

planation for the anomalous behavior of this substance as an inhibitor to the oxidation of sulfite solutions.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 191]

MECHANISM OF THE PHOTOCHEMICAL DECOMPOSITION OF NITROGEN PENTOXIDE

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Introduction

The photochemical decomposition of nitrogen pentoxide into nitrogen dioxide and oxygen was first studied by Daniels and Johnston.¹ Their method of experimentation was to illuminate, with sunlight or light from a tungsten lamp, a glass bulb containing nitrogen pentoxide crystals immersed in ice water and measure the pressure increase attending the illumination. By the use of light filters these authors were able to demonstrate that only light of wave length shorter than 4600 Å. was effective in producing decomposition. They also established the important result that, at least with radiations in the neighborhood of the violet part of the spectrum, the presence of nitrogen dioxide is necessary for the reaction, that is, this decomposition of colorless nitrogen pentoxide is photosensitized by the brown dioxide.

Two important suggestions have been made as to the mechanism of this reaction. Fazel and Karrer² have advanced the hypothesis that a light quantum is absorbed by a nitrogen dioxide molecule, which is thereby raised to a higher quantum state, and that this excited molecule, NO_2' , then makes a collision of the second kind with a pentoxide molecule, transferring energy of activation to the pentoxide molecule. The activated nitrogen pentoxide molecules subsequently decompose. Norrish,³ on the other hand, has shown that nitrogen dioxide is decomposed by light from a mercury arc into nitric oxide and oxygen. He has accordingly suggested that in the sensitized decomposition of the pentoxide, the first reaction is the decomposition of the dioxide, and that this is then followed by a dark reaction between nitric oxide and nitrogen pentoxide, $NO + N_2O_5 = 3NO_2$. For this mechanism to play an important part in the pentoxide decomposition, it is necessary that the thermal reaction between nitric oxide and nitrogen pentoxide have a rate at least comparable with the rate of recombination of nitric oxide and oxygen. Busse

¹ Daniels and Johnston, *THIS JOURNAL*, **43**, 72 (1921).

² Fazel and Karrer, *ibid.*, **48**, 2837 (1926).

³ Norrish, *J. Chem. Soc.*, 761 (1927).

and Daniels,⁴ by mixing nitric oxide and nitrogen pentoxide and observing the immediate appearance of the brown dioxide, have shown that this reaction is indeed very rapid.

It is to be noticed that if photochemical equivalence obtained, the decomposition of two molecules of nitrogen pentoxide per quantum absorbed could result no matter whether the initially activated NO_2 molecule transferred its activation to an N_2O_5 molecule, or whether it reacted with another NO_2 molecule. For in the first case we might have $\text{NO}_2' + \text{N}_2\text{O}_5 = \text{N}_2\text{O}_5' + \text{NO}_2$, followed by $\text{N}_2\text{O}_5' + \text{N}_2\text{O}_5 = 4\text{NO}_2 + \text{O}_2$ or by $\text{N}_2\text{O}_5' = \text{NO} + \text{NO}_2 + \text{O}_2$ and $\text{NO} + \text{N}_2\text{O}_5 = 3\text{NO}_2$; while in the second case we might have $\text{NO}_2' + \text{NO}_2 = 2\text{NO} + \text{O}_2$ followed by $2(\text{NO} + \text{N}_2\text{O}_5 = 3\text{NO}_2)$. However, the authors have shown⁵ that in the decomposition of the dioxide, various wave lengths are quite unequally effective; thus the yields expressed in molecules of oxygen produced per quantum absorbed were 0.0046, 0.36, and 0.77 for the wave lengths 4350, 4050 and 3660 Å., respectively. Since the decomposition of the dioxide depends so markedly on the wave length of the light used, measurement of the pentoxide decomposition with monochromatic light might distinguish between these two mechanisms. Should, for example, the radiation 4350 Å. prove to be effective in the pentoxide decomposition, this could hardly be explained by the Norrish mechanism because of the ineffectiveness of this radiation in decomposing the dioxide.

In the present paper are described measurements of the relative rates of nitrogen pentoxide decomposition produced by these three radiations and measurements of the relative rates of pentoxide and dioxide decomposition.

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Experimental Arrangement

The present work was carried out at 0° with the reactants and products present only in the gas phase. The apparatus is shown in Fig. 1. The reaction vessel, A, made of Pyrex glass, was oblong shaped with flat sides 2.2 cm. wide and 6.5 cm. high. Three of these sides were silvered, while the front surface was unsilvered and served as a window for the entrance of light. The clicker-type glass-diaphragm gage, B, described by Smith and Taylor⁶ was used to measure the pressure after the reaction chamber was sealed off at C and C'. Pressure readings were reproducible to 0.2 mm. or better. A Moll thermopile, mounted in a water-tight brass container with a glass window and a shutter, was rigidly fastened immediately beside the reaction vessel, as indicated at D. This was used to make relative measurements of light intensity during the illumination.

The thermostat, K, was a flat-sided glass jar. On the front of the thermostat was

⁴ Busse and Daniels, *THIS JOURNAL*, 49, 1257 (1927).

⁵ Dickinson and Baxter, *ibid.*, 50, 774 (1928).

⁶ Smith and Taylor, *ibid.*, 46, 1393 (1924).

fastened a flat copper sulfate absorption cell 1.2 cm. in thickness in such a way as to have a pocket 2.2 cm. in thickness between the cell and the front of the thermostat. A light filter mounted on a brass sheet with an opening 4.5 cm. square was placed in this pocket; the space was then filled with water to minimize light reflection losses. These filters were for the isolation of the mercury radiations at 4350, 4050 and 3660 Å. and were the same as used previously.⁷ A mercury arc lamp together with a reflector was placed immediately outside the copper sulfate cell and directly in front of the reaction vessel; the distance from the lamp to the reaction chamber was 6 cm. A shutter was provided between the lamp and the copper sulfate cell.

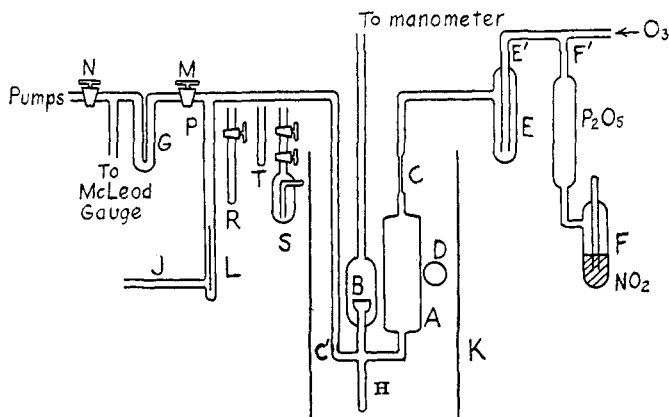


Fig. 1.

Temperature control was maintained by keeping the thermostat well packed with ice. A fine jet of air blown into a glass tube 1 cm. in diameter pumped water continuously from the bottom of the thermostat to near the top. A thermocouple with one junction near the bottom of the reaction chamber and the other in a Dewar tube filled with ice and water showed that the temperature was maintained constant to 0.1° or better.

The Experimental Procedure

Nitrogen pentoxide was prepared by oxidizing nitrogen dioxide in a stream of ozone and collecting the pentoxide in the trap, E, surrounded by ice and hydrochloric acid. The nitrogen dioxide had been previously prepared by heating *c. p.* lead nitrate in an all-glass apparatus, passing the gas evolved over phosphorus pentoxide and condensing it in the trap, F, using ice and salt. The ozone was prepared by passing tank oxygen over phosphorus pentoxide and then through a Siemen's ozonizer. During the pentoxide preparation the cock, M, was closed and the excess gases passed out through J.

When sufficient nitrogen pentoxide had been collected in E, the supply of nitrogen dioxide was sealed off at F' and the stream of ozone continued for a short time. The ozonizer was now turned off and, after sweeping out the ozone with oxygen, the apparatus was sealed at E'. A bulb of nitrogen dioxide was now placed in the tube, J, which was then sealed off. Liquid air was applied at E and G, the stopcock M opened and the whole system evacuated. The click gage was protected from breakage by evacuating both sides simultaneously. When the system was well evacuated, the bulb of nitrogen dioxide was broken by the magnetically operated plunger, L, the nitrogen dioxide im-

⁷ Dickinson and Baxter, ref. 5, p. 778.

mediately freezing out in the trap, E. After a final evacuation, the apparatus was sealed off at C'. Then ice-baths were placed around the reaction vessel and around E. After the pressure had risen sufficiently, the tube, C, was sealed off. In order to determine the original pressure of oxygen produced by decomposition on sealing off, liquid air was applied at the side-tube, H, and the pressure read. In no case was this pressure as large as 0.5 mm. The liquid air was now removed, the thermostat put in place, packed with ice and the initial pressure read.

The mercury arc was started and run for a time to become steady, pressure readings being taken at intervals. The shutter was now opened with pressure readings still being made during illumination. During this time measurements were made on the light intensity by reading the galvanometer connected with the thermopile when the shutter on the thermopile was opened and closed at intervals of one minute. The illumination was now discontinued but pressure readings were still made. The times of opening and closing the shutter were accurately noted. Another illumination was now carried out with a different filter interposed. In this way several illuminations could be made during a run with each of the wave lengths used before the supply of nitrogen pentoxide was exhausted.

The illuminations were continued until the nitrogen pentoxide was exhausted. The final total pressure was obtained from readings made several hours after the last illumination. The final pressure of oxygen was obtained by freezing out the nitrogen dioxide in the tube, H, with liquid air, measuring the pressure of uncondensed oxygen at room temperature; this measured pressure was first increased by 2% because of the fact that a definite volume of oxygen was at liquid-air temperature, and was then reduced to 0°.

Experimental Results

Fig. 2 shows the results of a typical series of successive illuminations (Nos. 3a, 3b and 3c) made with light of the wave lengths 3660, 4350 and

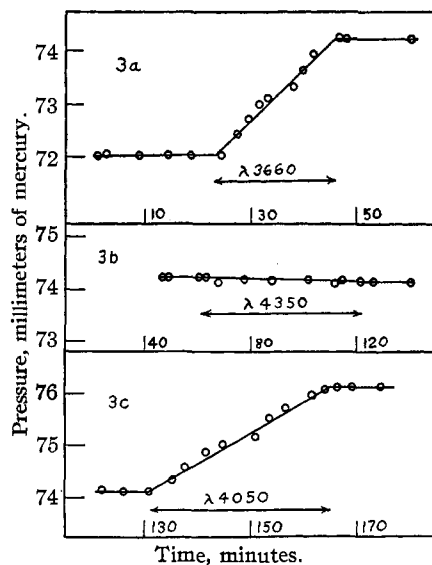


Fig. 2.

4050 Å., respectively. The ordinates are total pressure in mm. and the abscissas time in minutes; the periods during which illumination occurred are indicated on the plots. In these particular experiments the partial pressure of NO_2 was about 12 mm. and that of N_2O_5 about four times as great. The absorption, estimated from previous measurements,⁸ was probably greater than 60% in each case. The radiations 3660 and 4050 produced continuous pressure increases which ceased when the radiations were shut off. The radiation 4350 produced no detectable pressure increase although its intensity was more than three times that of the other radiations.

⁸ Dickinson and Baxter, ref. 5, p. 780.

The results of these and other similar experiments are given in the first nine columns of Table I. In Cols. 3-6 are given the mean partial pressures of the gases present during each illumination; their calculation involved, in addition to the pressure measurements described above, the

TABLE I
EXPERIMENTAL RESULTS WITH N₂O₅ + NO₂ AND WITH NO₂

No.	Wave length, Å.	p_{NO_2} , mm.	$p_{\text{N}_2\text{O}_5}$, mm.	$p_{\text{N}_2\text{O}_4}$, mm.	p_{O_2} , mm.	Intensity, cm. of scale defl.	Exposure, min.	Δp_{total} , mm.	$-\frac{\Delta p_{\text{N}_2\text{O}_5}}{\text{min. per cm. defl.}}$	$\frac{2\Delta p_{\text{O}_2}}{\text{min. per cm. defl.}}$
4a	3660	4.1	42.0	1.5	0.7	6.44	20.8	2.8	0.24	0.25
4c		8.2	35.8	5.7	3.9	4.50	26.8	3.6	.39	.38
4d		11.2	29.4	10.7	7.2	4.54	43.7	5.5	.39	.42
3a		11.6	48.6	11.5	1.1	4.16	22.8	2.2	.33	.43
3d		14.4	41.0	17.7	5.0	3.60	33.2	3.2	.40	.45
2b		16.3	23.4	22.7	0.8	3.39	20.0	2.1	.48	.46
4f		16.4	14.6	23.0	14.5	10.29	21.5	5.8	.40	.46
3g		17.2	32.2	25.2	9.4	6.07	31.5	4.7	.38	.46
2d		18.2	16.7	28.3	4.3	2.70	34.0	2.8	.48	.47
4g		18.7	6.0	29.9	19.0	8.84	^a	.	.42	.47
3h		19.4	24.2	32.1	13.3	6.00	39.4	5.3	.36	.47
2g		20.7	7.3	36.6	8.8	4.88	30.2	3.4	.37	.47
2h		21.7	3.0	40.2	12.2	4.06	^a	.	.46	.47
3j		23.2	8.4	45.9	21.2	5.95	39.4	5.3	.37	.48
3k		24.3	3.5	50.4	23.7	5.80	^a	.	.41	.48
4b	4050	6.1	39.2	3.2	2.2	5.70	35.7	2.2	.13	.17
3c		12.7	45.9	13.8	2.6	4.65	33.7	2.0	.19	.22
4e		13.9	22.5	16.5	10.5	7.28	40.6	4.0	.20	.23
3e		15.6	37.2	20.8	6.9	4.04	44.7	2.2	.19	.23
2c		17.2	20.2	25.2	2.4	3.95	21.8	1.6	.29	.24
2e		19.4	12.6	32.1	6.3	6.43	30.0	2.7	.22	.25
3i		21.3	16.5	38.8	17.3	6.00	55.7	4.5	.21	.25
3b	4350	12.2	47.3	12.7	1.9	15.9	60.0	-0.1
2a		15.8	25.0	21.3	0.0	13.5	10.0	+	.2	...
3f		16.1	35.6	22.2	7.7	13.8	60.1	-	.1	...
2f		20.0	10.0	34.2	7.5	18.4	30.2	.0

^a These illuminations were continued until the decomposition of nitrogen pentoxide was complete. The rates given in the tenth column were obtained from the slopes of the curves plotted as in Fig. 2 for the interval in which nitrogen pentoxide was known to be present.

constant⁹ for the equilibrium between NO₂ and N₂O₄ at 0°. The amount of nitrogen pentoxide decomposed is not proportional to the observed pressure increase, Δp_{total} , in different parts of a run. Instead, it may be shown that when the total pressure changes as a result of pentoxide decomposition

$$\frac{d p_{\text{N}_2\text{O}_5}}{d p_{\text{total}}} = -\frac{2K + 8p_{\text{NO}_2}}{3K + 4p_{\text{NO}_2}}$$

where $K = p_{\text{NO}_2}^2/p_{\text{N}_2\text{O}_4}$ and has the value 11.7 at 0° when pressures are expressed in mm. of mercury. The change in the partial pressure of N₂O₅ during an illumination was then calculated from the expression

⁹ Schreber, *Z. physik. Chem.*, **24**, 651 (1897).

$$\Delta p_{\text{N}_2\text{O}_5} = -\Delta p_{\text{total}} \frac{2K + 8p_{\text{NO}_2}}{3K + 4p_{\text{NO}_2}}$$

using the mean partial pressure of NO_2 ; p_{NO_2} ordinarily underwent only a small change during an illumination. In the tenth column are given the changes in $p_{\text{N}_2\text{O}_5}$ per ten minutes per cm. of galvanometer scale deflection. It will be noted that at all values of p_{NO_2} , including the larger ones at which absorption was presumably fairly complete, the radiation 3660 Å. is considerably more effective than the radiation 4050 Å. This fact, as well as the ineffectiveness of the radiation 4350 Å., is entirely accountable if the mechanism is the decomposition of NO_2 into NO and O_2 followed by a dark reaction between NO and N_2O_5 ; for these N_2O_5 rates closely parallel the quantum yields in the NO_2 decomposition. In order to determine whether the N_2O_5 rates have the proper absolute magnitude to be accounted for in this manner, as well as to eliminate, so far as possible, uncertainties arising from incomplete absorption and from the fact that the previous NO_2 work had been done at room temperature rather than at 0° , we have undertaken measurements of the rate of NO_2 decomposition in the same reaction vessel.

For this purpose the apparatus was sealed at C and P (Fig. 1) and a reservoir, S, containing nitrogen dioxide, was sealed on at the point indicated, as were also a trap, T, and a receptacle, R, which served as a sink for nitrogen dioxide after it had been illuminated once. Liquid air was maintained at a constant level around the trap, G, and the thermostat kept packed with ice. The nitrogen dioxide in S was kept frozen out with liquid air, out of contact with stopcock grease, except at the time of its introduction into the reaction vessel.

The method followed was to evacuate the whole system, close stopcock M, remove the liquid air from the reservoir, S, thus introducing some nitrogen dioxide into the apparatus, freeze this out in T, evacuate well, then remove the liquid air from around T with the stopcock M closed. The pressure of nitrogen dioxide and tetroxide was now measured and a measured illumination of from two to four minutes made with $\lambda 4050$ or 3660. Immediately after illumination, liquid air was applied at T, the stopcock, M, opened and the pressure of oxygen read on the McLeod gage. It has been shown in the previous research that nitric oxide is frozen out along with nitrogen dioxide. The amount of decomposition was kept low enough so that the recombination of NO and O_2 could be neglected. A blank run, in which the illumination was omitted, showed the development of non-condensable gas while the NO_2 was in contact with the stopcocks to be entirely negligible.

The volume of the apparatus between the points C and C' was found by filling with water to be 37.8 cc. In order to be able to calculate the pressure the oxygen formed would exert if it were all in this volume at

0°, air was trapped in the McLeod gage of known volume and its pressure read. In the meantime the rest of the apparatus, with liquid air and ice in place as in the oxygen measurements, was well evacuated. Then with the cock, N, closed the air was released from the McLeod gage and the pressure again read.

The rates of production of oxygen in the NO_2 experiments, expressed as millimeters per ten minutes per centimeter of scale deflection and reduced to the volume and temperature of the reaction vessel, were plotted against p_{NO_2} , and a representative curve was drawn. From this curve were read the rates of oxygen production corresponding to the particular values of p_{NO_2} occurring in the N_2O_5 experiments. Twice these rates are given in the last column of Table I. The multiplication by two is made in order to permit direct comparison of the last two columns.

Discussion of Results

The last two columns of the table, which summarize the results for the wave length 3660 and 4050 Å., may be considered to agree within the experimental error. It may be noted that in Expts. 4a and 4b the ratios of $p_{N_2O_5}$ to p_{NO_2} were about 10 and 6.5, respectively. The agreement of the rate of N_2O_5 decomposition with twice the rate of O_2 production in the absence of N_2O_5 but at the same NO_2 pressure is to be expected if the N_2O_5 does not interfere with the photochemical decomposition of NO_2 ($2NO_2 = 2NO + O_2$), and if the N_2O_5 decomposition is simply a dark reaction with NO ($N_2O_5 + NO = 3NO_2$). In other words, the comparative rates in the two sets of experiments are in agreement with the N_2O_5 mechanism proposed by Norrish. The fact that the effect of $\lambda 4350$ is too small to detect with the arrangement we have used is likewise in agreement with this mechanism if consideration be taken of the low quantum yield of this radiation in decomposing NO_2 .

The possibility that the N_2O_5 decomposition results from collisions of the second kind between activated NO_2 molecules and N_2O_5 molecules is not completely ruled out. But this mechanism would, in view of the present results, require very special assumptions concerning the efficiencies of these collisions as compared with the efficiencies of the collisions involved in NO_2 decomposition. However, since the efficiencies of collisions of the second kind are ordinarily highly specific with respect to the colliding molecules,¹⁰ such assumptions could only fortuitously be in agreement with present views. The possibility that such collisions might account for a small part of the decomposition would appear to be difficult to eliminate. However, certainly the major part of the N_2O_5 decomposition which we have observed is predicted satisfactorily by the Norrish mechanism.

¹⁰ Frank and Jordan, "Anregung von Quantensprüngen durch Stösse," Julius Springer, Berlin, 1926, p. 225.

Summary

The photochemical decomposition of gaseous nitrogen pentoxide in the presence of nitrogen dioxide has been investigated with approximately monochromatic radiations of the wave lengths 4350, 4050 and 3660 Å. From a comparison of the rates of photochemical decomposition of nitrogen pentoxide and nitrogen dioxide, it is concluded that the mechanism of this sensitized photochemical decomposition is essentially that suggested by Norrish, namely, the formation of nitric oxide and oxygen from the photo-decomposition of nitrogen dioxide, followed by dark reaction between nitric oxide and nitrogen pentoxide.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE COLLEGE OF THE CITY OF DETROIT]

VAPOR PRESSURES OF RELATED COMPOUNDS. THE APPLICATION OF DÜHRING'S RULE

BY A. R. CARR AND D. W. MURPHY

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Several methods have been proposed to show the relation between the vapor-pressure data for various substances. The approximate Clausius-Clapeyron equation states that the slope of the vapor-pressure curve of any substance is proportional to its molal entropy of vaporization. In other words, the slopes of the vapor-pressure curves of non-associated substances at the same pressure should be the same. However, due to deviation from the gas laws and for other reasons, over wide pressure ranges this is not the case. Hildebrand¹ has suggested that this equation would be more nearly correct if the comparisons between various liquids were made at equal vapor concentrations rather than at equal pressures. Wilson and Bahlke² found that this method is applicable to the paraffin hydrocarbons.

Another common method, also based on the Clapeyron equation, is to plot the logarithm of the vapor pressure against the reciprocal of the absolute temperature. Over short ranges of temperature the data for related substances give straight lines which are nearly parallel. However, as the temperature range increases, the straight lines are replaced by curves. Still other methods are empirical, such as those proposed by Ashworth³ and Cox.⁴ Calingaert and Davis⁵ applied the Cox method to several groups of related substances and found that the lines representing

¹ Hildebrand, *THIS JOURNAL*, **37**, 970 (1915).

² Wilson and Bahlke, *Ind. Eng. Chem.*, **16**, 115 (1924).

³ Ashworth, *J. Inst. Petroleum Tech.*, **10**, 787 (1924).

⁴ Cox, *Ind. Eng. Chem.*, **15**, 592 (1923).

⁵ Calingaert and Davis, *ibid.*, **17**, 1287 (1925).