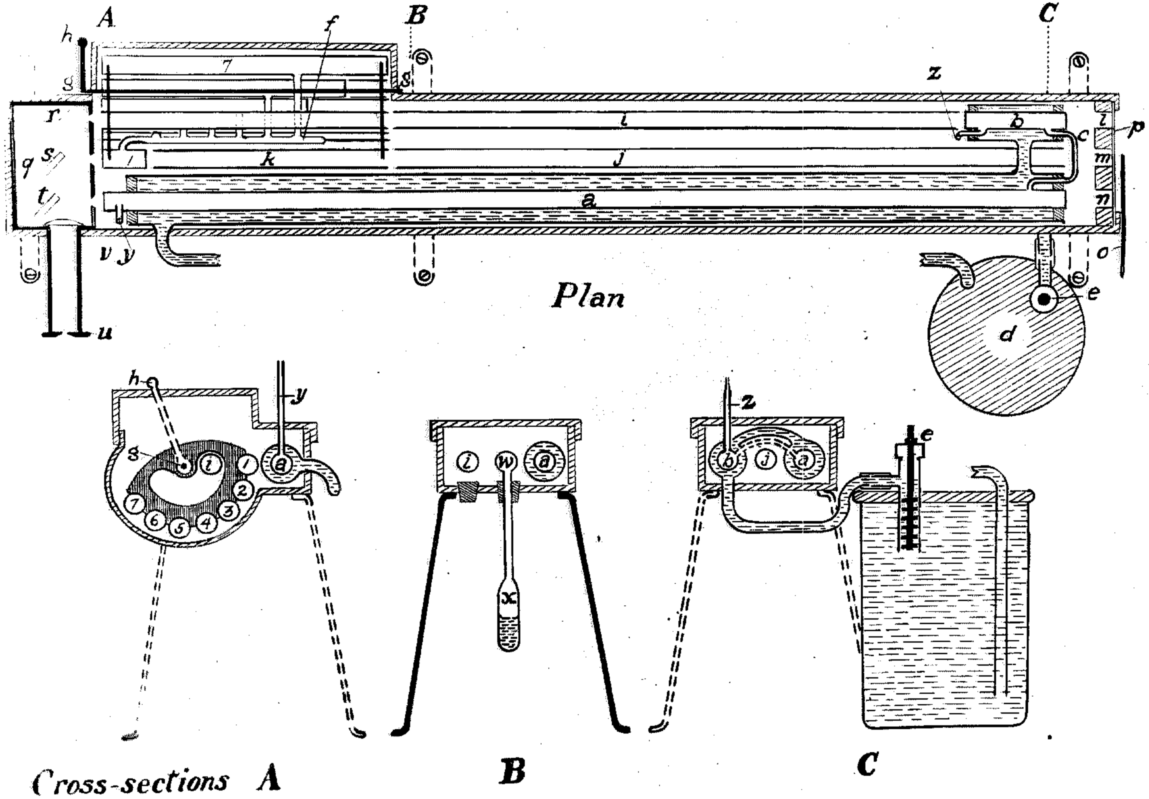
(4) Lueck, J. A. C. S. 44, 757 (1922).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Cross-sections A
B
C

FIG. 1

constructed an apparatus which was essentially a gas colorimeter.

Fig. 1 shows the plan and three vertical cross sections of the colorimeter. The reaction chamber consisted of the tubes a and b, 888 and 88.8 mm. long respectively, connected by the side arm c. Their ends were formed of plane microscope slide glass about 1 mm. thick, fused on by a special process. These tubes were jacketed as shown and kept at constant temperature by circulation of water from and to the thermostat d, which was provided with a screw pump e and the conventional apparatus for automatic temperature regulation (not shown in the diagram).

The tubes 1, 2, 3, 4, 5, 6, 7 will be referred to as the "one-phase standards." Each had plane glass ends and a side arm connected to the manifold f, thus forming a single gas chamber with seven branches, whose inside lengths ranged from 37 mm. to 259 mm. by successive multiples of 37. This system was evacuated, then charged with a measured quantity of NO_2 and sealed off. It was securely fastened to a cradle-shaped metal frame capable of being rotated about the axis g by means of the lever h and arrested in the desired position by means of a spring-latch. Thus each of the tubes could be brought into the horizontal plane of the reaction tubes and parallel to them. The open-ended tubes i, j and k were of the same diameter (15 mm.) as the standard and the reaction tubes, and served to equalize reflections along the paths of the three light beams, which entered through the circular apertures l, m, n, after diffusing through the opal-glass plate p, the source being a filament lamp. The shutter o excluded the light during intervals between readings. After passing through the tubes the light beams entered the mirror-box q through glass-windowed apertures 6 mm. square and were reflected at right angles by the sharp-edged speculum metal mirrors r, s, t, adjusted in such a position that the images of the square apertures were contiguous when viewed through the eye-piece u and the lens v focused upon them. Green or blue color screens were sometimes introduced to aid the eye in obtaining a sensitive match.

Cross section B , Fig. 1, illustrates the "two-phase standard", consisting of a short, plane-ended tube w connected by a narrow tube to the bulb x containing liquid NO_2. This system was evacuated at a low temperature before being sealed, so as to remove all foreign gases. The pressure of NO_2 in the compartment w could be varied between wide limits, being calculable from the temperature of the liquid and that of the vapor, with the aid of the experimental vapor pressure curve and Schreber's equation for the equilibrium between NO_2 and N_2O_4. This "two-phase standard" could be inserted in the middle, as illustrated in the drawing, or at the left. In the former position it was used for comparison with tube a or tube b, and in the latter position for comparison with the "one-phase standards" in order to check their titre, in which case it was necessary to remove the tube b or to compensate its absorption of light by interposing extra glass slides in the middle path.

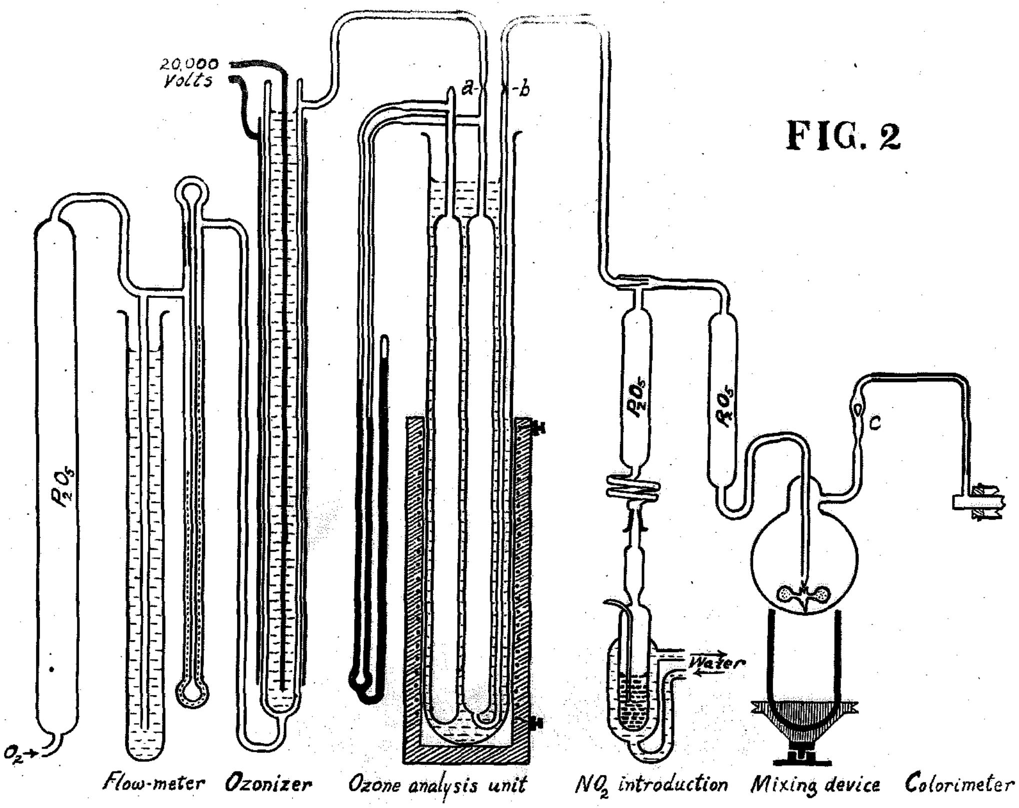
20,000 Volts
a
b
P2O5
P2O5
P2O5
O2
Water
c
Flow-meter
Ozonizer
Ozone analysis unit
NO2 introduction
Mixing device
Colorimeter

FIG. 2

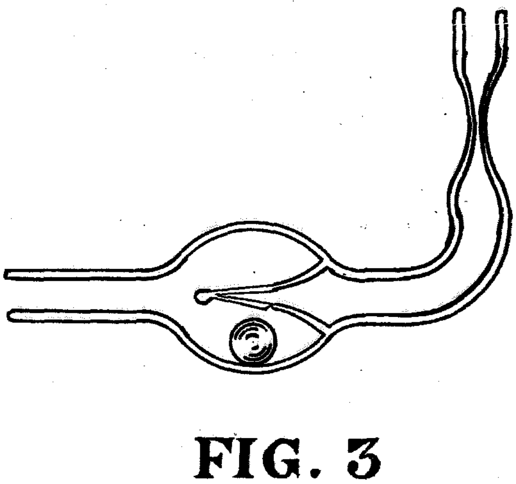

FIG. 3

Cross sections A and C need little further explanation. They show the inlet y and the outlet z of the reaction chamber, and more clearly illustrate the arrangement of the "one-phase standards", the water circulating system, and the light-tight cabinet with removable lid.

Initially several variations were tried in the method of preparing the N_2O_5 free from NO_2, and of introducing it into the reaction chamber. As all of these gave similar results, it was decided to adopt the most convenient procedure, which will be described here with the aid of Fig. 2. This final method as described was used in all work later than Run No. 4.

Oxygen from a commercial cylinder was dried in contact with P_2O_5 and passed into the train at the left of the figure, its flow being regulated by a blow-off immersed in liquid petrolatum and registered by a capillary flow-meter employing the same liquid. A Siemens ozonizer yielded a mixture of about 4% ozone by volume when operated steadily on 20,000 volts at room temperature and a flow of 150 c.c. per minute. This oxygen-ozone mixture passed thence through a device for analyzing it by the pressure change attending the subsequent decomposition of the ozone on heating, the pressure being measured with concentrated sulphuric acid in a capillary manometer, an arm of which was sealed to a closed buffer tube containing dry air at a known pressure and equal in volume to the analysis chamber, namely that portion of the train between the two constrictions a and b. The analytical procedure consisted simply in fusing at the constrictions and taking readings of temperature and of pressure before and after heating for about four hours at 150° in the oil bath, which was heated electrically and stirred by bubbling air from a tube not shown in the sketch. This analysis was not performed, of course, until after the desired mixture of gases had been introduced into the colorimeter.

The N_2O_5 was produced by forcing NO_2 and N_2O_4 into the gas stream under its own vapor pressure from the liquid in the jacketed bulb, as illustrated in the figure. By carefully controlling the temperature of the water circulating through the jacket, the liquid oxides could be vaporized at a steady rate, which could be varied in different runs so as to give relatively high or low concentrations of the N_2O_5 that formed upon contact with the stream of ozone. P_2O_5 driers were used as shown, and the resulting mixture of N_2O_5, O_2 and O_3 passed thence into a mixing device, where stirring was accomplished by means of a glass propeller, with hollow blades filled with iron filings, driven by rotating a horseshoe magnet.

After leaving this chamber the gases passed through a tube having a constriction and a glass check-valve c, beyond which a capillary led to the reaction chamber of the colorimeter. The valve and the capillary served to retard diffusion into the colorimeter of the slight quantity of gas decomposed in the process of fusing off the constricted tube. The volume of the entire train was approximately a liter, and usually the gas flow was maintained steadily at about

150 c.c. per minute for half an hour, by which time the reaction chamber contained a fairly homogeneous mixture entirely free from NO_2 and of a distinctly bluish color from the excess of ozone. The partial pressure of the N_2O_5 was determined from subsequent colorimetric analysis of the NO_2 present after the complete decomposition, as will be described in a later section. In all except the first four runs the partial pressure of the ozone was also estimated from the combined data. The temperature of the water bath having been adjusted to the desired point and kept constant within about 0.02°, the system was now ready for the main experiment and the reaction chamber was quickly sealed off by fusion of the inlet and outlet tubes. The exact time of this operation was recorded, but in the calculations five minutes was allowed for the interval during which the gas had been traversing the mixing bulb.

In the later runs the procedure from the time of sealing off the reaction chamber was to take brief observations of the color in the main tube a (Fig. 1), by comparison with a colorless blank at frequent intervals. As the excess ozone was being converted to oxygen by the simultaneous reactions

$$N_2O_5 = N_2O_4 + \tfrac{1}{2}O_2 \qquad \text{and} \qquad N_2O_4 + O_3 = N_2O_5 + O_2$$

the blue color gradually faded out. The first appearance of yellow therefore marked the exhaustion of the ozone and the beginning of the unretarded decomposition of the pentoxide. Since a pressure of NO_2 as low as 0.01 mm. could be detected easily, an effort was made to get a precise observation of the time at this point of "zero" concentration. Next the "one-phase standard" tube No. 1 was brought into position and rapid observations were taken at intervals of increasing frequency until the intensity of its color was matched by that of the reaction mixture. After the intensity had exceeded that of standard No. 1, the latter was replaced by No. 2 and similar observations were taken until this was matched, and so on until all, or as many as desired, of the standards had been matched and the times noted. Due to the limited sensitivity of the eye, there was usually a period of from one to ten or more minutes - depending mainly on the rate at which NO_2 was being formed - during which no difference could be distinguished between the intensities of the two fields. The middle point of such a period was selected as the "time" of equal intensity, and was probably correct to within a fifth of the length of the period, corresponding usually to about 5% of the interval between the match of one standard and that of the next highest. In many of the runs a later point on the time-pressure curve was obtaining by matching against the "two-phase" tube. Finally the temperature of the reaction mixture was raised to about 40°, where the decomposition is 99% completed in five hours, and upon cooling again the NO_2 was analyzed by matching one or the other of the reaction tubes <u>a</u> or <u>b</u> against the two-phase standard. This and the other analyses will be the special subject of a later section.

Preparation of Materials.

The source of the N_2O_5 had no noticeable effect on the results. In the earlier runs fuming nitric acid was dehydrated by forming a paste with phosphorus pentoxide, from which the gases were distilled off in a current of ozone and dried over powdered phosphorus pentoxide in a long tube. Pure white crystals of N_2O_5 were condensed in a U-tube at about -50° and these were later vaporized and swept with an excess of ozone into the mixing bulb, whence the mixture was later transferred to the previously evacuated reaction chamber by means of a glass connection like the illustration in Fig. 3. This was opened by a smart tap from beneath, which knocked the glass bead against the thin, file scratched tip, and was closed by fusing the constriction. The same device was used in place of a stopcock in other operations as well.

In all the later runs, as described above, the source of the NO_2 and N_2O_4 was the liquid, a supply of which was prepared by the destructive distillation of lead nitrate crystals (Kahlbaum), water vapor being carefully removed by passing through three tubes of phosphorus pentoxide before condensing in the jacketed container shown in Fig. 2. When not in use the container was sealed by fusing the constricted opening at the top, and to open it the tip was melted in a torch flame while the pressure inside was slightly above atmospheric. Connection was made to the train by inserting into the beveled tube, which had been ground to fit snugly over the neck of the container.

The ozone was formed from commercial oxygen (Linde), containing no impurities recognized as affecting the decomposition of N_2O_5, with the possible exception of water vapor, for which drying tubes were provided. That the ozone was reasonably stable was proven by tests of the slow rate at which it decomposed spontaneously at room temperature. The concentrations in various runs ranged from 2.5% to 5.2% by volume.

Analyses and Computations.

The methods of analysis of the NO_2 were based on Beer's Law that equal amounts of light are absorbed by passage through equal quantities of a substance independently of the concentration. Although deviations from this law are known to occur in gases,(5) they are not of such a nature as to introduce serious errors in this work.

Analysis of NO_2 in Reaction Tube during Run. - The gradually increasing partial pressure of NO_2 in the reaction tube was analyzed by matching against the various "one-phase standards." The pressure of NO_2 first introduced into this standard system was 11.88 mm. Hg at 22.0°, so that the shortest tube, No. 1, absorbed the same amount of light as would be absorbed by 0.495 mm. NO_2 pressure in the long reaction tube at the same temperature, the ratio of the lengths being 37:888. Similarly the pressure equivalent of No. 2 was 0.990 mm. and so on. After Run No. 7 the standard was evacuated and refilled with a smaller quantity (6.45 mm. at 21.2°) of gas, so that the lowest pressure measurable was reduced to 0.269 mm. at the same

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(5) R. W. Wood, "Physical Optics", Second Ed., p. 444; Macmillan 1921.

temperature. The temperature of the "one-phase standard" was always that of the room while that of the reaction tube usually differed from it, hence corrections were calculated and applied for the effects of variation in temperature both on the pressure-volume product and on the equilibrium between NO_2 and N_2O_4.

Calibration of the One-phase Standard.- The two-phase tube constituted the ultimate standard, and the calibration of the one-phase standard is here illustrated by reproducing an actual example.

Observations

Date: May 8, 1924.

Tube No. 7 (length 259 mm.) matched two-phase tube (length 28.5 mm.)

Temperature of liquid in two-phase tube: -16°

" " vapor " " " " : +20.7°

Temperature of one-phase system: 21.2°

Derived Data

Total pressure in two-phase tube; $p_{NO_2} + p_{N_2O_4} = 108$ mm.(6)

Partial pressure of N_2O_4; $p_{N_2O_4} = 0.01448\, p^2_{NO_2}$ (7)

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(6) 108 mm. is the vapor pressure at -16°, obtained by interpolation from the data given in Tables Ann. Int., 2, 113 (1911).

(7) 0.01448 is the value of K_p at 20.7° obtained from Schreber's equation; $\log K = \log \frac{p_{N_2O_4}}{p^2_{NO_2}} = \frac{2866}{T} - \log T - 9.1324$ (Z. physik. Chem., 24, 651, 1897).

Computations

From the above equations,

Partial pressure of NO_2 in two-phase tube;

$$p_{NO_2} = \frac{-1 + \sqrt{1 + (4 \times 0.01448 \times 108)}}{2 \times 0.01448}$$

$$= 58.5 \text{ mm.}$$

Pressure NO_2 in one-phase system; p'_{NO_2}

$$p'_{NO_2} = \frac{58.5 \times 28.5 \times (273 + 21.2)}{259 \times (273 + 20.7)}$$

$$= 6.45 \text{ mm.}$$

Determination of Final Pressure in Reaction Tube.- **The analysis of the final pressure of NO_2 after the completion of a run was usually obtained in a similar manner by matching the color in the reaction tube against the two-phase standard. For the higher pressures, the shorter tube b was matched against this standard. It was sometimes found convenient to make use of the one-phase standard also in these analyses.**

Accuracy of the Analyses.- It is somewhat difficult to make an exact estimate of the accuracy of the various analyses.

In the case of the comparison between the reaction tube and the various one-phase standard tubes during the run, it was found that the apparent match persisted throughout a period in which the partial pressure of NO_2 must have changed by about 8%. Since the time of the match was taken as the middle of this period, it is believed that "observational" error in these concentrations was less than 2%.

In the use of the two-phase standard, the comparison was made by adjusting the temperature of the liquid or of the vapor in the two-phase tube until a match was secured. It was generally found that a change of about 1° in either temperature was sufficient to destroy the match. Calculation showed that an error of 1° in either of these temperatures would correspond to an error of about 3% in the result. Since the temperatures were probably known to considerably better than this, it is thought that the "observational" error in the concentrations thus measured was certainly less than 5%.

In addition to the above "observational" errors, "systematic" errors were also undoubtedly present, owing to deviations from Beer's Law, and to incorrectness in the figures taken for the degree of association of the NO_2 and for the vapor pressure of the NO_2 in the two-phase standard.

Effect on Computations.- It is evident from the foregoing that the relative values of the partial pressure of NO_2 obtained in the early stages of the run are fairly accurate, while the absolute values of these pressures and the values of the final pressure are more uncertain. Fortunately a greater degree of accuracy in these latter figures was not necessary for the main purpose of the experiment, which was to compare the rates in successive stages of the early part of the reaction, as represented by the familiar equation

$$\frac{1}{t_2 - t_1} \ln\frac{P_1}{P_2} = k$$

where P_1 and P_2 are pressures of the disappearing constituent N_2O_5

at times t_1 and t_2 respectively, and k is constant for a given temperature. If substitutions in this equation gave a constant value of k for every stage of the reaction, its unimolecular character would be substantiated. In this reaction we obviously may set

$$\frac{p_1}{p_2} = \frac{2\,p_\infty - 2\,p_1}{2\,p_\infty - 2\,p_2} = \frac{p_\infty - p_1}{p_\infty - p_2}$$

where p_1, p_2 and p_∞ are pressures of the appearing product NO_2, provided we take into account the equilibrium $2\,NO_2 \rightleftharpoons N_2O_4$ and include the N_2O_4 as equivalent NO_2 in the p terms. Thus, if the pressure of NO_2 were 0.552 mm., as indicated by matching against the one-phase standard No. 2, the corresponding value of p in a 20° run would be (taking 0.01523 as the value of K_p at 20°, cf. Note 7);

$$p = p_{NO_2} + 2p_{N_2O_4} = p_{NO_2} + 2\,(0.01523\ p^2_{NO_2}) = 0.561 \text{ mm.}$$

It will be observed that, for values of the final pressure relatively large in comparison with the pressures in early stages, a moderate error in the determination of p_∞ would affect the magnitude of k to a slight extent, but would not appreciably affect its constancy throughout the early stages of the run. The same is true for an error in the calibration of the one-phase standard system, for this would but slightly influence the relative values of p_1, p_2 ...p_7, or of the k's.

Typical Run.- Below are arranged the summarized data and computations for a typical run (No. 9). Time is in minutes from the initial formation of the N_2O_5, and pressure is in mm. Hg under standard conditions.

Run No. 9. Summary.

Date: June 10, 1924. Temperature of reaction: 20.0°

Time.		Standard Matched.		Pressure.		
Period	Point	No.	Temp.	p_{NO_2}(8) + 2 $p_{N_2O_4}$(9)	=	p_t
	230	Blank		0		0
267 - 271	269	1	21.7	$0.269 + 2(0.01523)(0.269)^2$	=	0.271
303 - 309	306	2	21.3	$0.537 + 2(0.01523)(0.537)^2$	=	0.545
349 - 357	353	3	21.5	$0.807 + 2(0.01523)(0.807)^2$	=	0.827
389 - 399	394	4	21.5	$1.075 + 2(0.01523)(1.075)^2$	=	1.111
428 - 440	434	5	21.3	$1.339 + 2(0.01523)(1.339)^2$	=	1.395
End of run	∞	Two-phase	l 18.5 v 21.5	$6.019 + 2(0.01523)(6.019)^2$	=	7.122

Unimolecular Tests.

Interval	$\frac{2.303}{t' - t} \log \frac{p_\infty - p_t}{p_\infty - p_{t'}}$	= k
t_0 to t_1	$\frac{2.303}{269 - 230} \log \frac{7.122 - 0}{7.122 - 0.271}$	= 0.00099
t_1 to t_2	$\frac{2.303}{306 - 269} \log \frac{7.122 - 0.271}{7.122 - 0.545}$	= 0.00110
t_2 to t_3	$\frac{2.303}{353 - 306} \log \frac{7.122 - 0.545}{7.122 - 0.827}$	= 0.00093
t_3 to t_4	$\frac{2.303}{394 - 353} \log \frac{7.122 - 0.827}{7.122 - 1.111}$	= 0.00112
t_4 to t_5	$\frac{2.303}{434 - 394} \log \frac{7.122 - 1.111}{7.122 - 1.395}$	= 0.00120
t_1 to t_5	$\frac{2.303}{434 - 269} \log \frac{7.122 - 0.271}{7.122 - 1.395}$	= 0.00109

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(8) These values are the partial pressures of NO_2 at 20° in the reaction tube, as determined by the match.

(9) These values are calculated with the help of Schreber's equation.

Results.

Runs Made at 20°.- Of the fourteen runs at 20°, two were unsuccessful on account of extremely low initial pressures of N_2O_5, requiring uninterrupted observations over a prohibitive length of time. A third run was discarded because NO_2 was found to be present at the start. Run No. 5 was the earliest in which an attempt was made to note the time of the first appearance of NO_2 and to estimate the concentration of ozone. Prior runs differed also in the method of preparing and introducing the N_2O_5, as noted above. The eleven completed runs at 20° are shown diagramatically in Table 1 below. The short horizontal lines indicate values of p_t as plotted on the scale in the column at the extreme left, while the intervening figures represent the value of $k \times 10^5$ calculated for the interval. The runs are arranged in columns in the order of diminishing values of p_∞, which are shown at the bottom together with the mean values of $k \times 10^5$ for the entire interval between the second and the last observations.

The low values of k for the first interval in Runs Nos. 5, 6 and 13 may be accounted for by a reasonable assumption. In addition to the ordinary experimental errors, there could be a distinct type affecting the earliest stage exclusively, namely a lack of homogeneity in the gas mixture; for it is quite conceivable that the ozone and the pentoxide were not uniformly distributed throughout the long narrow tube, and consequently that all of the pentoxide did not begin decomposing freely at the same instant. In the other runs it would appear that the mixing has been more thorough.

Table 1.

p	$k \times 10^5$										
	No. 4	No. 14	No. 13	No. 7	No. 16	No. 5	No. 11	No. 2	No. 9	No. 8	No. 6
0											
		102	70		95		103		99	96	
						75					72
0.5		104	108	94	89		126		110	118	
	100	111	106		101	91	100	109	93	103	105
1.0		107	92		98		91		112	100	
	98	100	108	111		89		97	120		
1.5		117	113		114						113
	107	102	91	99		85					
2.0											
	87			113		91					
2.5											
								98			
3.0	90	101		101	99						
			102								
3.5	117			92							
4.0											
4.5											
	91										
5.0											
5.5											
6.0											
Mean k	99	104	102	102	102	90	105	99	109	105	111
p_∞	110	42	37.7	35	19.7	16.4	9.40	8.50	7.122	5.035	2.652

Varied Runs.- Since in all of these experiments the analytical method required the admission of light at frequent intervals, the reaction was exposed intermittently to photochemical acceleration, though only for a small fraction of the time, probably never exceeding one-tenth. In the majority of the runs the intensity of illumination, after the light has passed through the opal glass, was approximately 570 ergs per second per $cm.^2$ at the aperture, whose area was 2 $cm.^2$, so that any appreciable photochemical action would have been surprising. However, to make certain that the effect was negligible, two runs, Nos. 20 and 21, were carried out at 20° with continuous illumination of the same intensity. The results, shown in Table 2, indicate that the photochemical effect was scarcely appreciable. Table 2 also contains the results of three runs at 25°, one at 35° and one at 40°. An exact observation of "zero" pressure was not taken in Run No. 1, and was missed accidentally in Nos. 12 and 20, as was also the first match in No. 20; but approximations arrived at from neighboring observations indicated no abnormal behavior.

Table 2.

p	$k \times 10^5$						
	20° Continuous illumination		25°			35°	40°
	No.21	No.20	No. 1	No.17	No.18	No.19	No.12
0							
	92			172	244	907	
0.5	103			192	208	866	1540
	101	95	244	187	211	696	1360
1.0	94	86		226	226	741	1340
	122	114	243	235		888	1860
1.5	105	120		235			1530
2.0	114	128	238	191	228	940	
2.5			235				
3.0	106		224	197		836	
3.5			219				
4.0							
4.5							
Mean k	106	108	233	202	222	837	1480
p_∞	11.78	8.548	58.1	35.5	4.965	5.895	4.950

Retardation by Ozone.- The phenomenon previously mentioned as having been observed by Daniels, Wulf and Karrer,(3) namely the delayed reappearance of NO_2 after the elapse of time calculated for the disintegration of the ozone, was not encountered in the fifteen experiments of the present work in which the ozone concentration was analyzed, with the possible exception of one doubtful case (Run No. 13). In every other instance the calculated time exceeded the observed time several fold, as shown by the results in Table 3. The value C_{O_3} in the third column is the molal fraction of ozone before mixing with N_2O_4, as obtained from the analysis of the oxygen-ozone mixture by the method previously described. The fourth column gives the pressure of N_2O_5 in the reaction chamber, namely one-half the value of p_∞ determined after the run. In the fifth column p_{O_3} is the excess pressure of ozone immediately after mixing, and is derived from the corresponding values of C_{O_3} and $p_{N_2O_5}$ by means of the relationship

$$p_{O_3} = C_{O_3}(P - p_{N_2O_5}) - p_{N_2O_5}$$

where P is the total, i.e. approximately barometric, pressure at the moment of mixing. This is equivalent to stating that the resultant pressure of ozone is its pressure on dilution, diminished by one equivalent of ozone for each equivalent of pentoxide formed, and hence assumes that the reaction is that found by Wulf, Daniels and Karrer,

$$N_2O_4 + O_3 = N_2O_5 + O_2.$$

The same assumption is also the basis on which were computed the values in column six, using the average observed rate k_T, as follows:

$$t \text{ (calc)} = \frac{p_{O_3}}{k_T' p_{N_2O_5}} \text{ minutes.}$$

Table 3.

Run No.	Temp.	C_{O_3}	$p_{N_2O_5}$	p_{O_3}	t (calc.)	t (obs.)
5	20	0.039	8.2	20.2	2,370	105
6	20	0.028	1.33	19.3	14,100	399
7	20	0.038	17.5	9.6	532	14
8	20	0.025	2.52	15.9	6,130	300
9	20	0.038	3.56	24.2	6,610	235
11	20	0.037	4.70	22.5	4,650	186
13	20	0.025	18.8	0*	0	33
14	20	0.052	21.0	16.4	759	60
15	20	0.050	1.04	36.6	34,200	510
16	20	0.048	9.85	24.8	2,440	125
17	25	0.050	17.8	18.6	502	50
18	25	0.047	2.48	32.4	6,000	215
19	35	0.030	2.95	19.2	794	75
20	20	0.040	4.27	23.6	5,360	200
21	20	0.040	5.89	23.9	3,940	183

* The actual calculation gives a negative value (see text).

Discussion of Results.

If the initial rate of the decomposition were other than unimolecular, we should expect that the equation

$$\frac{1}{t' - t} \ln \frac{p_\infty - p}{p_\infty - p'} = k$$

would give values of k differing in the initial stages from those in the later stages. In case the reaction had proved to be autocatalytic at the start and of the first order later on, as originally suspected, the velocity would have presumably increased for a while as a function of the increasing concentration of the catalytic product, until a "critical concentration" of the catalyst has been established, after which it would have no longer been dependent on this variable. In such a case the value of k calculated in the unimolecular equation above would be low for the early stages of the decomposition, especially for the first interval examined, and would eventually reach a constant value coinciding with that found in the previous investigations of Daniels and Johnston.(1)

In every experiment of the present research, the value of k proved to be reasonably constant throughout, though in a few instances there were moderate deviations for which a plausible explanation was advanced above. Hence the results supply no confirmation of the hypothesis that this reaction is autocatalytic.

It is of some interest to note that in experiments with low initial pressures of N_2O_5, the rate of formation of NO_2 would be somewhat retarded at first, if the mechanism of the decomposition were that proposed by Bodenstein, namely

$$N_2O_5 \longrightarrow N_2O_3 + O_2 \qquad (I)$$

$$N_2O_3 \longrightarrow NO + NO_2 \qquad (II)$$

$$2\ NO + O_2 \longrightarrow 2\ NO_2 \qquad (III)$$

Reaction II is assumed by Bodenstein to be very rapid, while reaction III has been studied separately and found to be of the third order, the rate being proportional to the concentration of the O_2 and to the square of the concentration of the NO. However, calculations based on the reported rate of reaction III have indicated that, under the conditions of the present experiments, the large excess of O_2 would raise the velocity of this oxidation to a par with the velocity of reaction I in a comparatively short time. As a result the rate of production of NO_2 by the consecutive mechanism of Bodenstein would not differ beyond experimental error of observation from the rate of its production by the direct mechanism assumed in this work.

There is substantial agreement between the values of k in the present results and those found by Daniels and Johnston,(1) as shown by the comparison in the following table. The agreement is more striking when attention is directed to the contrast between the initial pressures in the two sets of experiments, and the fact thus established that the rate is independent of the initial pressure furnishes additional confirmation of the unimolecular character of the reaction.

Table 4.

Temp.	Present Results.		Results of Daniels and Johnston.		
(C.)	Range of initial $p_{N_2O_5}$	k (Obs.)	Range of initial $p_{N_2O_5}$	k (Obs.)	k (Calc.)
20°	1.3 to 55 mm.	0.00103	275 mm.	0.00117	0.00099
25°	2.5 to 29 mm.	0.00219	269 to 290	0.00203	0.00203
35°	2.9	0.00837	56 to 308	0.00808	0.00790
40°	2.5	0.0148	---	---	0.0151

In regard to the rapid disappearance of the excess ozone, which was contrary to expectations in view of the observations of Daniels, Wulf and Karrer,(3) it is felt that no explanation should be attempted before the phenomenon has been subjected to a more rigorous investigation, as it probably depends on conditions whose importance has been underestimated. In Run No. 13, the one instance in which appeared an exception to the general character of the present results, there was reason to suspect that the ozone concentration was greater than the value found by analysis, for the latter would have been insufficient for the comlete oxidation of the N_2O_4; moreover it is noteworthy that the most probable sources of error in the analytical procedure, such as leaks or insufficient heating, would yield low results.

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Summary.

That the thermal decomposition of gaseous nitrogen pentoxide is a unimolecular reaction after the initial stage has been shown by previous investigators.

The rate of the decomposition in the initial stage has been found by the present investigation to be unimolecular.

Evidence of an autocatalytic induction period did not appear at the lowest concentrations of NO_2 measurable.

A colorimetric method of NO_2 analysis has been developed, capable of measuring as low as 0.27 mm. with an accuracy of about 5%.

The rate of the reaction was determined at temperatures from 20° to 40°, showing a good agreement with the results obtained by Daniels and Johnston.

The preliminary procedure consisted in mixing freshly prepared nitrogen pentoxide with oxygen and ozone, the latter serving to re-oxidize the decomposition products until it was exhausted. In contradiction to the results of Daniels, Wulf and Karrer, the measured excess of ozone did not retard the decomposition of the nitrogen pentoxide for an unduly long period of time. The explanation of the difference in the behavior found in the two sets of experiments is an important problem for further investigation.