Stage of Development

An idea of the range of usefulness of the machine in the present state of its development can be gained from the following. Without heating the air or attempting in any way to control the natural temperature gradient existing in the rotor, the second type of rotor herein described sedimented at every trial such heavy molecules as the respiratory protein of the earthworm (5% solution; 1% in potassium chloride).[17] With the first crude air heating arrangement tried (manually adjusted electric heater inside the air supply tubing) which enabled us to keep the temperatures above and below the cell at the same value to within ± 0.3°, the same rotor easily sedimented molecules as small as the hemp seed protein edestin (molecular weight about 208,000). With the driving air arbitrarily thermostated to within ±0.02° and the room temperature controlled, the same rotor will sometimes sediment molecules as small as purified egg albumin (molecular weight about 35,000).

More remains to be done before the instrument is uniformly reliable for the smallest molecules. The authors are confident that once the exact relations between the temperatures recorded by the thermocouples and the temperatures of the cell walls have been determined, the problem will have been solved completely, for it is comparatively easy to maintain any desired temperature gradient between the air above and below the cell. Devices are contemplated which promise to make the temperature of the air above, within and below the rotor, wholly independent of the room temperature.[18]

Summary

1. The air-driven spinning top has been developed as a transparent convectionless ultracentrifuge.

2. The three types of instability of the air-driven rotor are described, with their causes and remedies.

3. Means are given for measuring, increasing and controlling the speed of the top, with a discussion of the best materials of construction.

4. Spinning top centrifuges are described in which it is possible to photograph the cell by transmitted light of any monochromatic wave length, visible or ultraviolet.

5. Two different types of cells are described.

6. Means are discussed for measuring and controlling the temperature gradient existing between the top and bottom of the cell.

7. The present stage of the development of the instrument is described.

[17] The best average value we have obtained for this protein (uncorrected for viscosity and density) is $s = 61.8 \times 10^{-13}$. The value of 72×10^{-13} published by us in THIS JOURNAL, **57**, 780 (1935), proved to be exceptionally high.

[18] Mr. H. J. Fouts in this Laboratory has since found that in order fully to equalize the temperature inside the rotor with the temperature of the slip stream from the driving air (on account of the friction caused by the periscope upon the air within the rotor) it is advisable to draw the air entering the periscope, as well as the air playing upon the top of the rotor, through a much colder thermostat, instead of taking it from the guard ring as described above.

STANFORD UNIVERSITY, CALIF. RECEIVED AUGUST 5, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Photochemical Decomposition of Nitric Oxide[1]

BY PAUL J. FLORY AND HERRICK L. JOHNSTON

Berthelot[2] observed that nitric oxide decomposed when irradiated with light from the quartz mercury arc and concluded that nitrogen and oxygen are the final products of the decomposition. Macdonald,[3] as part of his investigation of the nitrous oxide decomposition, made a brief study of the decomposition of nitric oxide under irradiation from the aluminum spark, between pressures of 50 and 650 mm. He observed that the rate seemed to depend entirely upon the amount of light absorbed and reported a quantum yield of 0.75. He interpreted his data in terms of a primary mechanism of activation. Noyes[4] found good evidence for the decomposition of nitric oxide through the agency of excited mercury atoms. Under the conditions of his experiments he observed no appreciable amount of direct photochemical reaction.

We have investigated the photochemical decomposition of nitric oxide both with the mercury arc and with sparks between various metal elec-

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Cleveland Meeting of the American Chemical Society, Sept., 1934.

[2] Berthelot, *Compt. rend.*, **150**, 1517 (1910).

[3] Macdonald, *J. Chem. Soc.*, 1 (1928).

[4] W. A. Noyes, Jr., THIS JOURNAL, **53**, 514 (1931).

trodes, as sources of radiation, and over a pressure range from 0.02 to 7 mm. We have been successful in correlating the primary process, which proves to be an act of predissociation, with the absorption spectrum of the gas. This interpretation appears, also, to provide a better explanation than that given by Macdonald for the decomposition at the higher pressures.

Experimental

Reaction System.—The reaction system consisted of a cylindrical quartz cell, 75 mm. long by 25 mm. in diameter, with plane end windows. The cell was connected through a graded quartz to Pyrex seal, to a calibrated McLeod gage and to mercury cut-offs which communicated to a high vacuum system and to a preparation line. No stopcocks were contained in the reaction system.

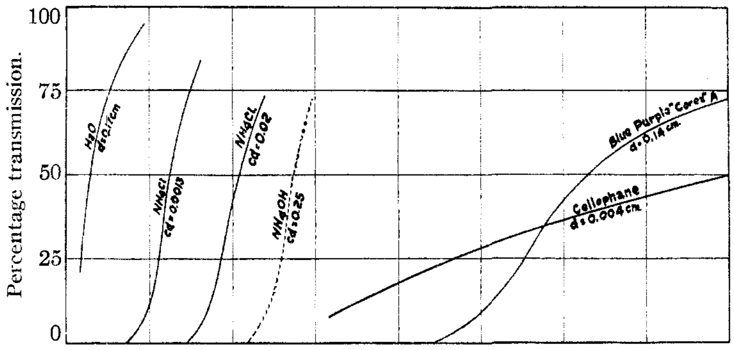

Fig. 1.—Absorption curves of filters (*d*, in centimeters; *c*, in moles per liter).

The reaction system was evacuated to a pressure of 10^{-6} mm. prior to each run, and was usually baked out during evacuation. Nitric oxide, prepared and purified by the method employed by Johnston and Giauque[5] was introduced to the desired pressure and the reaction followed by means of pressure measurements.

In some of the experiments a condenser-diaphragm manometer, similar to the one described by Olson and Hirst[6] was used.

Sources of Illumination.—Most of the experiments were done with a quartz mercury arc which was relatively weak in unreversed λ 2537 resonance radiation. A number of experiments were also made with condensed spark discharges between suitable metal electrodes. It was found necessary to electrically shield the cell, with a tin foil covering, to prevent decomposition under the influence of an induced field set up within the cell.

Filters.—Filters were used to locate the active regions of the spectrum. The absorption characteristics of these filters are shown in Fig. 1. The curves for water and for aqueous ammonium chloride and the solid portion of the curve for ammonium hydroxide are constructed from the absorption data of Ley and Arends.[7] The dotted portion of the ammonium hydroxide curve was constructed from visual estimates obtained with a small ultraviolet fluorescing spectroscope, and is considered reliable to within 25 Å. The curves for cellophane[8] and for the Corex glass were determined by means of a Bausch and Lomb spectrograph equipped with a rotating sector comparator. An under-water spark was the source of continuous radiation.

To prevent photolysis the filter liquids were made to flow through a thin filter cell (one or two mm. liquid thickness) cemented to the reaction cell in such a way that the window of the latter formed one window of the filter cell.

Preliminary Observations

The Gage Reaction.—From considerations of stoichiometry alone nitrogen dioxide, nitrous oxide, nitrogen and oxygen are possibilities as ultimate products of the dissociation.[9] However, Macdonald[3] has shown that nitrous oxide is photochemically decomposed ten times as rapidly as nitric oxide while Norrish[10] has found that nitrogen dioxide is decomposed rapidly into nitric oxide and oxygen at wave lengths shorter than 4000 Å. The reverse thermal reaction is third order and it can be shown from the data of Bodenstein[11] that the rate of recombination of nitric oxide and oxygen is negligible at the pressures of our experiments.

From these considerations it would appear that nitrogen and oxygen should be the final products of the dissociation, regardless of the primary mechanism, and that the final and initial pressures should be equal. Contrary to this expectation preliminary experiments showed that the pressure decreased rapidly to less than one-half of the initial pressure (and went through a minimum at about $^1/_4P_0$).[12] Furthermore, the pressure in the reaction system rose slowly when the arc was shut off but dropped rapidly again, for a short period, when the cell was re-illuminated. As the result of several such alternate periods of light and of dark (*cf.* Fig. 2) the pressure eventually approaches a value which is very near to one-half of the initial pressure.

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[5] Johnston and Giauque, This Journal, **51**, 3194 (1929).

[6] Olson and Hirst, *ibid.*, **51**, 2378 (1929).

[7] Ley and Arends, *Z. physik. Chem.*, **B6**, 243 (1929); **B17**, 177 (1932).

[8] The cellophane was placed between two pieces of quartz plate to protect it from the action of ozone. Although the cellophane did show some solarization the effect was not great.

[9] Nitrogen tetroxide and nitrogen trioxide may be excluded since at the low pressures of our experiments these molecules would, themselves, dissociate into the simpler oxides.

[10] Norrish, *J. Chem. Soc.*, 761 (1927).

[11] Bodenstein, *Z. Electrochem.*, **24**, 183 (1918).

[12] The position of the minimum is based on subsequently more careful measurements with the technique finally adopted (*cf. seq.*) for removing the accumulation of oxygen.

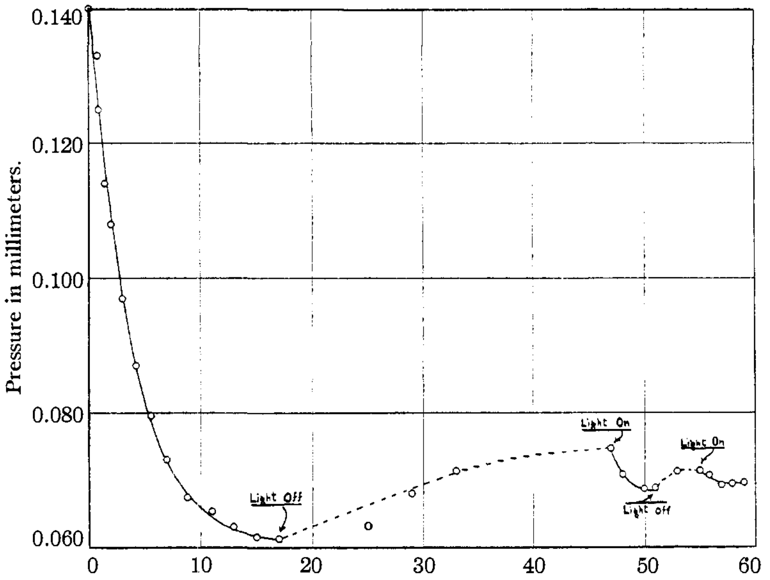

Fig. 2.—Anomalous behavior following the initial period of illumination.

A clue to this behavior was found in the observation that a film was deposited on the mercury surface in the stem of the McLeod gage, which indicated that something was being removed from the reaction system during compressions in the gage. This indication was confirmed in a series of runs in which the McLeod gage was replaced by the diaphragm manometer. The results are shown graphically in Fig. 3, for several initial pressures. The broken curve, plotted to the same scale, is from data obtained with the McLeod gage and shows the true course of the decomposition. It is clear that our expectations regarding the constancy of pressure during the early course of the photochemical decomposition[13] are verified.

Additional confirmation was obtained in later experiments with the McLeod gage, in which the reaction was allowed to continue for five or six hours without running up the gage. Pressures measured at the end of this period were about $^5/_6$ of the initial pressure, in good accord with the diaphragm gage curves.

The presence of liquid mercury, either on the walls of the connecting tubing or in the reaction cell itself, did not affect the results in either of these experiments.

We interpret this as evidence for the following series of reactions[14]

$$NO + h\nu = {}^1/_2N_2 + {}^1/_2O_2 \qquad (1)$$

$$NO + {}^1/_2O_2 = NO_2 \qquad (2)$$

$$Hg + NO_2 = HgNO_2 \qquad (3)$$

of which (2) and (3) occur only in the gage.

The increase in pressure after the illumination is shut off results from the slow, dark reaction

$$HgNO_2 = HgO + NO \qquad (4)$$

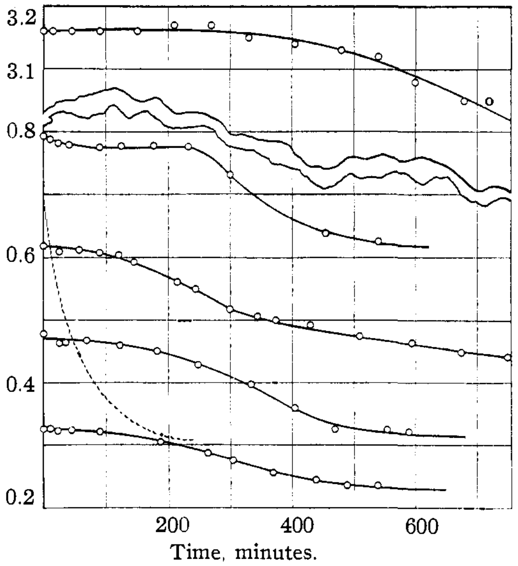

Fig. 3.—Experiments with the membrane manometer; - - - - -, decomposition curve measured with the McLeod gage.

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(13) The marked pressure drop which comes two hours or more after the reaction is initiated is interesting although it appears to be irrelevant to the subject of our investigation since it comes *after* the decomposition of the nitric oxide is ended (comparison with the broken curve). This fact itself is significant since it seems to indicate that the change which produces the decrease in pressure is either prevented, or compensated, through the agency of nitric oxide. It also appears that the change is produced through the action of light, or of excited mercury, on oxygen since we were able to duplicate the pressure decrease, to the correct order of magnitude, with the cell filled with *oxygen alone*. In this experiment the oxygen pressure decreased to about $^3/_4$ P_0 in seven and one-half hours and was still falling.

Experiments in which a Blue Purple Corex A filter, which prevented decomposition of the nitric oxide, was placed in the path of the radiant energy prevented the appearance of this delayed pressure drop.

The presence of a yellowish-brown deposit (probably mercuric oxide) on the cell window and on the walls for a few millimeters back from the window provided evidence for some reaction, either of oxygen or of ozone, with excited mercury. There is probably some relation between these results and those observed by Neujmin and Popov [*Z. physik. Chem.*, **B27**, 15 (1934)] for illumination of oxygen with light of wave length shorter than λ 1750 but we did not investigate the reaction further.

(14) We refer here only to the stoichiometrical equations for the successive steps. The arguments advanced against the nonoccurrence of (2) in the reaction cell do not apply to the gage, where the pressure reaches 200 millimeters during the compression. Our data do not permit us to assign the formula $HgNO_2$ with certainty although (*cf. seq.*) they do indicate that the nitrogen/oxygen ratio in the compound is very close to $^1/_2$.

This proves to be a first order reaction, as shown in Fig. 5, with a rate constant of 1.5 × 10^{-2} per hour. This figure is based on data obtained in a run, illustrated in Fig. 4, which was taken primarily to study this phase of the process. P_∞ represents the limiting pressure to which the curve of Fig. 4 (dark reaction) extrapolates asymptotically and is indicated in that figure.

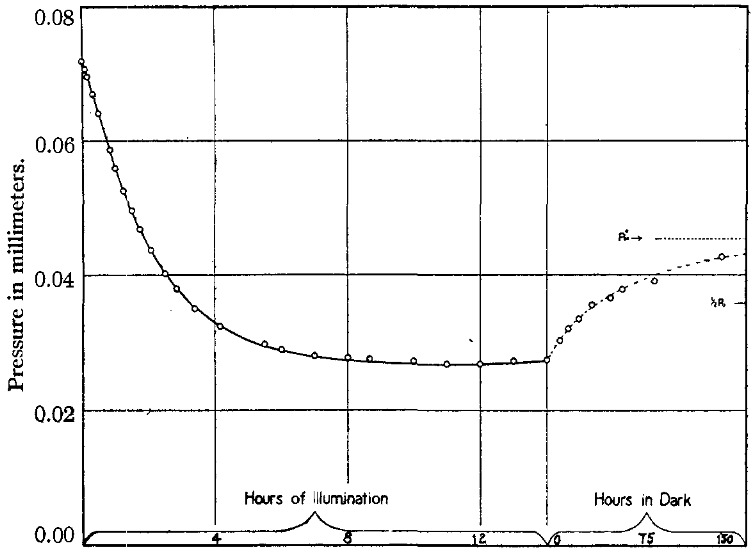

Fig. 4.—Course of a single run, showing the final dark reaction.

Although the reactions which occur in the McLeod gage may appear to be an encumbrance to the study of the photochemical reaction, they actually are an aid since it becomes possible to follow the reaction by measurements of pressure. The expedient was adopted, in all of our later, more careful, quantitative work, of compressing the gas in the gage to a pressure of 200 mm. or more every five minutes, whether pressure readings were wanted or not. Since the gage constituted about 75% of the total volume of the reaction system three-fourths of the accumulated oxygen was thus removed every five minutes. Preliminary trials showed that compression for a period of thirty seconds was more than ample time to remove the oxygen from the gas, and also that the rate of diffusion was sufficient to accomplish removal of the accumulated oxygen by this procedure.

Elimination of Photosensitization as a Mechanism for the Decomposition.—The absence of a mercury sensitized step in the decomposition, under the conditions which pertained to our experiments, was proved by three independent tests.

(1) A mercury vapor filter formed by placing a drop of mercury in the side-arm of an evacuated and baked quartz cell 4.5 cm. long, did not reduce the reaction rate by more than was to be expected for the introduction of two quartz windows into the light path.

(2) The use of a Blue Purple Corex A filter which cuts off the radiation completely below λ 2300 but shows 70% transmission of λ 2537 (*cf.* Fig. 1) reduced the rate to 1.3% of its value without the filter. A similar experiment with a cellophane filter, which cuts out radiation below about λ 2200 but is 45% transparent to λ 2537, reduced the rate to about 1% of its value without the filter.

(3) Insertion of a U-tube cooled with a dry ice–chloroform–carbon tetrachloride bath between the quartz cell (previously baked out thoroughly) and the rest of the reaction system, to keep the cell free of mercury vapor, had no effect on the rate of reaction.

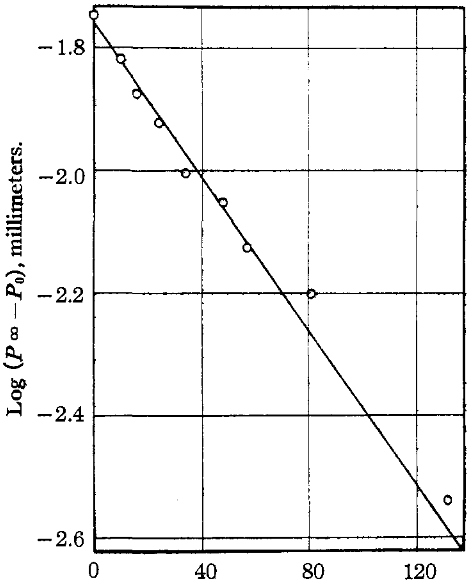

Fig. 5.—The first order gage reaction.

We conclude that the reactions, in our experiments, are at least 98% non-sensitized.[15]

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[15] Our results in no wise contradict those of Noyes (Ref. 4) who reported a mercury sensitized reaction with negligible photochemical reaction. Noyes used a water-cooled arc which doubtless gave a high intensity of λ 2537 while the cooling water, if tap water were used, must have removed almost all of the radiation which we find to be effective for the photochemical process. Our own air-cooled arc

Dependence on Light Intensity.—The influence of the light intensity on the rate of nitric oxide decomposition was determined by the use of calibrated wire screens[16] placed in the light path.

The results of these experiments, with three different screens, are shown in Table I. These runs were all made at about 0.12 mm. initial pressure, which falls in the region (*cf. seq.*) where, for a given light intensity, the percentage decomposition is a function of time and almost independent of the pressure. "t" and "t_0" refer to the times required for the recorded percentage changes in pressure, with and without the screens in the light path, respectively. The last column in the table is obtained from the screen calibrations.

TABLE I

DEPENDENCE OF REACTION RATE ON LIGHT INTENSITY

Screen no.	Change in pressure, %	t, min.	t_0, min.	t_0/t	I/I_0
1	11.1	30	19.8	0.66	0.681
	16.9	50	31.6	.63	
2	8.9	40	15.6	.39	.361
	12.7	60	22.8	.38	
	19.1	100	36.4	.364	
3	7.5	150	15	.10	.13

The Primary Process

Influence of Pressure on the Rate of Reaction.—In order to obtain information as to the general character of the primary process the dependence of reaction velocity on the pressure of nitric oxide was determined for a series of pressures varying between 0.02 and about 7 mm. So as to minimize the possible influence of the decomposition products on the reaction velocity, the comparisons were made between the *initial* rates of decomposition. The values of $(\mathrm{d}P/\mathrm{d}t)_0$ for the several individual runs are recorded in Table II, in which the third column gives the probable error in the several determinations, as deduced from a consideration of the accuracy of the McLeod gage, the completeness of oxygen removal, etc.

TABLE II

VARIATION OF REACTION RATE WITH PRESSURE

Initial pressure P_0, mm.	$(\mathrm{d}P/\mathrm{d}T)_0$, mm./min.	% Error	$\left(\frac{\mathrm{d}\ln P}{\mathrm{d}t}\right)_0$ Obsd.	Calcd.
0.0215	1.12×10^{-4}	6	5.2×10^{-3}	5.22×10^{-3}
.0428	2.40	4	5.6	5.16
.0677	3.58	2.5	5.28	5.06
.0907	4.54	2	5.00	4.98
.1258	6.14	2	4.88	4.86
.1258	6.00	2	4.76	4.86
.1315	6.50	2	4.94	4.84
.1354	6.72	2	4.96	4.84
.1990	9.4	2	4.72	4.62
.235	10.7	2	4.52	4.52
.306	13.6	2	4.44	4.30
.467	19.4	2	4.12	3.88
.694	22.6	2	3.26	3.36
.977	26.8	2	2.74	2.86
2.24	36.8	3	1.64	1.58
4.37	39	4	0.90	0.84
7.12	44	4	.62	.51

The table indicates that, for very low pressures, $(\mathrm{d}P/\mathrm{d}t)_0$ is about linear with the pressure and, at high pressures, approaches a constant value. This behavior, together with the linear relationship between rate and light intensity (Table I), suggests at once that the main factor in determining the rate may be the amount of light absorbed. This suggestion is confirmed by the agreement of the experimental values for $(\mathrm{d}\ln P/\mathrm{d}t)_0$ in column four with those, in column five, which are calculated from the relationship

$$\left(\frac{\mathrm{d}\ln P}{\mathrm{d}t}\right)_0 = -3/2\ kaI_0\left(\frac{1 - e^{-aP_0}}{a\,P_0}\right) \qquad (8)$$

which is derived[17] on the assumption that the decomposition rate is directly proportional to the rate of light absorption and that the absorption of effective radiation obeys Beer's law. The fit is

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gave out very little unreversed radiation of λ 2537, due largely to self reversal in the arc, and accounts for our low mercury sensitized yield. Subsequent experiments with the same arc operated under conditions that very greatly increased the output of λ 2537 resonance radiation gave evidence of a very considerable mercury sensitized reaction.

(16) Forbes, *J. Phys. Chem.*, **32**, 482 (1928).

(17) Here, k is a constant in which is incorporated the quantum yield and the relation of the pressure decrease to the number of molecules which disappear in unit time; I_0 is the intensity of the incident light of effective wave length and a is its absorption coefficient which includes the fixed length of light path applicable to our experiment. P_0 is the initial pressure.

The derivation is as follows.

$$\mathrm{d}P/\mathrm{d}t = \mathrm{d}P_{\mathrm{NO}}/\mathrm{d}t + \mathrm{d}P_{\mathrm{N_2}}/\mathrm{d}t \qquad (5)$$

$$= -3/2\ kI_{\mathrm{abs}} + k_4A \qquad (6)$$

by the stoichiometry of equations 1–3. Here A represents the pressure equivalent of the NO withdrawn by equation (3) and k_4 is the first order velocity constant of reaction (4).

Introduction of Beer's law gives

$$\mathrm{d}P/\mathrm{d}t = -\ 3/2\ kI_0\,(1 - e^{-aP_{\mathrm{NO}}}) + k_4A \qquad (7)$$

which reduces, in the limit of (t = 0), to equation (8) above.

The several factors $3/2kaI_0$ were constant under the experimental conditions which we employed and were evaluated collectively, by extrapolation of the experimental values of $(\mathrm{d}\ln P/\mathrm{d}t)_0$ (*cf.* Fig. 6) to zero pressure. In this limit the quantity in parenthesis, on the right of equation (8), becomes unity.

The values in the fifth column of Table II were then computed through the choice of an arbitrary "best fit" for the absorption coefficient a which proved to be, for these experiments, 1.44 in reciprocal millimeters of pressure. Justification for regarding this fit as a confirmation of the dependence of initial rate on the amount of absorbed light is provided in the excellent agreement with the experimental results over a thirty-five fold change in the initial pressure, obtained with only this one arbitrary constant.

shown graphically in Fig. 6 where the smooth curve is calculated by equation (8) and the circles represent experimental points.

Influence of Nitrogen on the Rate of Reaction.—We find that nitrogen has no effect on the rate of reaction. This was tested both by studying the influence of an excess of nitrogen added at the beginning of an experiment and by studying the effect of nitrogen accumulation on the progress of a full reaction. The latter study also provides additional confirmation of the dependence of rate on the light absorption.

Table III shows the results obtained in two experiments which were run to test the effect of an initial excess of nitrogen. Within the limits of experimental error the rates of nitric oxide decomposition are the same.

TABLE III

COMPARISON OF THE DECOMPOSITION RATES WITH AND WITHOUT NITROGEN AS A DILUENT

$P_0(N_2)$, mm.	P_0(NO), mm.	$(dP/dt)_0$, mm./min.	$(d \ln P_{NO}/dt)_0$,
0	0.1121	4.4×10^{-4}	$3.9\ (\pm 0.1) \times 10^{-3}$ min^{-1}
0.360	.0916	4.0×10^{-4}	$4.3\ (\pm 0.4) \times 10^{-3}$ min^{-1}

Figure 7 shows the course of a complete run (carried out under the more careful conditions of our later experiments) in which the experimental pressures are shown in their relation to a curve calculated from the same basic assumptions that were employed in the preceding section and with the same value of the absorption coefficient which was derived from the initial rates (namely, 1.44 mm.$^{-1}$).[18]

As the graph shows, the experimental values are a little high in the final period of the reaction. Although the discrepancy is definitely greater than the probable error of the rate measurements themselves,[19] the results are, nevertheless, in sufficiently good agreement with the general shape of the calculated curve to show that the rate-controlling factor throughout the decomposition is the absorption of light and that the accumulated nitrogen has no marked influence on the reaction.

Dissociation as the Primary Step.—It is possible from the above results to deduce the general character of the primary process. At 0.1 mm. pressure of nitric oxide the average time between collisions is about 10^{-6} seconds. If the photoreaction involves the collision of an excited and a normal molecule, then at low pressures where only a small fraction of the active radiation is absorbed and where most of the excited molecules would lose their energy by fluorescence, the rate should be proportional to the square of the nitric oxide pressure. The experimental observation (Table II and Fig. 6) that the rate becomes linear with pressure at low pressures therefore rules out the collision process. A primary dissociation of the molecule is the only alternative. Failure of nitrogen, either as an accumulation product or as an initial diluent, to modify the rate also indicates the absence of primary activation.

We may also conclude that any secondary processes which occur subsequent to the dissociation are little influenced by variation in the pressure either of nitric oxide or of nitrogen.

The Active Region of the Spectrum

Effective Mercury Arc Radiation.—It is difficult to be quite certain of the lower limit of the

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[18] This curve was calculated from the equation

$$(P_0 - P) + \frac{3}{4a} \ln \left[\frac{1 - e^{-aP_0}}{1 - e^{-a(4P-P_0)/3}}\right] + \frac{k_4}{2a}\left[\frac{(e^{2akI_0t} - 1)}{2a\ kI_0} - t\right] = 3/2\ kI_0t \qquad (14)$$

This equation is derived from (7) as follows. As a first approximation reaction (4) is neglected so far as it influences either the total absorption of light or the amount of $HgNO_2$ remaining at time t. Then, it follows from the stoichiometry of reactions 1–3 that we may rewrite (7) in the form

$$\mathrm{d}P/\mathrm{d}t = -\ 3/2\ kI_0(1 - e^{-a(4P-P_0)/3}) + 2/3\ k_4(P_0 - P) \qquad (9)$$

which rearranges to give

$$\mathrm{d}P + (3a/4)\ \mathrm{d}\ln\ (1 - e^{-a(4P-P_0)/3}) - \frac{2k_4(P_0 - P)\mathrm{d}t}{3(1 - e^{-a(4P-P_0)/3})} + 3/2\ kI_0\ \mathrm{d}t = 0 \qquad (10)$$

Expansion of (9) by MacLaurin's theorem with disregard of higher powers of $(P - P_0)$ and of the term in k_4 yields, on integration, the following approximate relationships

$$4P - P_0 = 3\ P_0e^{-2aI_0kt} \qquad (11)$$

and

$$P_0 - P = 3/4\ P_0(1 - e^{-2aI_0kt}) \qquad (12)$$

These values are then substituted in the *third term only* (which is a small correction term) of equation (10) and the denominator of this term is then expanded by MacLaurin's theorem, and powers of the exponent higher than the first are neglected. This treatment yields the equation

$$\mathrm{d}P + \frac{3a}{4}\,\mathrm{d}\ln\ (1 - e^{-a(4P-P_0)/3}) - \frac{k_4}{2a}(e^{2aktI_0} - 1)\ \mathrm{d}t + 3/2\ kI_0\ \mathrm{d}t = 0 \qquad (13)$$

which integrates to give (14) above.

The several approximations introduced in this derivation are exact in the limit of $t = 0$ and remain good throughout the greater portion of the reaction. We cannot expect this equation to reproduce accurately the experimental data in the immediate neighborhood of the pressure minimum (shown in Fig. 4), where reaction (4) plays a relatively great influence.

[19] The formation of a little mercurous nitrate (or other compound with an O to N ratio greater than 2), in the gage may be the cause of the discrepancy.

wave lengths which may have entered our reaction cell but in view of the intense continuous absorption which sets in with air below λ 1750 we are safe in concluding that no radiation below λ 1750 need be considered in seeking the details of the photochemical process. In order to determine what line, or lines, may be responsible for the photochemical decomposition with the mercury arc a number of runs were carried out with the filters whose absorption characteristics are shown in Fig. 1. Reference has already been made to the results obtained with the Corex and the cellophane filters which showed that radiation below λ 2300 is responsible for at least 98% of the reaction, under the conditions which pertained to our experiments. The results obtained with the other filters are given in Table IV, which also includes comparative rates which show the influence of filters on the reaction promoted by radiation from aluminum and zinc sparks. The influence of the ammonium chloride and ammonium hydroxide filters places the effective radiation below λ 1900.[20] The effect of water in reducing the reaction rate by about 50% corresponds to the absorption of water for wave lengths in the neighborhood of λ 1830.

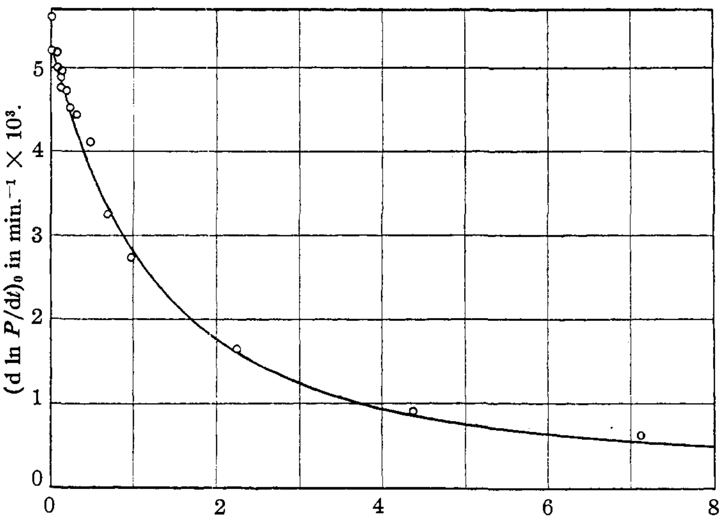

Fig. 6.—Dependence of the initial decomposition rate on the pressure: o, observed: ————, calculated.

The only mercury lines which fall within this active region are those at λλλ 1775, 1832 and 1849, respectively (*cf.* Fig. 8). Hg 1775 falls in a region which is free of nitric oxide absorption. Furthermore, it should be removed completely by the water filter. The results of the several experiments with the mercury arc suggest therefore that the primary process is either the absorption of unreversed radiation from the strong line at λ 1849 in the (9,0) band of the β-system or the absorption of the weak line at λ 1832 (together with continuous radiation surrounding λ 1849) in the (1,0) band of the δ-system. To gain further information on this point an approximate measurement of the absorption coefficient of λ 1849 was carried out spectrographically. An absorption cell 5 cm. long (approximately the mean light path of the divergent light which passed through the 7.5-cm. reaction cell) was placed in front of the spectrograph slit and several exposures of different time lengths were made, both for the evacuated cell and for different pressures of nitric oxide. By visual estimate of the line intensities (all taken on the same plate which was sensitized with Eastman ultraviolet sensitizing solution) the absorption of the λ 1849 line was determined. Application of Beer's Law, which Lambrey[21] has

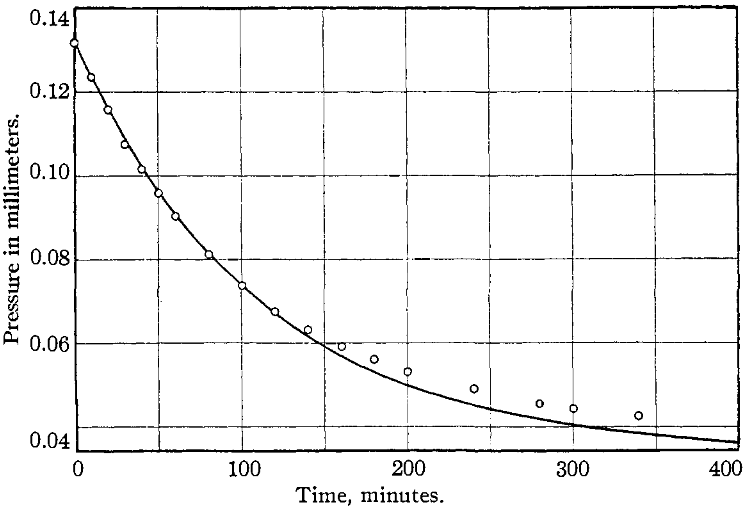

Fig. 7.—Course of a complete run: o, observed; ————, calculated.

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(20) Quantitatively, the 3% residual rates with these filters agree, within limits of error, with the 1% rates obtained with the cellophane and Corex filters and indicate: (1) that none of the mercury arc radiation between λ 1900 and λ 2300 is effective in promoting the decomposition and (2) that the small effect due to radiation of longer wave length is due to unreversed radiation of the λ 2537 line.

(21) Lambrey, *Ann. Phys.*, **14**, 95 (1930).

TABLE IV

INFLUENCE OF LIGHT FILTERS ON THE RATES OF NITRIC OXIDE DECOMPOSITION

Source of radiation	Comparative rates (per cent. pressure decrease per minute)			
	Empty cell	H_2O d = 0.15 cm.	NH_4Cl cd = 0.0013	NH_4OH cd = 0.25
Hg arc	0.30	0.14	0.01	0.01
Al spark	..	.70	.05	..
Zn spark	..	.35	.06	..

shown to be applicable to β-band absorption, yielded 1.9 (±0.3) × 10^{-2} mm.$^{-1}$ for *el* (equivalent to *a* in equation (8)). The rate dependence on pressure, considered in an earlier section of this paper, yielded 1.4 for the mean absorption coefficient, *a*, of the active radiation. The absorption of λ 1849 is thus much too weak to account for the observed reaction. No reliable quantitative measurement of the absorption of λ 1832 was possible, due to the low intensity of the line. However, it was found that nitric oxide at only 3 mm. pressure caused almost complete removal of the line. This result is not incompatible with an absorption coefficient of 1.4.

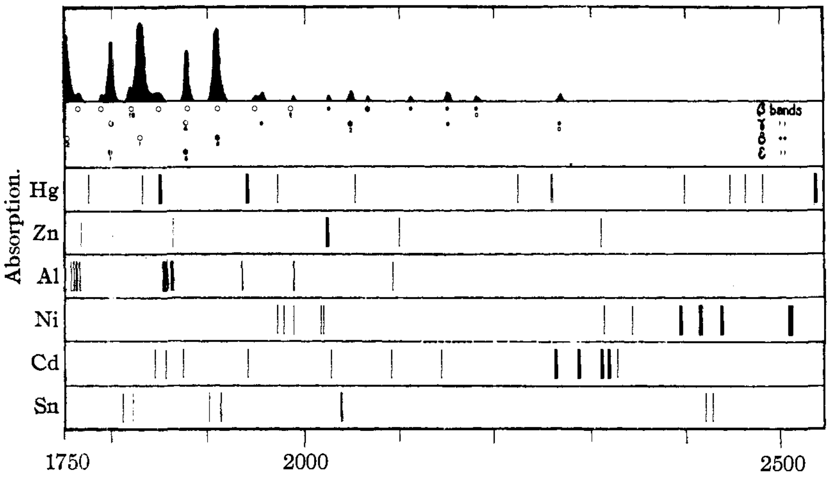

Fig. 8.—Absorption spectrum of nitric oxide in relation to the chief lines of the mercury arc, and of the spark sources employed in this investigation. (The positions and relative intensities of the absorption bands are constructed from the data of Liefson [*Astrophys. J.*, **63**, 73 (1926)] and that of Lambrey [*Ann. phys.*, **14**, 95 (1930)]. The positions and relative intensities of the emission lines are taken from the tabulations in Kayser's "Hauptlinien der Linienspektra aller Elemente." The mercury arc spectrum below λ 1900 is based on the work of Lyman [*Astrophys J.*, **38**, 282 (1913)], who used a mercury arc operated under conditions similar to those we employed except that Lyman's arc was constructed with a fluorite window. Lyman observed that the strong resonance line at λ 1849 was accompanied by continuous radiation extending over more than 40 Å. We confirmed this, for our own arc, by observations taken with a small Gaertner quartz spectrograph. In addition to the broad continuum adjacent to λ 1849 the 1832 line showed up faintly.

The numbers below the circles, which mark the positions of the several absorption bands, represent vibrational quantum numbers of the upper states. White circles mark bands which are absent in emission. Frl. Guillery (*Z. Physik*, **42**, 1212 (1927)) reports emission from the 4′ and 5′ levels of the γ bands but a consideration by one of us (P. J. F.) makes it appear probable that these are, in reality, 0′ and 1′ levels of the ϵ system.

From this we conclude that most, if not all, of the reaction is due to absorption in the δ (1,0) band. Absorption of λ 1849 in the β (9,0) band may have a lesser effect which becomes significant at higher pressures in agreement with the observed rates above 3 mm. pressure (Table II).

Photochemical Effect of Spark Sources.—Results obtained with sparks between metal electrodes confirm the conclusions of the previous section and also indicate some photochemical influence of β-band absorption. The influence of water and ammonium chloride filters on reactions promoted by the aluminum and zinc sparks is included in Table IV. Comparative results obtained with six different spark sources with a 2-mm. water filter are shown in Table V.[22]

The most general observation that we can draw from Table V is that all of the sparks are effective to the same order of magnitude, from which we conclude that their activity is primarily due, not to absorption of their specific lines,[23] but to absorption in the rather considerable continuous background which all of these sources possess.

Removal of the water filter resulted in a two- to four-fold increase in the rates given in Table V. This indicates that most of the active radiation lies below λ 1850. We conclude, therefore, that the same absorption is responsible for dissociation with the several sparks, as with

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[22] The figures in Table V cannot be compared with those in IV since the nature of the power supply, which produced the sparks, was different in the two cases.

[23] The somewhat lesser influence of the ammonium chloride filter in reducing the activity of the zinc spark, than with either mercury or aluminum, may be due to weak absorption of the strong λ 2025 line of zinc in the β (4,0) absorption band of nitric oxide. The low intensity of emission bands with v' = 4 constitutes evidence for some predissociation from this level.

TABLE V

COMPARATIVE RATES OF DECOMPOSITION WITH DIFFERENT SPARKS

Spark source	Rate (% pressure decreases per minute)
Al	0.30
Zn	.23
Cd	.21
Ni	.19
Cu	.11
Sn	.25

the mercury arc—namely, absorption in the δ (1,0) band of nitric oxide, together with some absorption in the bands of the β-system, of which weak absorption of Hg 1849 (and perhaps of Zn 2025) constitute special examples.

The nature of the dependence of the reaction rate on nitric oxide pressure and its independence of nitrogen pressure indicated that the primary step is dissociation. The fact that the active radiation falls in a banded region of the spectrum proves that the dissociation process is one of predissociation.

This conclusion receives support in the emission spectrum of nitric oxide. Thus Kaplan[24] attributes the absence of bands with v' greater than 4 (and the unexpected weakness of ($v' = 4$) bands) to predissociation to a repulsive level which must intersect the upper $^2\Pi$ potential energy curve (*cf.* Fig. 9) somewhere in the neighborhood of $v' = 4$. A similar explanation may be offered to explain the fact that no δ emission bands have been observed[25] with v' greater than zero, although strong emission bands would be expected for higher vibration states, both on the basis of the Franck–Condon principle and of the distribution in absorption.

We expect that radiation absorbed by any of the bands which are marked with open circles in Fig. 8 would be photochemically active while radiation absorbed by bands marked with black circles would be inactive (except for some activity in the β (4,0) band).

Secondary Processes

Nature of the Dissociation Products.—The dissociation energy of nitrogen now seems to be pretty definitely fixed in the neighborhood of 7.34 volts.[26] Combining this value (equivalent to 169,350 calories per mole) with that of the heat of dissociation of oxygen[27] and with the heat of formation of nitric oxide at the absolute zero,[28] we obtain 121,950 calories as the molal heat of dissociation of nitric oxide into atoms, at zero degrees Kelvin. The energy associated with radiation of wave length 1830 Å. exceeds this dissociation energy of nitric oxide by approximately 33,600 calories. Since this is less than the energy necessary to put either atom into an excited electronic state the dissociation products must be the normal atoms. And since momentum, as well as energy, must be conserved in the dissociation, it is a simple matter to compute the kinetic energies given to the respective atoms in the process. These prove to be: for nitrogen, 17,630 calories per gram atom; for oxygen 15,690 calories per gram atom.

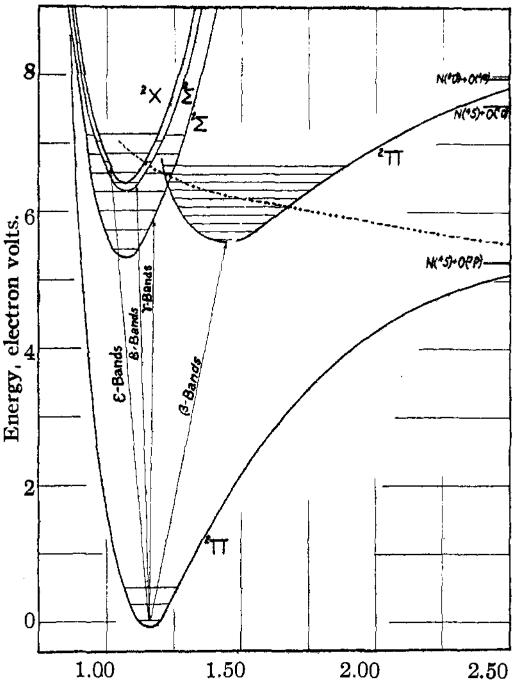

Fig. 9.—Potential energy curves for the known states of nitric oxide: – – – –, estimated position of the $^2\Sigma$ repulsive level responsible for predissociation in the region λ 1800–2000.

Atomic Reactions.—Stoichiometrically possible secondary processes are:

$N + NO = N_2 + O \qquad + 47{,}400 \qquad (15)$

$O + NO = O_2 + N \qquad - 4{,}600 \qquad (16)$

$2N + W = N_2 \qquad +169{,}350 \qquad (17)$

$2O + W = O_2 \qquad +117{,}350 \qquad (18)$

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[24] Kaplan, *Phys. Rev.*, **37**, 1406 (1931).

[25] Knauss, *ibid.*, **32**, 417 (1928); Schmid, *Z. Physik*, **59**, 42, 850 (1929); *ibid.*, **64**, 279 (1930).

[26] Herzberg and Sponer, *Z. physik. Chem.*, **B26**, 1 (1934); Mulliken, *Phys. Rev.*, **46**, 144 (1934). *Cf.* also Vegard, *Nature*, **134**, 696 (1934), and Lozier, *Phys. Rev.*, **44**, 575 (1933); *ibid.*, **45**, 840 (1934).

[27] Herzberg, *Z. physik. Chem.*, **B10**, 189 (1930).

[28] Giauque and Clayton, THIS JOURNAL, **55**, 4885 (1933).

$N + O + W = NO \qquad +121{,}950 \qquad (19)$

$O + N_2 = NO + N \qquad -47{,}400 \qquad (20)$

$O + N_2 = N_2O \qquad -12{,}600 \qquad (21)$

$N + O_2 = NO + O \qquad +4{,}600 \qquad (22)$

$N + O_2 + W = NO_2 \qquad +53{,}250 \qquad (23)$

$N + NO + W = N_2O \qquad +34{,}800 \qquad (24)$

$O + NO + W = NO_2 \qquad +48{,}650 \qquad (25)$

where W represents reaction with an adsorbed layer of atoms (or molecules) on the walls.

Of these, (20) and (21) are ruled out completely, and (16) reduced to an improbable occurrence, from energy considerations alone.[29]

A simple calculation, based on the measured rate constants, indicates that the accumulation of oxygen in the reaction system rarely exceeded 1×10^{-3} mm., and was, as a rule, considerably lower than this. This eliminates reaction (22), in comparison with (17) or (19), as a contender for the removal of nitrogen atoms.

At the lowest pressures (0.02 mm.) at which the photodecomposition was studied wall recombination of atoms by reactions (17), (18) and (19) should become a competing process with any gas phase reaction, such as (15). If this latter reaction should occur to an appreciable extent the rate would fall off, at these low pressures, more rapidly than with the first power of the pressure, which is contrary to the experimental results (Fig. 6). Furthermore, the quantum yield at high pressures, where bimolecular gas phase reactions would be favored, is less than unity while reaction (15) would, itself, lead to a quantum yield of two. Therefore we conclude that the recombinations of atoms on the walls, by reactions (17), (18) and (19), constitute nearly the entire secondary process. If the specific velocity constants of (17), (18) and (19) are numerically equal there should be a quantum yield of 0.5, but values from 0 to 1 are possible depending on the ratio of the mean of the rates of (17) and (18) to that of (19).[30]

Correlation with the Decomposition at Higher Pressures

Macdonald,[3] who made a brief study of the decomposition for the pressure range 50 to 650 millimeters, found an extinction coefficient for the active radiation which is only 2% of that we have computed for the active radiation at low pressures and about double that which we have measured for the absorption of λ 1849. From this we conclude that β-band absorption, followed by predissociation, is the primary mechanism of the high pressure decomposition. This is reasonable since, through this range of pressures, absorption in the β-bands must increase in almost direct proportion to the pressure while δ-absorption, already substantially complete even at four or five millimeters, can show little gain.

This conclusion differs from that of Macdonald, who pictured the primary mechanism as one of activation, followed by independent bimolecular reactions between activated and normal molecules. However, we find nothing in Macdonald's work (which was restricted almost entirely to the measurement of quantum yield and to the relation between reaction rate and light absorption) which precludes the predissociation mechanism.

Although the details of the secondary processes appear less certain, most of the arguments advanced in favor of atomic recombinations at the walls, for the low pressure decomposition, appear applicable also at the higher pressures. The one objection to this conclusion is Macdonald's purported observation of appreciable nitrous oxide among the reaction products. This may be accounted for in terms of reaction (24) although to produce 10% nitrous oxide among the products would require a very considerable amount of this reaction since nitrous oxide itself decomposes much faster than nitric oxide. This would require a quantum yield approaching 1.5, which is contrary to the facts. On the basis of what de-

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[29] In collision of a fast oxygen atom, with either nitrogen or nitric oxide in the gas phase, conservation of linear momentum exacts a minimum toll of 35% of the kinetic energy of the oxygen. This leaves only 10,000 calories, as a maximum, for activation. In only a small fraction of the collisions will this maximum energy be available. The great majority of collisions will be elastic due to steric and statistical factors and will dissipate the high energy of the oxygen in successive small losses. A further argument against (16) is the fact that nitrogen as a diluent did not affect the rate.

[30] Reactions (23), (24) and (25) are not excluded on any of the grounds advanced above, although wall reactions of this character appear considerably less probable than (17), (18) or (19). In any case (23), (24) or (25) must be considered in connection with the ultimate products which result from the photodecomposition of the NO_2 or N_2O, which are more rapidly decomposed than the NO. Norrish (ref. 10) has shown that NO_2 decomposes photochemically, by a bimolecular process, to yield NO and O_2. The net effect of (23) would thus be the complete reversal of the initial photodecomposition of nitric oxide, and a consequent quantum yield of zero if this process represented the normal method of removing the nitrogen atoms. It is clearly not of much relative importance in the actual decomposition. The net influence of (25) would be the substitution of a more complex process than (18) for the formation of molecular oxygen. Reactions (17) or (19) would still be required to account for the removal of atomic nitrogen. Macdonald (ref. 3) finds that the photodecomposition of N_2O yields N_2, NO and O_2 in the proportions of 3, 2 and 1. Thus the net effect of (24) is the substitution of a more complex process than (17) or (19) for the removal of nitrogen atoms and would lead to a quantum yield of 1.5, which is double the value observed by Macdonald. Any of these mechanisms (23, 24 or 25) require that one or more of the simple reactions (17, 18 or 19) be operative for the removal of one species of atom. It appears reasonable to credit the entire secondary process, in the main, to the simpler set of reactions.

scription Macdonald gives of his analytical procedure we feel that the presence of nitrous oxide in the reaction products may not be fully established.

Summary

The photochemical decomposition of nitric oxide has been studied, as a function of the pressure, over the pressure range 0.02 to 7 mm. with irradiation both from the mercury arc and from sparks between electrodes of aluminum, zinc, cadmium, nickel, copper and tin, respectively.

The final products of the reaction are nitrogen and oxygen although the latter is removed by a reaction which takes place during compression of the gas in the McLeod gage. This reaction produces a solid product, probably mercurous nitrite, which decomposes to liberate nitric oxide by a first order process which has a velocity constant of 1.5×10^{-2} hr.$^{-1}$.

The rate of decomposition proves to be directly proportional to the rate of light absorption for light of the effective wave length and is, at very low pressures, directly proportional to the pressure. The absorption of effective radiation follows Beer's law and has, for the reaction with the mercury arc, an extinction coefficient of about 2.9×10^{-2} per millimeter light path per millimeter of pressure. Nitrogen as a diluent does not appreciably influence the rate of decomposition. These results, alone, indicate primary dissociation as the first step in the process.

The use of filters containing solutions of ammonium chloride and of ammonium hydroxide places the effective mercury arc radiation below λ 1900. The use of a water filter indicates that the effective region is in the neighborhood of λ 1830. The strong resonance line at λ 1849 is ruled out, except for a relatively small influence at the higher pressures, by measurement of its absorption coefficient which proves to be one hundred times too small for the observed reaction. The alternative is the weak λ 1832 line of mercury which is strongly absorbed by the $(1', 0'')$ band of the δ-system of nitric oxide. The essential features of this interpretation are confirmed by the measurement of the decomposition under the influence of both filtered and unfiltered radiation from sparks between metal electrodes. The latter owe the greater portion of their effectiveness to a background of continuous radiation below λ 1900.

This interpretation of the primary process, which must be a predissociation since it occurs in a banded region of the spectrum, agrees well with the evidence for predissociation provided by the emission spectrum of nitric oxide.

Possible secondary processes are considered. All are believed ruled out on theoretical or experimental grounds, in comparison with combination of nitrogen and oxygen atoms on the walls.

Macdonald's work with high pressures of nitric oxide has been considered and it is concluded that the mechanism determined for the low pressure decomposition may also be applied to the results at higher pressures. However, predissociation from the upper levels of the β-bands, rather than the δ-bands, provides the primary step at these higher pressures.

COLUMBUS, OHIO RECEIVED JUNE 25, 1935

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Reduction Studies in the Morphine Series. VII. Pseudocodeinone[1]

BY ROBERT E. LUTZ AND LYNDON SMALL

Pharmacological studies which have been carried out at the University of Michigan coördinate with the chemical investigations at this Laboratory have shown that as regards general physiological action, the four codeine isomers may be grouped in pairs, codeine with allopseudocodeine, and isocodeine with pseudocodeine.[2] This pairing is based primarily upon the relative degree of convulsive and depressant actions exhibited by each of the drugs, upon their toxicity and upon their effective ratios in other respects when toxicity is taken into account. The same relationship holds for the four corresponding isomeric morphines, and suggests that the spatial arrangement of the alcoholic hydroxyl group may be of

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(1) The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia and the University of Michigan.

(2) Eddy, *J. Pharmacol.*, **45**, 361 (1932).