through the medium of a constant volume gas thermometer. The usual experimental corrections, appropriate to careful work in gas thermometry, are applied.

Data of state were determined, for pure NO, between 122 and 308°K. and, for pure N_2O between 197 and 298°K., and the second virial coefficients were computed, for each gas, over the experimental range of the observations. These are well represented by power series in $(1/T)$ (equations 5 and 6, respectively). The accuracy of the data is, normally, about two units in the second virial coefficient.

The values of the virial coefficients are shown graphically as functions of temperature, where comparison is also made with the virial coefficient calculated from Berthelot's equation. For both NO and N_2O Berthelot's equation reproduces molar volumes with a fair degree of accuracy but fails to reproduce the temperature derivatives of the volume, in NO, at temperatures near the boiling point, where the $(B-T)$ curve changes slope rapidly.

The equation of Eucken and d'Or, which is based on an assumed partial association to N_2O_2 in the gaseous phase, is discussed and it is concluded that evidence for association, if it exists, must be found in some source outside of $P-V-T$ data.

Johnston and Giauque's value for the molal heat of vaporization of nitric oxide, from vapor pressure data, has been recalculated with the aid of the improved equation of state. The recalculation improves the already good agreement with their reliable calorimetric value.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Photolysis of Nitrogen Oxides: N_2O_5, N_2O_4 and NO_2

BY HARRISON H. HOLMES AND FARRINGTON DANIELS

Improvements in photochemical technique and increased importance of the nitrogen oxides in chemical kinetics have made desirable an amplification of the early work on the photolysis of nitrogen pentoxide.[1,2] Although the careful work of Baxter and Dickinson[3] on nitrogen pentoxide and of Norrish,[4] and Dickinson and Baxter[5] on nitrogen dioxide established the nature of some of the reactions, a wider range of observations was needed, particularly at shorter wave lengths. The photolysis of nitrogen tetroxide and of uncatalyzed nitrogen pentoxide had not yet been investigated. A knowledge of the influence of foreign gases and solvents was important, also. For these reasons the present investigation was undertaken.

Under many experimental conditions these three oxides are mixed together, and photolysis is complicated, but in the present investigation the individual behavior of each has been determined by suitably changing the wave length, the temperature and the pressure.

Experimental Procedure

The monochromator and lamp, described previously,[6] provided monochromatic radiation of high intensity and purity, using a slit width of 0.6 mm.

The thermopile, 8 × 40 mm. in area, measured all the light passing through the cell. It was calibrated at 0 and 25° against U. S. Bureau of Standards radiation lamp C-132 with the aid of a 1000-watt secondary standard.[7] Deflections were 3.3% higher at 0° than at 25°. Quantum yields of 0.597 and 0.556 were obtained at 436 $m\mu$ for the photolysis of uranyl oxalate whereas Leighton and Forbes[8] found 0.610, 0.555 and 0.585. In the opinion of the authors all important measurements should be cross-checked under actual working conditions against this standard work of Leighton and Forbes.

The rectangular quartz reaction cell, 4.6 × 1.2 × 2.75 cm., was similar to one described before.[9] Pressure measurements were made in it with a reproducibility of 0.2 mm. using a diaphragm, mercury manometer and cathetometer, while the gases were sealed off in contact only with quartz. The beam of light, rendered parallel by a quartz lens, nearly filled the cell without touching the sides. A block of polished, crystalline quartz mounted by the side of the cell served as a blank in determining the incident energy. The thermostat containing the cell and thermopile was constant within less than 0.05°.

The nitrogen oxides were prepared by standard methods

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

[2] A further unpublished research was carried out in this Laboratory by Waldemar Vanselow.

[3] Baxter and Dickinson, THIS JOURNAL, **51**, 109 (1929).

[4] Norrish, *J. Chem. Soc.*, 761 (1927); 1158, 1604, 1611 (1929).

[5] Dickinson and Baxter, THIS JOURNAL, **50**, 774 (1928).

[6] Heidt and Daniels, *ibid.*, **54**, 2381, 2384 (1932).

[7] Forbes, *J. Phys. Chem.*, **32**, 490 (1925).

[8] Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930).

[9] Damon and Daniels, *ibid.*, **55**, 2363 (1933).

and stored with phosphorus pentoxide. The foreign gases were usually freed from reducing agents by passing through hot 100% nitric acid and stored over concentrated sulfuric acid. The carbon tetrachloride, although highly purified, showed slight absorption at 313 mμ and probably contained a trace of carbon disulfide.

The quartz cell was flamed and evacuated, purified nitrogen pentoxide was sublimed in through stopcocks lubricated with phosphoric acid, and the crystals were then partially evacuated. Sometimes ozone was admitted to oxidize nitrogen dioxide, and after evacuating and admitting more ozone the cell was cooled to −80° and sealed off during further evacuation. The technique for nitrogen dioxide and tetroxide was the same except that ozone was not used. After reaching thermal equilibrium the incident and transmitted light were determined and pressure changes measured for several successive periods of time.

Solid crystals covered the bottom of the cell and ensured that the partial pressure of nitrogen pentoxide was maintained constant (51.5 mm. at 0°). Careful experiments showed that there were no "after effects" following the illumination, the pressure rising only by an amount expected from the thermal decomposition. The energy readings were corrected for (a) the slight non-linearity of the thermopile–galvanometer system, (b) the difference in transmission between the quartz block and the cell, (c) the transmission of the cell and thermopile windows and (d) the light absorbed by the reactants through reflection from quartz–gas interfaces, four of which intervened between the reactants and the thermopile receivers. This last correction varied from 5% of the absorbed light at the beginning of a determination to zero at the end, when the absorption was nearly complete.

The moles of nitrogen pentoxide decomposed were calculated from the pressure increase by the graphical method[10] using Bodenstein's value[11] of 13.53 for the equilibrium constant $p^2_{NO_2}/p_{N_2O_4}$ at 0° (p in mm.). A correction for the thermal decomposition at 0° amounted to 0.14 mm. of nitrogen pentoxide per hour.[12]

Experimental Results

Photolysis of the Mixed Oxides.—Typical data are shown in Table I. The incident radiation at 366 mμ, varying between 89,300 and 91,200 ergs per second, was recorded at frequent intervals. The time of exposure is given in the first column, and the transmitted light in the second. The actual energy absorbed in ergs per second at these times is shown in the third column, all corrections having been applied. The pressure of the decomposition products nitrogen dioxide, nitrogen tetroxide and oxygen, over and above the 51.5-mm. constant pressure of nitrogen pentoxide is given in the fourth column where P represents total pressure. The corresponding pressure of nitrogen pentoxide which has decomposed (obtained by graphical interpolation) is given in the fifth. In the sixth column $\Phi^{N_2O_5}$ represents the number of molecules of nitrogen pentoxide decomposed between the times given in the first column divided by the corresponding number of quanta absorbed.

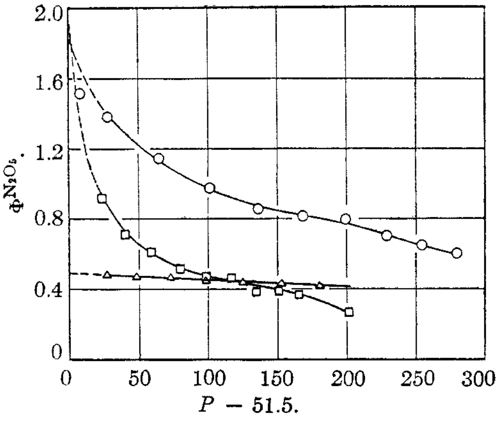

Fig. 1.—Quantum yields $\Phi^{N_2O_5}$ at different pressures of decomposition products: △, 405, ○, 366, □, 313 mμ.

These results are given by circles in Fig. 1 where $\Phi^{N_2O_5}$ is plotted against the pressure of the decomposition products ($P - 51.5$). Similar data for 405 mμ (triangles) and for 313 mμ (squares) are also summarized in Fig. 1.

TABLE I

QUANTUM YIELDS WITH N_2O_5, NO_2 AND N_2O_4

WAVE LENGTH 366 Mμ, TEMP. 0°

Time, min.	$I_{trans.}$ $\times 10^{-3}$ ergs/sec.	$I_{abs.}$ $\times 10^{-3}$ ergs/sec.	$P -$ 51.5, mm.	$P_{N_2O_5}$ dec., mm.	$\Phi^{N_2O_5}$ molecules$_{N_2O_5}$/quanta	Frac. abs. by NO_2
0	75.0	16.1	5.3	2.6	...	..
5	60.5	32.8	11.8	5.9	1.53	0.88
20	25.6	67.5	44.9	25.0	1.39	.75
35	11.3	80.6	83.7	48.4	1.15	.63
50	5.6	85.9	120.2	70.8	0.978	.56
65	3.0	88.6	153.0	91.3	.861	.51
80	1.7	89.6	184.5	111.3	.819	.48
95	1.1	89.9	214.3	129.9	.800	.45
110	0.7	90.4	242.4	147.5	.709	.43
125	.4	90.5	268.2	164.0	.665	.42
140	.3	90.8	292.3	179.3	.612	.41

Radiation at 436 mμ was found to be photochemically inactive at 0° in full agreement with the findings of Baxter and Dickinson[3] and of Norrish[4] but contrary to earlier unpublished data[13] obtained in this Laboratory. In one case

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[10] Daniels and Johnston, THIS JOURNAL, **43**, 53 (1921).

[11] Bodenstein, *Z. physik. Chem.*, **100**, 68 (1922).

[12] Reference 10, page 68.

[13] Reference 2. This investigation was referred to in "Activation et Structure des Molecules," Reunion Internationale de Chimie Physique, Paris, 1928, p. 393.

energy was absorbed at the rate of 146 × 10^{14} quanta per second and $\Phi^{N_2O_5}$ was found to be 0.013 (zero within the limits of experimental error), and in another case with weak radiation (1.28 × 10^{14} quanta per second) $\Phi^{N_2O_5}$ was 0.00. It is interesting to note that the intensity was varied over 100-fold and that the light had no effect in accelerating the thermal reaction.

The apparent quantum efficiency $\Phi^{N_2O_5}$ (Fig. 1) decreases with time on account of a screening effect, more and more of the light being absorbed by nitrogen tetroxide under conditions such that nitrogen pentoxide is not decomposed. The value of $\Phi^{N_2O_5}$ follows closely the averaged fraction of the light absorbed by nitrogen dioxide as recorded in the last column of Table I. This calculation is explained in the following section.

Absorption Coefficients.—The application of the Beer–Lambert law to the mixture of the three absorbing gases gives

$$\ln I_0/I = k_{NO_2}p_{NO_2}l_{NO_2} + k_{N_2O_4}p_{N_2O_4}l_{N_2O_4} + k_{N_2O_5}p_{N_2O_5}l_{N_2O_5}$$

The absorption coefficient for nitrogen dioxide (k_{NO_2}) was first evaluated by measuring the absorption of nitrogen dioxide in the absence of nitrogen pentoxide at 45° and at total pressures below 30 mm. Under these conditions the absorption of nitrogen tetroxide is negligible.

The cell was gradually pumped out and transmitted intensities, I, were measured at various pressures. The incident light I_0 was taken as the thermopile reading with the empty cell. The partial pressure of nitrogen dioxide was calculated from the total pressure using the equilibrium constant of Verhoek and Daniels.[14] The pressure thus found was then reduced by application of the simple gas laws to the hypothetical value it would have at 0° in order to have the same concentration units throughout. Eight to twelve values of ln I_0/I were plotted against p_{NO_2} (0°) between 4 and 30 mm. at each wave length, and a straight line was passed through them. The average deviation from the straight line along the ln I_0/I axis was ±0.023. The length of the cell, l, was in all cases 2.75 cm., and the constant k_{NO_2} was calculated from the slope of the line. The cell was next thermostated at 0° and the absorption, at various wave lengths, of NO_2–N_2O_4 mixtures up to a total pressure of 125 mm. was measured. A quantity corresponding to $(\ln I_0/I)_{N_2O_4}$ was obtained by subtracting $k_{NO_2} p_{NO_2}l_{NO_2}$ from ln I_0/I, and this function was then plotted against $p_{N_2O_4}$. Nine to twelve points were thus found for each of the wave lengths 366, 313, 280, 265 mμ; the pressures of N_2O_4 ranged from 2 to 98 mm., and the average deviation from a straight line was ±0.018 unit along the $(\ln I_0/I)_{N_2O_4}$ axis. Then $k_{N_2O_4}$ was calculated from the slopes of these lines. Two assumptions are involved in this procedure, namely, that k_{NO_2} is independent of temperature and of the presence of foreign gases (*e. g.*, N_2O_4). This point of view seemed justified when it was found that at 436 and 405 mμ (where N_2O_4 is transparent) mixtures containing equal amounts of NO_2 showed the same absorption at 0° as at 45°.

In mixtures of the three gases, $k_{N_2O_5}$ at 280 and 265 mμ were found in a similar manner by subtracting from the total values of ln I_0/I, the absorption due to nitrogen dioxide and to nitrogen tetroxide. This value was in agreement with direct measurements on nitrogen pentoxide at 0 and 10° when decomposition products were insignificant.

The various absorption coefficients k are summarized in Table II, where p is the gas pressure reduced to 0° and expressed in mm. of mercury and l is the cell length in cm.

TABLE II

ABSORPTION COEFFICIENTS, $k = 1/pl \ln I_0/I$

Wave length, mμ	k_{NO_2}	$k_{N_2O_4}$	$k_{N_2O_5}$
436	0.0192	0	0
405	.0216	0	0
366	.0187	0.00824	0
334	.013	.015	0
313	.00773	.0119	0
302	.0055	.0085	0
280	.00263	.0174	0.0029
265	.00136	.0243	.0063

The values of k at 334 and 302 mμ are less accurate, for a less reliable technique was used.

The existence of two absorption maxima for nitrogen tetroxide is clearly shown by the data, and their positions are in approximate agreement with the findings of Harris.[15]

Matsui and Noda[16] found that for blue light (4100–4650 Å.) k_{NO_2} = 0.0180 and that for 3660 Å. k_{NO_2} = 0.0182 and $k_{N_2O_4}$ = 0.0077.

The exactness with which Beer's law applies to these data throughout the whole range of pressure, and the fact that the absorption at 405 mμ does not change when nitrogen tetroxide and

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[14] Verhoek and Daniels, THIS JOURNAL, **53**, 1250 (1931).

[15] Harris, *Proc. Nat. Acad. Sci.*, **14**, 690 (1928).

[16] Matsui and Noda, *J. Soc. Chem. Ind. Japan*, **33**, 518 (1930); *Chem. Abs.*, **25**, 1337 (1931).

nitrogen pentoxide are added, can be taken as arguments that there is no appreciable combination between the different oxides to give a light absorbing complex.

Quantum Yield, NO_2.—In a mixture of nitrogen dioxide and nitrogen tetroxide, the fraction of light absorbed by NO_2 is given by the expression $k_{NO_2}p_{NO_2}/(k_{NO_2}p_{NO_2} + k_{N_2O_4}p_{N_2O_4})$.

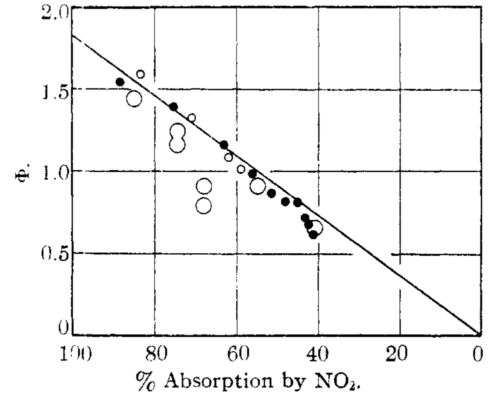

Fig. 2.—Quantum yield at 366 mμ as a function of the light absorbed by nitrogen dioxide. (The large circles represent less accurate measurements in the absence of nitrogen pentoxide.)

The data of the last column of Table I were calculated with this formula, using the average pressure of nitrogen dioxide during a given time interval. The values of $\Phi^{N_2O_5}$ at 366 mμ in the sixth column of Table I are plotted as black circles against these fractions in Fig. 2. The small white circles represent additional points using a cell 9.8 cm. deep instead of 2.75 cm. deep. In Fig. 3 a similar set of data is shown for light of 313 mμ. It is evident from these graphs that there is no photolysis when all the light is absorbed by nitrogen tetroxide; and that the quantum yield is directly proportional to the fractional absorption by nitrogen dioxide. In other words, the intercepts show that $\Phi_{NO_2}^{N_2O_5}$[17] has a constant value equal to 1.83 for 366 mμ and 1.93 for 313 mμ; and that $\Phi_{N_2O_4}^{N_2O_5}$ is equal to zero. The variation of $\Phi^{N_2O_5}$ with pressure is due then to the screening effect of nitrogen tetroxide. At 405 mμ nitrogen tetroxide is transparent; accordingly there is no screening effect and $\Phi^{N_2O_5}$ is nearly independent of pressure (the slight pressure effect will be explained later).

The large circles in Figs. 2 and 3 represent quantum yields for the decomposition of nitrogen dioxide in the absence of nitrogen pentoxide. The results are considerably less accurate than those obtained in the presence of nitrogen pentoxide, but it was desired to obtain an independent check and to show that nitrogen pentoxide is not a complicating factor. Most of these results were obtained by the photochemical equilibrium method of Norrish[18] in which the cell is radiated until a steady pressure is reached. Typical data are given in Table III.

TABLE III

QUANTUM YIELDS Φ^{NO_2} IN THE ABSENCE OF NITROGEN PENTOXIDE AT 313 mμ

Temp., °C.	Initial $NO_2 + N_2O_4$	Pressure NO_2, (mm.)	Pressure increase	Pressure oxygen, (mm.)	Mol. dec. per sec. $\times 10^{-14}$	Quanta absorbed per sec. $\times 10^{-14}$	Φ^{NO_2}
45	32.0	30.2	5.0	4.25	54.8	27.7	1.98
25	73.2	49.9	6.4	3.90	54.7	38.0	1.44
25	69.3	47.8	7.1	4.30	71.5	61.0	1.17
25	232.9	112.3	7.4	4.15	66.0	105.4	0.63
25	152.0	84.4	5.9	3.33	34.1	56.2	.61
0	80.9	26.9	5.1	2.70	28.9	73.7	.39
0	195.5	45.1	5.0	2.58	25.2	84.2	.30

Although the quantum yields obtained in this way are much less accurate, it is evident from Figs. 2 and 3 that they agree with those obtained with the addition of nitrogen pentoxide. As explained before, the data of Tables I and III give a quantum yield approaching 2 when corrected for the screening effect of nitrogen tetroxide, but it is not evident from the published details that such a correction was made in Norrish's work.[18] In the work of Baxter and Dickinson the pressures were

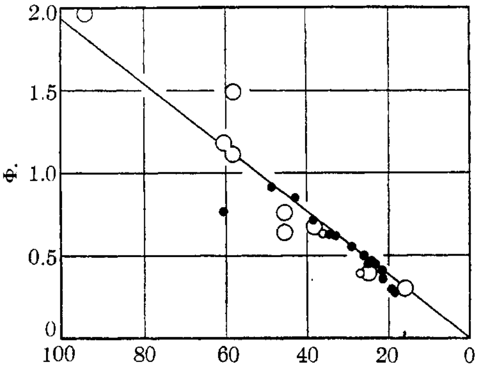

Fig. 3.—Quantum yield at 313 mμ as a function of the light absorbed by nitrogen dioxide. (The large circles represent less accurate measurements in the absence of nitrogen pentoxide.)

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[17] In describing the photolysis of complicated, absorbing systems such as this, it is proposed to designate as superscript that material which decomposes, as measured experimentally; and to designate as subscript that material which absorbs the quanta.

$$\Phi_{NO_2}^{N_2O_5} = \frac{\text{molecules } N_2O_5 \text{ decomposed}}{\text{quanta absorbed by } NO_2}$$

[18] Norrish, *J. Chem. Soc.*, 1165 (1929).

so low that the screening effect of the nitrogen tetroxide would be negligible. In one experiment the bottom of the cell was covered 1 mm. deep with powdered quartz. The fact that no change in quantum yield was obtained shows that the walls had no influence on the reaction. A single determination at 436 mμ gave for Φ^{NO_2} a value of 0.0025.

Quantum Yield, N_2O_5.—Nitrogen pentoxide itself absorbs radiation below 300 mμ.[19] With radiation of 280 and 265 mμ, at the beginning of an experiment when nitrogen dioxide and tetroxide were absent, it was found that 0.6 molecule of nitrogen pentoxide was decomposed for each quantum absorbed by the nitrogen pentoxide. The quantum yield at 280 mμ was calculated also from the mixtures, knowing the partial pressures and absorption coefficients of N_2O_5, N_2O_4 and NO_2 and assuming that $\Phi_{NO_2}^{N_2O_5} = 2$ and $\Phi_{N_2O_4}^{N_2O_5} = 0$. In three experiments at 280 mμ and 0°, $\Phi_{N_2O_5}^{N_2O_5}$ ranged from 0.6 at 51.5 mm. to 0.8 at a total pressure of about 100 mm. The slight increase of $\Phi_{N_2O_5}^{N_2O_5}$ in the presence of decomposition products suggests that $\Phi_{N_2O_4}^{N_2O_5}$ at 280 mμ is not quite zero. Two experiments with pure nitrogen pentoxide at 10° gave, within the limit of experimental error, the same quantum yield as at 0°, namely $\Phi_{N_2O_5}^{N_2O_5} = 0.6$. At 265 mμ and 0° when nitrogen dioxide and nitrogen tetroxide were negligible, $\Phi_{N_2O_5}^{N_2O_5}$ was found to be 0.6.

Quantum Yield, N_2O_4.—The addition of nitrogen tetroxide to nitrogen pentoxide does not lower the apparent quantum yield at 265 mμ as it does at the longer wave lengths. Even when a considerable amount of the decomposition products are present and 85% of the light is absorbed by nitrogen tetroxide, 2% by nitrogen dioxide and 13% by nitrogen pentoxide, the apparent yield is 0.42 molecule of nitrogen pentoxide decomposed per quantum absorbed by the mixture. From these facts it is concluded that at 265 mμ $\Phi_{N_2O_4}^{N_2O_5}$ is 0.4. The photoactivity of nitrogen tetroxide at 265 mμ was further established by filling the cell at 0° with 217.7 mm. of nitrogen tetroxide and nitrogen dioxide in the absence of nitrogen pentoxide. At this pressure 98% of the light is taken up by the nitrogen tetroxide. Four experiments gave a quantum yield $\Phi_{N_2O_4}$ of 0.4 ± 0.1. The decomposition products were nitric oxide and oxygen as shown by the rate at which the pressure decreased after exposure to light. The period of half recombination calculated from the rate constant[20] for the oxidation of nitric oxide was 87 minutes. The observed time was sixty-six minutes in one case and eighty-seven minutes in another. The pressure returned exactly to its original value on standing overnight.

At 280 mμ when 96% of the absorption was due to nitrogen tetroxide $\Phi_{N_2O_4}$ was found to be 0.2 ± 0.1.

Effect of Foreign Gases.—The nitrogen pentoxide was sealed up in the quartz cell with various pressures of transparent, foreign gases and exposed to the radiation. Measurements were made at intervals while the decomposition products, nitrogen dioxide and nitrogen tetroxide were accumulating, as before. The yields at 366 and 313 mμ were plotted against the percentage of light absorbed by nitrogen dioxide as in Fig. 2. The intersection on the left-hand axis gave $\Phi_{NO_2}^{N_2O_5}$ uncomplicated by the screening effect of nitrogen tetroxide. At 405 mμ $\Phi_{NO_2}^{N_2O_5}$ was obtained by extrapolation to zero pressure of decomposition products using the same slope as given in Fig. 1.

The results are summarized in Table IV.

TABLE IV

EFFECT OF FOREIGN GAS ON THE PHOTO-DECOMPOSITION OF NITROGEN DIOXIDE

Foreign gas	Pressure of gas	$\Phi_{NO_2}^{N_2O_5}$ 405 mμ	$\Phi_{NO_2}^{N_2O_5}$ 366 mμ	$\Phi_{NO_2}^{N_2O_5}$ 313 mμ
None	0	0.50	1.83	1.93
Helium	614	.51	1.66	1.72
Argon	699	.44	1.38	1.32
Nitrogen	574	.46	1.48	1.27
Nitrogen	595	.44	1.45	1.27
Oxygen	584	.45	1.40	1.38
Oxygen	619	.42	1.20	1.23
Hydrogen	532	.37	1.43	1.27
Carbon dioxide	120	.45	1.62	1.50
Carbon dioxide	326	.42	1.44	1.35
Carbon dioxide	431	.40	1.32	1.24
Carbon dioxide	652	.36	1.32	..
Carbon dioxide	683	.36	1.21	1.12
Nitrous oxide	679	.34	1.16	1.10
Nitrous oxide	567	.34	1.27	1.18

The effect of varying the foreign gas pressure was studied only with carbon dioxide. The results are shown in Fig. 4.

Since all the foreign gases studied had a noticeable effect on the quantum yield, it is to be expected that the products of the reaction, nitrogen tetroxide and oxygen, would also reduce the yield. The suggestion is supported by the data

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[19] Urey, Dawsey and Rice, THIS JOURNAL, **51**, 3190 (1929).

[20] Bodenstein and Lindner, *Z. physik. Chem.*, **100**, 87 (1922).

at 405 mμ in Fig. 1 where Φ is seen to be a function of pressure just as it is in Fig. 4 with carbon dioxide. At this wave length there is no absorption by nitrogen tetroxide and no screening effect. In Fig. 1 it may also be seen that Φ at 366 and 313 mμ decreases more rapidly where the pressure of the reaction products becomes large.

Effect of Solvent.—The photolysis of nitrogen pentoxide and nitrogen dioxide dissolved in carbon tetrachloride was studied because a solvent may be regarded as an extreme case of a foreign gas. The influence of solvents on the thermal decomposition had been studied previously in this Laboratory.[21]

The photolysis was measured by the evolution of oxygen using a quartz cell 1.35 cm. deep, 1 cm. wide and 8 cm. high with plane, polished sides, fused to a narrow quartz gas buret of 1-cc. capacity. The height of the concentrated sulfuric acid in the buret was read with a cathetometer. A few beads were placed in the bottom of the cell, and the buret and cell were permanently mounted together in the thermostat. It is difficult to shake a photochemical cell of this type continuously but tests on the thermal decomposition which agreed within 5% of those calculated from the results of Eyring and Daniels showed that it was sufficient to shake the cell and buret thoroughly before each reading.

Dried nitrogen pentoxide and then dried carbon tetrachloride were distilled into the cell, which had been flamed and evacuated. The buret liquid was drawn in and the buret and cell were then sealed off. Sufficient thermal decomposition was allowed to give a pale straw color. Thermal decompositions were run between some of the photo-decompositions to make sure that supersaturation of oxygen and other errors had been eliminated. The volume of the solution was 5 cc. and the concentration 0.1 mole per liter, as determined by measuring the oxygen evolved in the complete thermal decomposition at a higher temperature. The photochemical decomposition was about one-third as much as the accompanying thermal decomposition. The slit of the monochromator was opened to 1.4 mm. for the determinations at 280 and 265 mμ. The results are summarized in Table V.

TABLE V

PHOTOLYSIS OF N_2O_5 AND NO_2 IN CARBON TETRACHLORIDE AT 0°

Wave length	Absorption, %	Time expos., min.	Quanta absorbed $\times 10^{-18}$	Total dec., cc. O_2	Photo-dec. molecules $\times 10^{-18}$	Quantum yield
405 mμ	29	30	5.12	0.019	0.24	0.05
405	35	30	5.90	.016	.10	.02
366	76	25	25.3	.023	.44	.02
280	100	60	23.1	.040	.87	.04
265	100	65	19.6	.041	.87	.04
265	100	30	8.97	.022	.48	.05
265	100	30	8.74	.025	.63	.07

On account of the relatively high concentration of nitrogen pentoxide most of the decomposition at 280 and 265 mμ is due to absorption by nitrogen pentoxide, but at the longer wave lengths the photo-decomposition of nitrogen dioxide is involved. In all cases the quantum yield is very low, but it is not zero. These conclusions are supported also by a long series of less accurate experiments in which the decomposition was followed by treatment with dilute sodium hydroxide solution and titration with the dilute potassium permanganate. They are also supported by the fact that the absorption of light by nitrogen dioxide at 366 and 405 mμ increased only very slightly during a long exposure.

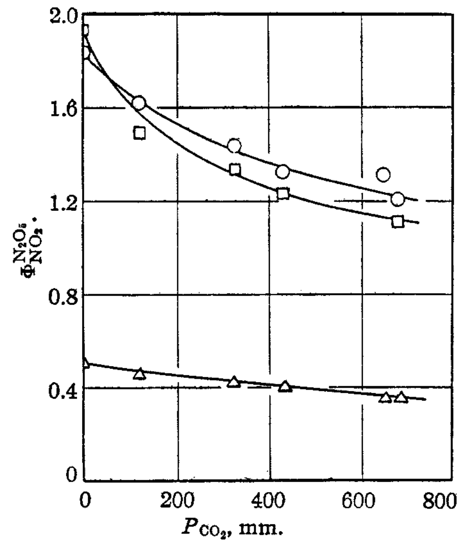

Fig. 4.—Effect of carbon dioxide in reducing the quantum yield $\Phi^{N_2O_5}_{NO_2}$ (corrected for screening by nitrogen tetroxide): △, 405, ○, 366, □, 313 mμ.

Discussion

Although nitrogen pentoxide is photochemically active at 265 and 280 mμ, at longer wave lengths it is to be regarded only as a chemical reagent which stops instantly the recombination of the decomposition products of the nitrogen dioxide and increases the accuracy with which the

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(21) Eyring and Daniels, THIS JOURNAL, 52, 1472 (1930).

quantum yield can be determined. Only by reducing the experimental errors in Φ to about 3% can the influence of foreign gases be studied.

The results of the corrected quantum yields are summarized in Table VI.

TABLE VI

QUANTUM YIELDS AT 0°

Wave length	$\Phi_{N_2O_5}$	$\Phi_{N_2O_4}$	Φ_{NO_2}
436 mμ	t	t	0
405	t	t	0.50
366	t	0	1.83
313	t	0	1.93
280	0.6	Small	(2)*
265	.6	0.4	(2)*

t, transparent. *, assumed.

The Norrish mechanism

$$\begin{array}{l} NO_2 + h\nu = NO_2^* \\ NO_2^* + NO_2 = 2NO + O_2 \\ \underline{2NO + 2N_2O_5 = 6NO_2} \\ (NO_2) + h\nu + 2N_2O_5 = (NO_2) + O_2 + 4\underset{2N_2O_4}{\underset{\downarrow\uparrow}{NO_2}} \end{array}$$

is entirely satisfactory for explaining the observed facts and no results in this or any other research appear to be opposed to it. The close similarities in the quantum yields and the quenching effects with and without nitrogen pentoxide indicate that the mechanism is the same, as already established by Norrish and by Baxter and Dickinson.[3] They render less likely the mechanism proposed by Fazel and Karrer,[22] according to which nitrogen pentoxide is decomposed directly by collision with an activated nitrogen dioxide molecule. The total stoichiometric results are the same.

The results of this investigation show that nitrogen tetroxide is not decomposed by the light which it absorbs at 366 and 313 mμ but that it is decomposed at 265 and slightly decomposed at 280 mμ. The prediction of Dawsey[23] that nitrogen tetroxide should be decomposed by the light which it absorbs is thus supported only in part by the experimental facts. Apparently much of the energy is expended in electronic excitation or in other ways and only below a threshold wave length can photodecomposition into nitric oxide occur. At longer wave lengths it is possible that the molecule undergoes photodissociation into two molecules of nitrogen dioxide but that no pressure change can be detected on account of immediate thermal recombination.

The photodecomposition of nitrogen pentoxide confirms the prediction of Urey, Dawsey and Rice[24] based on the absorption spectra. These authors also pointed out that the energy below 300 mμ is sufficient to effect the reaction $N_2O_5 + h\nu = N_2O_5^* = (N_2O_4 \rightleftarrows 2NO_2) + O$. If this is the reaction the photo process is 60% efficient and part of the failure to give a quantum yield of unity may be due, possibly, to reoxidation of the nitrogen dioxide by atomic oxygen (or ozone). If the reaction proceeds according to the equation

$$N_2O_5 + h\nu = N_2O_5^* = N_2O_3 + O_2 = NO + NO_2 + O_2$$
$$NO + N_2O_5 = (3NO_2 \rightleftarrows 3/2N_2O_4)$$

the photo process has an efficiency of 30% and the low efficiency cannot be attributed to reoxidation of the nitrogen dioxide. In either case the low yield may be attributed in part to a difficulty in transforming the energy of electronic activation into vibrational energy with subsequent disruption of the molecule.

The present investigation shows that about one atmosphere of a polyatomic gas reduces the quantum yield by 25 to 35%, whereas only a few millimeters is required to quench the fluorescence.[25] These facts suggest that the electronic and vibrational-rotational energies, at least in the activated nitrogen dioxide molecule, are only slowly interchangeable, as suggested by Norrish. The electronic energy can be much more easily removed by collisions than the energy of chemical activation, which probably exists in the form of vibrational excitation.

The quenching of the electronic energy cannot be explained on the hypothesis that this energy is transferred to vibrational energy by the collisions in such a way as to cause chemical decomposition—for then the increased vibrational energy should lead to an increase in quantum yield at 405 mμ rather than to a decrease. The blurring of the fine-lined spectrum of nitrogen dioxide at about 380 mμ combined with the photochemical threshold in this region has been used to support the theory of predissociation. Moreover, it has been found that the addition of foreign gases such as oxygen to small amounts of nitrogen dioxide increases the absorption and shifts the apparent predissociation limit as far as 424 mμ.[26] But

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[22] Fazel and Karrer, THIS JOURNAL, **48**, 2837 (1926).

[23] Dawsey, *Proc. Nat. Acad. Sci.*, **16**, 546 (1930).

[24] Urey, Dawsey and Rice, THIS JOURNAL, **51**, 3190 (1929).

[25] Norrish, *J. Chem. Soc.*, 1611 (1929); Baxter, THIS JOURNAL, **52**, 3920 (1930).

[26] Kondratiew and Polak, *Z. Physik*, **76**, 386 (1932).

conditions which produce this "induced predissociation" do not increase the photochemical activity. It is likely that theories of predissociation, particularly induced predissociation, are of little importance in explaining the photolysis of nitrogen dioxide. The quenching effect of foreign gases can be explained on the assumption that the foreign gas molecule dissipates some of the vibrational energy as well as the electronic energy of the excited nitrogen dioxide molecule before the latter can collide with a second nitrogen dioxide molecule and decompose into nitric oxide and oxygen.

Regarding the relative efficiencies of the different foreign gases in reducing the quantum yield, it can be stated that helium is the least effective of all gases tried, and that the triatomic gases are more effective than the diatomic gases. The effect, as shown by carbon dioxide, is nearly proportional to the pressure of the foreign gas.

In a typical experiment the quantum yield ($\Phi^{N_2O_5}_{NO_2}$) of 1.83 in the gas phase at 366 mμ was reduced to 1.21 when 30 mm. of nitrogen dioxide was mixed with 683 mm. of carbon dioxide and sufficient decomposition products to give a total pressure of 870 mm.; and $\Phi^{N_2O_5}_{NO_2}$ was reduced to 0.15 by liquid carbon tetrachloride, allowing for the fact that in the solution 87% of the light at 366 mμ was absorbed by nitrogen tetroxide. The fraction of the molecules which survived collisions with gaseous carbon dioxide molecules was 1.21/1.83 or 0.66. Assuming that the carbon dioxide and nitrogen dioxide molecules have about the same weight and cross section, there must have been in the gas phase 840/30 or 28 collisions of a nitrogen dioxide molecule with a foreign gas molecule for every collision with another nitrogen dioxide molecule. On the average, then, a photochemically activated molecule of nitrogen dioxide survives 0.66 × 28 or 18.5 collisions with a foreign gas (carbon dioxide) and still retains sufficient energy to react as soon as it collides with a nitrogen dioxide molecule.

The fraction of activated nitrogen dioxide molecules which survived "collisions" with liquid carbon tetrachloride was 0.15/1.83 or 0.08. Liquid carbon tetrachloride then is about 0.66/0.08 or 8 times as effective as one atmosphere of carbon dioxide in quenching the activated molecules of nitrogen dioxide.

If we assume that the relations of gas kinetics may be applied as well to solutions, and that carbon tetrachloride molecules have the same deactivational efficiency as carbon dioxide molecules, then in solution there are $8 \times 28 = 224$ "collisions" between nitrogen dioxide and carbon tetrachloride for every collision between two nitrogen dioxide molecules. These assumptions, however, lead to an improbably large value for the mean free path when the simple gas kinetic formula is applied to a solution of known nitrogen dioxide concentration.

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Summary

1. Absorption coefficients at wave lengths from 436 to 265 mμ have been determined for N_2O_5, N_2O_4 and NO_2.

2. Nitrogen pentoxide is decomposed by the light which it absorbs at 280 and 265 mμ with a quantum efficiency of 0.6.

3. Nitrogen tetroxide is decomposed at 265 mμ with a quantum efficiency of 0.4. At 366 and 313 mμ it absorbs light but gives no measurable decomposition.

4. Nitrogen dioxide is decomposed with the following quantum efficiencies: 1.93 at 313, 1.83 at 366, 0.50 at 405 (at 0°) and 0.0 at 436 mμ, after allowance for the screening effect of N_2O_4.

5. The effect of foreign gases, He, A, N_2, O_2, H_2, CO_2 and N_2O, in decreasing the photodecomposition of NO_2 has been measured. The effect of pressure of CO_2 on the quantum yield has been measured. Photodecomposition in carbon tetrachloride solution is slight but not negligible.

6. Foreign gases are much more effective in reducing the fluorescence of nitrogen dioxide than in reducing the photochemical action.

7. Theoretical interpretations of these facts have been discussed.

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