

Although odd and even rotation species exist in diatomic iodine gas, the data show that molecular rotation of the type existing in solid hydrogen does not occur in solid iodine. However, the results indicate that both para and ortho iodine carry their respective spin multiplicities into the solid state.

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PHOTOCHEMICAL STUDIES.

XII. THE PHOTOCHEMICAL REACTION BETWEEN NITRIC OXIDE AND MERCURY VAPOR

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The field of investigation initiated by the fundamental researches of Cario¹ and of Cario and Franck,² in which the spectra of thallium and of silver and the dissociation of hydrogen were produced through the agency of excited mercury atoms, has proved to be of great theoretical interest. These phenomena, ascribed to inelastic collisions of the second kind, have been shown to be quite universal and have been demonstrated for a large variety of reactions by many different workers. It is not necessary at this point to give a detailed list of such reactions.³

The exact mechanism of such photosensitized reactions is of some interest. The various experimental facts and theoretical ideas concerning the action of excited mercury on hydrogen and water vapor have been summarized and discussed recently by Beutler and Rabinowitsch.⁴ The production of ozone from oxygen, first studied by Dickinson and Sherrill,⁵ has been investigated from different angles by other investigators.⁶ Various mechanisms have been proposed to account for this reaction⁷ and among others one which depends, essentially, on the fact that oxygen is paramagnetic. It was with the object of throwing further light upon the mechanisms of some types of photosensitization that the present investigation, involving also the action of excited mercury on a paramagnetic gas, nitric oxide, was undertaken.

¹ Cario, *Z. Physik*, **10**, 185 (1922).

² Cario and Franck, *ibid.*, **11**, 161 (1922).

³ For a recent summary see Griffith and McKeown, "Photo-processes in Gaseous and Liquid Systems," Longmans, Green and Co., London, 1929, p. 582 *et seq.*

⁴ Beutler and Rabinowitsch, *Z. physik. Chem.*, **8B**, 403 (1930).

⁵ Dickinson and Sherrill, *Proc. Nat. Acad. Sci.*, **12**, 175 (1926).

⁶ Noyes, *THIS JOURNAL*, **49**, 3100 (1927); Leipunsky and Sagulin, *Z. physik. Chem.*, **1B**, 362 (1928); **3B**, 215 (1929); Noyes, *ibid.*, **2B**, 445 (1929).

⁷ See also Gaviola, *Phys. Rev.*, **33**, 309 (1929).

I. Experimental

The nitric oxide used in these experiments was prepared by the method of Winkler,⁸ introducing some of the modifications suggested by Johnston and Giauque.⁹ This method is based upon the reaction: $2\text{NO}_2^- + 4\text{H}^+ + 2\text{I}^- = 2\text{NO} + \text{I}_2 + 2\text{H}_2\text{O}$. The flask C (Fig. 1) was partially filled with a solution made by dissolving 75 g. of potassium nitrite and 38 g. of potassium iodide in 225 cc. of distilled water. The flask A contained a 50% (by weight) solution of sulfuric acid. The column D was filled with glass beads and contained concentrated sulfuric acid (about 93%). The column G also contained glass beads and was filled with a 50% solution of potassium hydroxide. The flask T served merely as a protective trap in case of accident. J contained anhydrous calcium chloride for removing most of the moisture and K contained phosphorus pentoxide.

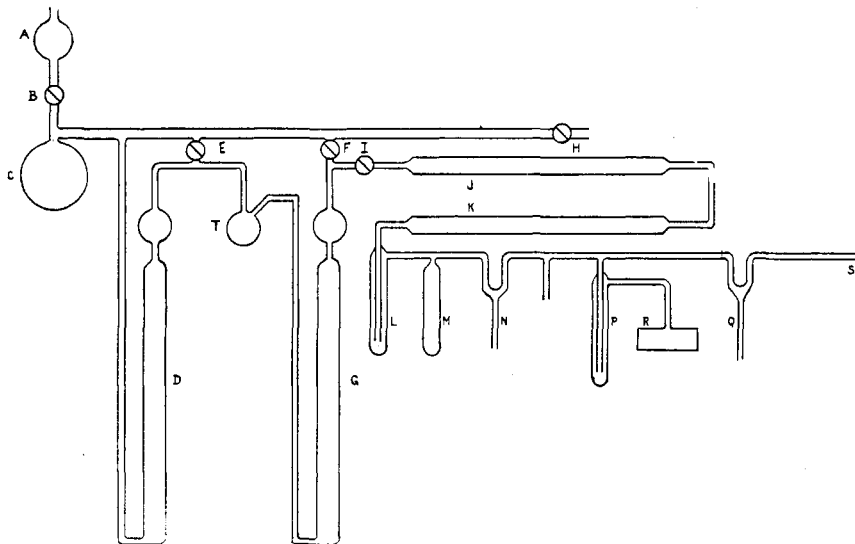


Fig. 1.

The stopcock I was closed and the mercury in cut-offs N and Q was lowered. The entire apparatus as far as I was then evacuated with continual flaming to as low a pressure as could be obtained with a mercury diffusion pump. The stopcocks E and F were then opened and the gas preparation apparatus was evacuated through H by means of an oil pump. This evacuation was carried on until a low pressure was attained, limited largely by the vapor pressure of water over the solution in C. In this way practically all of the air in the gas phase and a large fraction of the air dissolved in the various solutions was eliminated. Stopcocks E, F and H were closed and a few drops of the sulfuric acid solution allowed to enter C through the stopcock B. The gas evolved bubbled through the 75-cm. column of sulfuric acid in D and then through the concentrated potassium hydroxide in G. Stopcocks E, F and H were opened and the gas pumped out. This process was repeated at least twice before gas was admitted to the main apparatus. Finally stopcocks E, F and H were closed and I opened. Nitric oxide was allowed to flow through the calcium chloride and phosphorus pentoxide tubes

⁸ Winkler, *Ber.*, **34**, 1408 (1901).

⁹ Johnston and Giauque. *THIS JOURNAL*, **51**, 3194 (1929).

for several minutes and then the mercury in the cut-off N was raised and liquid air was placed around the trap L. When sufficient nitric oxide had collected in L the stopcock I was closed. The amount of nitric oxide prepared was never large, usually only sufficient to exert about five centimeters pressure when the liquid air was removed from L. The liquid air was now removed from L and placed around M and the nitric oxide sublimed over. The last fraction was allowed to escape by lowering the mercury in N with the vacuum pumps attached to S in operation. This process of purification by sublimation was repeated at least three times before using any nitric oxide for an experiment.

The nitric oxide as it leaves C would contain as impurities some hydriodic acid, traces of nitrogen and iodine and unknown amounts of other oxides of nitrogen (with perhaps a small amount of free oxygen). The hydriodic acid is probably partially removed by the sulfuric acid. Passage of the gas through the concentrated potassium hydroxide should remove most of the iodine, the remaining traces of hydriodic acid and nitrogen dioxide. The only nitrogen oxide not accounted for would be N_2O , although this would probably not be formed in any appreciable quantity. It is quite soluble in water but probably would not be completely removed. The repeated distillations with liquid air would tend to eliminate practically all of the highly volatile impurities such as nitrogen and oxygen completely. The others, namely, hydriodic acid and the various foreign oxides of nitrogen, would have exceedingly low vapor pressures at the temperature of liquid air. They would probably not be removed completely by the distillation process.

The vapor pressure⁹ of nitric oxide at the temperature of boiling oxygen ($90.13^\circ K.$)¹⁰ is about 3.2 mm. and at the temperature of boiling nitrogen it is about 0.1 mm.¹¹ In most of the experiments described in the present paper, the pressure of nitric oxide used was not greater than 0.15 mm., so that the gas could be admitted to the reaction vessel from a trap immersed in liquid air. In these experiments the only possible volatile impurities were nitrogen and oxygen. These were swept away as far as possible by submitting the solid at liquid-air temperatures to a high vacuum, as well as by the process of sublimation already described. When pressures of several millimeters of nitric oxide were necessary, the liquid air was removed from the trap L and the gas coming off allowed to bubble through about one centimeter of mercury in the cut-off N. This would tend to remove those oxides of nitrogen which react readily with mercury and would also make it possible to use only the first portion of gas coming off from the solid. Since nitric oxide is much more volatile than any of the impurities (other than nitrogen and oxygen), this method should ensure a high purity of the gas used.

The pressures were all measured by means of a McLeod gage.

The reaction vessel was of fused quartz, 25 mm. in diameter and 48 mm. in length. It was sealed to the vacuum line by a graded quartz to pyrex seal. No stopcocks or other sources of organic impurities were present in the line between the two cut-offs N and Q. The admission of gas to the line while L was immersed in liquid air should ensure absence of organic vapors as impurities. In certain of the later experiments a reaction vessel made of Corex glass was used. This glass may be sealed directly to pyrex.

The quartz mercury arc lamp and the reaction vessel were both immersed in a water-bath. The distance from the lamp to the window of the reaction vessel was negligible. The current through the lamp was supplied by a motor generator. The variations between runs is to be ascribed undoubtedly to variations in voltage of the line supplying the lamp.

¹⁰ Giauque and Johnston, *THIS JOURNAL*, 51, 2313 (1929).

¹¹ Calculated from the formula given by Giauque and Johnston,⁹ although their data did not extend to such low temperatures.

II. Results

The first object of the experiments was to determine the effect of pressure of nitric oxide on the rate of the reaction. In the reaction of excited mercury with oxygen,^{5,6} a film of mercuric oxide was produced on the side of the reaction vessel toward the source of radiation. In the present experiments no such film was noticed.

It seems evident that the gas remaining in the reaction vessel after the completion of the reaction is nitrogen. This is rendered reasonable by the fact that the final pressure attained after very long exposure is always very close to one-half the initial pressure. That conditions are actually not quite as simple as this is indicated by the variation in pressure, both with and without illumination, after the pressure had attained approximately one-half the initial value. With continuous illumination the pressure would decrease to a value less than one-half the initial pressure, but on standing there would be a gradual pressure increase. It seemed impossible, however, to repeat this process indefinitely, for sooner or later the pressure decrease during illumination would cease and the pressure would gradually increase with or without illumination. Every precaution was taken to be sure that this increase was not due to a leak in the apparatus.

The reaction seems to lead to the production of nitrogen dioxide. The action of this gas on liquid mercury has been studied previously.¹² It is not exceedingly rapid at low pressures. The final reaction is supposed to be represented by the equation¹³ $4\text{Hg} + 2\text{NO}_2 = 4\text{HgO} + \text{N}_2$, but the initial step is almost certainly the formation of a mercuric or mercurous salt, perhaps a nitrite, which may then evolve nitrogen more slowly.

TABLE I
RESULTS OF A TYPICAL RUN

Reaction vessel, quartz.	Current, 5.8 amp.	Temp., 25°
Time, min.	Pressure, mm.	Pressure (calcd.), mm.
0	0.0339	(0.0339)
55	.0307	.0299
213	.0229	.0224
303	.0206	.0208
968	.0171	.0171

Table I shows the results obtained during a typical run. The values in the third column are calculated by means of the equation

$$(2.303/t) \log_{10} (p_0 - 1/2 p_0)/(p - 1/2 p_0) = 4.91 \cdot 10^{-3} \quad (1)$$

Many other runs were made and in all cases the reaction rate followed the equation

¹² Moore and Noyes, *THIS JOURNAL*, **46**, 1367 (1924); Moore, *ibid.*, **47**, 2932 (1925); Noyes, *Trans. Faraday Soc.*, **21**, 569 (1926); Pierce and Noyes, *THIS JOURNAL*, **50**, 2179 (1928).

¹³ "Watts' Dictionary of Chemistry," Longmans, Green and Co., London, **1894**, Vol. III, p. 566.

$$-dp/dt = k_1 (p - 1/2 p_0) \quad (2)$$

within the experimental error, p_0 being the initial pressure and p the pressure at the time t . Table II shows a typical run with Corex glass.

TABLE II

TYPICAL RUN WITH COREX GLASS

Reaction vessel, Corex.	Current, 6.3 amp.	Temp., 25°.	$k_1 = 1.45 \cdot 10^{-4}$
Time, min.	Pressure, mm.	Pressure (calcd.), mm.	
0	0.1285	0.1285	
175	.1260	.1270	
950	.1199	.1203	
1660	.1148	.1148	

In order to determine the possible effect of pressure on the values of the constant, k_1 , a series of runs was made at varying pressures with other conditions identical as nearly as possible. Nitric oxide from the same preparation was used and the runs followed each other as closely as possible. Table III shows the results obtained.

TABLE III

EXPERIMENTAL DATA

Time interval, min.	Initial pressure, mm.	Final pressure, mm.	Current, amp.	k_1
31	0.1178	0.1128	6.2	$2.9 \cdot 10^{-3}$
30	.0340	.0330	6.1	2.0
30	.00353	.00338	6.0	3.1

Similar series were made on two other occasions with results which showed no systematic variation of k_1 with pressure.

In order to ascertain whether the reaction was really due to the action of excited mercury, or whether it should not be ascribed either to some foreign gas acting as sensitizer or to direct photochemical decomposition of the nitric oxide, the trap P was, during several runs, immersed either in liquid ammonia (-33°) or in liquid air. Constants obtained under these conditions were uniformly much lower, in some cases being actually zero. The fact that the zero value was not always obtained is undoubtedly due to the insufficient time allowed for the complete removal of mercury vapor. In one case in which liquid air had no apparent effect, close examination showed mercury droplets to be present in the reaction vessel. These had undoubtedly been placed there in the process of flaming the line before the run. Table IV shows a summary of the constants obtained under various conditions.

One run was made at considerably higher pressures of nitric oxide. The initial pressure was 24.13 mm., the time three hours and the final pressure 23.37 mm., giving a value for k_1 of $3.7 \cdot 10^{-4}$. This indicates, as would be expected, that k_1 decreases with pressure. An experiment was made with the same nitric oxide after evacuating the line to a lower pressure. In this

TABLE IV
SUMMARY OF REACTION RATE CONSTANTS

Experimental conditions	k_1 (min. ⁻¹)
Quartz vessel	$4.7 \cdot 10^{-3}$
Quartz vessel, liq. NH ₃ on <i>P</i>	0.8
Quartz vessel, liq. air on <i>P</i>	.4
Corex vessel	$2.1 \cdot 10^{-4}$
Corex vessel, liq. air on <i>P</i>	0.35

way the presence of inhibiting impurities due to the preparation at higher pressures (see Sec. I) would be detected. A value of $4 \cdot 10^{-3}$ for k_1 was obtained, indicating that the rate was the same as for other lots of nitric oxide.

An attempt was made to determine the percentage transmission of the Corex glass for a wave length of 2536 Å. An average of four determinations gave 0.038 as the ratio of this radiation transmitted by Corex to that transmitted by quartz. That is, an exposure of about five seconds with quartz gave about the same darkening of the plate as an exposure of one hundred and thirty seconds with Corex. The experimental arrangement used in the study of the fluorescence of this line was used. This value should be considered as approximate. An attempt to make the measurement with a rotating sector gave even less reliable results due to the feeble transmission.

The experiments with Corex were carried out with a slightly higher average current through the mercury arc lamp than those with the quartz vessel. The ratio of rates (Corex/Quartz) as given in Table IV is 0.045, which should be considered as too high rather than too low. The square root of 0.038 is 0.19 and the square is 0.0014. Both of these values are considerably removed from 0.045, so that we feel safe in stating that the rate is proportional to the intensity of the resonance radiation.

Studies were also made of the quenching of the fluorescence of mercury vapor by nitric oxide. The apparatus shown schematically in Fig. 2 was used. A is a mercury arc lamp of the vertical type with the lower part immersed in water kept at room temperature. B is a quartz lens and C is the fluorescence tube, approximately 80 cm. in length and tapered and bent over at the end to reduce back reflection in the manner described by Hughes and Thomas.¹⁴ The slit of the spectrograph is shown at D. The various parts of the apparatus were placed in such a manner that radiation was not directly reflected into the spectrograph.

With short exposures (up to about one minute) the 2536 Å. line of mercury alone was shown on the photographic plate. With exposures of several minutes a few other lines could be detected, but especially those at 3132, 3654, 4046, 4358 and 5461 Å. These lines are denoted as ($3^3D_1 \rightarrow 2^3P_2$), ($3^3D_2 \rightarrow 2^3P_2$), ($2^3S_1 \rightarrow 2P_0$), ($2^3S_1 \rightarrow 2^3P_1$) and ($2^3S_1 \rightarrow 2^3P_2$),

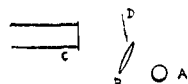


Fig. 2.

¹⁴ Hughes and Thomas, *Phys. Rev.*, 30, 466 (1927).

respectively, all of which have initial energy levels which may be produced from the excited state (2^3P_1) by the absorption of lines emitted by the mercury arc. It seems safe to say that very little, if any, reflected radiation need be considered in interpreting these experiments. We assume, therefore, that the intensity of the 2536 Å. as indicated by the spectrograph is proportional to the intensity of the fluorescence.

In determining the extent to which nitric oxide quenches the fluorescence of mercury vapor, exposures were made of five seconds' duration at intervals of one centimeter on the photographic plate with mercury vapor in the fluorescence tube in a high vacuum. Nitric oxide was then admitted and exposures of 5, 10, 15, etc., seconds were made in such a way that they alternated on the photographic plate with those without nitric oxide. Visual comparison was used to ascertain equality of intensity. The average of three plates showed that thirty-three seconds with nitric oxide at a pressure of 6.1 mm. gave the same blackening of the plate as five seconds without. With 2.0 mm. of nitric oxide the ratio was 18/5. Hydrogen was used as a comparison. The hydrogen was not specially purified except by passage through a liquid-air trap. With 6.0 mm. of hydrogen the ratio found was 100/5.

III. Theoretical

The present work was undertaken because nitric oxide is a paramagnetic gas. All, or nearly all, of the homogeneous gas reactions which have been proved definitely to be of the third order, involve nitric oxide.¹⁵ This may indicate that the paramagnetic character of these molecules renders reactions involving triple collisions more probable than for ordinary gases. Hinshelwood¹⁵ has summarized arguments against the existence of N_2O_2 as a definite intermediate.

The line spectrum of mercury has been quite satisfactorily analyzed.¹⁶ The normal state is designated as 1S_0 , with no resultant electron spin to be ascribed to the kernel and the two valence electrons (s electrons) with their spins antiparallel, giving a resultant of zero. This state, then, should be essentially non-magnetic. The resonance line (2536 Å.) involves in absorption a $^1S_0 \rightarrow ^3P_1$ transition. In the triplet state produced when mercury vapor absorbs this radiation, the electron spins are parallel instead of antiparallel and the atom as a whole now possesses a net electronic orbital angular momentum. This should mean that excited mercury is paramagnetic. Further details concerning the mercury spectrum need not be given here.

The spectrum of nitric oxide has received a great deal of attention. The

¹⁵ Hinshelwood, *Chem. Reviews*, **3**, 237 (1926).

¹⁶ See, for example, Grotrian, "Graphische Darstellung der Spektren von Atomen und Ionen mit ein, zwei und drei Valenzelektronen," Julius Springer, Berlin, 1928, Vol. II, p. 78.

nitric oxide molecule contains an odd number of electrons and the normal state is a ${}^2\Pi_{1/2, 1/2}$ state. For reasons which need not be given here¹⁷ the ${}^2\Pi_{1/2}$ state will be nearly non-magnetic for small values of the resultant quantum number J , while the ${}^2\Pi_{3/2}$ state will be paramagnetic. The works of Sponer,¹⁸ Sponer and Hopfield,¹⁹ Jenkins, Barton and Mulliken,²⁰ Guillery²¹ and Schmid²² have shown that the β , γ and δ bands in all probability have as the same final state the normal ${}^2\Pi$ state. The upper states seem to be best described as ${}^2\Sigma$, ${}^2\Pi$ and ${}^2\Sigma$ states, respectively.²³ In addition to the normal doublets, NO shows λ -type doubling.²⁴

The various electron energy levels for NO are given as follows:²³

X level (${}^2\Pi$)	0 volt
A (${}^2\Sigma$)	5.45 volts
B (${}^2\Pi$)	5.60 volts
C (${}^2\Sigma$)	6.45 volts
D (${}^2\Sigma$)	6.58 volts

The β , γ and δ band systems (X-B, X-A, X-C, resp.), extend from about 2250 Å. toward shorter wave lengths. Since all of these bands have the normal ${}^2\Pi$ state as the final state in emission, they should also be observed in absorption. In the experiments described in the present paper, the absorption should be exceedingly feeble, both on account of the low pressures used and because of the fact that a cooled mercury arc lamp gives practically no continuous emission in this region. In view of the results obtained at higher pressures and the fact that the elimination of mercury vapor by liquid air practically stops the reaction, direct absorption of radiation by nitric oxide would seem to be unimportant in the present work.

Mulliken²³ has concluded that the normal ${}^2\Pi$ state of nitric oxide should separate adiabatically into a normal oxygen atom (3P) and a normal nitrogen atom (4S) at the convergence limit of its vibration levels. He gives the value of 7.9 volts for the energy of dissociation. This value is certainly subject to a large uncertainty. The heat of dissociation of nitrogen is fixed at a probable value corresponding to 9–9.5 volts,²⁵ while that of oxygen is subject to an even greater uncertainty,²⁶ but may be placed between the

¹⁷ Van Vleck, *Phys. Rev.*, **31**, 608 (1928).

¹⁸ Sponer, *Nature*, **117**, 81 (1926).

¹⁹ Sponer and Hopfield, *Phys. Rev.*, **27**, 640 (1926).

²⁰ Jenkins, Barton and Mulliken, *ibid.*, **30**, 150 (1927).

²¹ Guillery, *Z. Physik*, **42**, 121 (1927).

²² Schmid, *ibid.*, **59**, 42 (1929); **64**, 279 (1930).

²³ Birge and Sponer, *Phys. Rev.*, **28**, 259 (1926); Mulliken, *ibid.*, **32**, 186, 761 (1928); *Chem. Reviews*, **6**, 524 (1929).

²⁴ Mulliken, *Phys. Rev.*, **33**, 508 (1929).

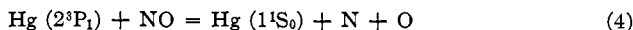
²⁵ Birge, *ibid.*, **34**, 1062 (1929).

²⁶ Birge and Sponer, *ibid.*, **28**, 267 (1926); Herzberg, *Z. physik. Chem.*, **4B**, 223 (1929); Copeland, *THIS JOURNAL*, **52**, 2581 (1930); Rodebush and Troxel, *ibid.*, **52**, 3467 (1930); Sommer, *Naturwissenschaften*, **18**, 752 (1930); Herzberg, *Z. physik. Chem.*, **10B**, 189 (1930).

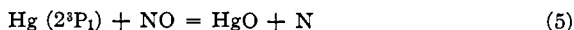
limits of 5.1 and 7 volts, with the probability that the correct value is near the lower limit. The heat of formation of nitric oxide from the elements corresponds to 0.94 volt.²⁷ We may now set up the following relationships:

$$\begin{array}{r}
 \text{NO} = \frac{1}{2} \text{N}_2 + \frac{1}{2} \text{O}_2; \Delta E = +0.94 \text{ v.} \\
 \frac{1}{2} \text{N}_2 = \text{N}; \Delta E = -4.5 \text{ to } -4.75 \text{ v.} \\
 \frac{1}{2} \text{O}_2 = \text{O}; \Delta E = -2.55 \text{ to } -3.5 \text{ v.} \\
 \hline
 \text{NO} = \text{N} + \text{O}; \Delta E = -6.1 \text{ to } -7.3 \text{ v.} \quad (3)
 \end{array}$$

Since the minimum energy of dissociation of nitric oxide exceeds the 4.9 volt energy of excitation of 2^3P_1 state of mercury by 1.2 volts, the reaction

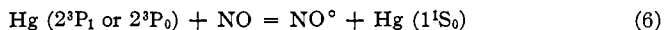


may be considered as impossible. However, if the heat of vaporization of mercury is taken as equivalent to 0.55 volt, the heat of formation of mercuric oxide from the elements as 0.93 volt, the reaction

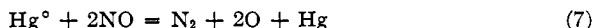


is found to be exoenergetic to the extent of 2.6 to 2.8 volts. This value is too large by an amount corresponding to the heat of sublimation of mercuric oxide. The latter is not known but certainly should not exceed one volt. Reaction 5 should, therefore, be considered as thermodynamically possible.

Two other possible primary steps may be considered: (1) that represented by the equation



where NO° represents an excited nitric oxide molecule. Since the lowest excited electron level of nitric oxide lies 5.45 volts above the normal, NO° would, in all probability, represent a molecule in the normal electron level but in a high vibration-rotation state. (2) An excited or metastable mercury atom may stay associated with a nitric oxide molecule a sufficient length of time to render the equivalent of a triple collision possible. The reaction could then be represented by



or some other reaction of this general type.

The effect of various gases in quenching the fluorescence of mercury vapor has been the subject of several recent investigations.^{28,29,30} The quenching may be ascribed to three different types of process: (1) loss of energy by the mercury atom due to a simple collision of the second kind with the production of a normal 1^1S_0 atom. This probably occurs when the spectra of thallium and of silver are produced.¹ (2) A definite chemical reaction

²⁷ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 560.

²⁸ Stuart, *Z. Physik*, **32**, 262 (1925).

²⁹ Gaviola, *Phys. Rev.*, **33**, 309; **34**, 1049, 1373 (1929); **35**, 1226 (1930).

³⁰ Zemansky, *ibid.*, **31**, 812 (1928); **36**, 919, 219 (1930).

may take place. This may be the case with oxygen and hydrogen.³¹ (3) Loss of only a small amount of energy (0.218 volt) with the production of a 2^3P_0 mercury atom. This small amount of energy may appear as energy of vibration and rotation of the quenching molecule. Using the ideas of Kallmann and London,³² Zemansky³⁰ has shown that quenching is most apt to occur by this mechanism when the quenching molecule has a vibration level differing from the normal by approximately $(0.218 + \frac{1}{2}kT)$ volt. This process is of importance for such molecules as CH_4 , H_2O , CO , CO_2 and N_2 .

The first vibration level of nitric oxide lies 0.231 volt above the zero vibration level.³³ This differs from 0.218 volt by 0.013 volt and, according to Zemansky,³⁰ this should mean that NO would have an exceedingly large "effective cross section for quenching." In fact the cross section should be larger than for any gas given in his diagram.

In the experiments described above, nitric oxide was shown to quench the resonance radiation of mercury to the extent of 72% at a pressure of 2 mm. and 85% at 6 mm. The method used was not capable of the highest precision; moreover the optical arrangement was different from that used by Zemansky,³⁰ so that a direct comparison with other gases is impossible. A rough calculation shows that the effective cross section for quenching is approximately $2 \cdot 10^{-16}$ sq. cm., not as high as for NH_3 , C_4H_{10} , CO and CO_2 , but larger than for H_2O , C_2H_6 , CH_4 and N_2 . The pressure for half quenching would be slightly less than one millimeter, which is lower than the values for other gases studied by Stuart²⁸ with the exception of H_2 , O_2 and CO . Hydrogen used in the same apparatus showed a quenching of 95%, which agrees within about 1% with the value calculated by the method of Gaviola.²⁹

If the quenching in nitric oxide is due to $2^3P_1 \rightarrow 2^3P_0$ transitions, at higher temperatures the quenching should be noticeably less because there are more collisions capable of causing the reverse process.³⁴ This experiment was tried, using a cell made entirely of fused quartz. There was much more scattering in this cell than in the one used previously. After proper corrections the results at room temperature agreed fairly satisfactorily with those obtained with the other cell. At a temperature of from 600 to 700°, 7 mm. of nitric oxide gave approximately 10% less

³¹ Cf. Zemansky, Ref. 30. A slight error seems to have crept into his consideration of the possibility of the reaction $Hg^+ + O_2 = HgO + O$. This reaction should be exoenergetic to the extent of about 3 volts, a value which is in error by an amount corresponding to the heat of sublimation of mercuric oxide. For other arguments against this mechanism see Dickinson and Sherrill, Ref. 5 and Noyes, Ref. 6.

³² Kallmann and London, *Z. physik. Chem.*, **2B**, 207 (1929).

³³ "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. V, p. 415.

³⁴ See Cario and Franck, *Z. Physik*, **17**, 202 (1923).

quenching than at room temperature. This is an average value obtained in seven different runs. At similar temperatures Cario and Franck⁸⁴ found nitrogen to be practically without effect in quenching the fluorescence of mercury vapor. Due to the possibility of introducing impurities it was not advisable to try high pressures of nitric oxide and there is, therefore, the probability that part of the 2^3P_0 atoms are removed by the walls. Moreover nitric oxide quenches the fluorescence of mercury vapor much more effectively than nitrogen. It is questionable whether the quenching should become zero at the temperatures used even if it were due entirely to the production of 2^3P_0 atoms. For reasons to be given later it seems certain that this mechanism is not the only one, but the results do not disprove the presence of some collisions of this type. In fact it seems probable that part of the quenching is to be ascribed to the production of 2^3P_0 atoms.

At 25° the following distribution of nitric oxide molecules among the various vibration states is obtained⁸⁵ (neglecting λ -type doubling)

$^2\Pi_{1/2}$	$v = 0$	65.04%
$^2\Pi_{1/2}$	$v = 1$	0.477%
$^2\Pi_{1/2}$	$v = 2$	0.004%
$^2\Pi_{3/2}$	$v = 0$	34.23%
$^2\Pi_{3/2}$	$v = 1$	0.250%
$^2\Pi_{3/2}$	$v = 2$	0.0021%

Thus a small but definite fraction of the molecules have a vibrational quantum number of 1. If the majority of the quenching is ascribed to the process $\text{NO} (^2\Pi, v = 0) + \text{Hg} (2^3P_1) = \text{NO} (^2\Pi, v = 1) + \text{Hg} (2^3P_0)$, certain of the facts presented above may be tentatively explained. At low pressures the 2^3P_0 atoms would diffuse largely to the walls and be converted to normal atoms. As the pressure is increased, the chance for reversal of the above process before the metastable atoms reached the walls would be increased. Thus the quenching at higher pressures could not be calculated by a simple formula from that at low pressures. This would be independent of any effect due to broadening of the absorption line, etc. The qualitative results presented above indicate this to be the case. The lower quenching at higher temperatures could also be explained in this manner.

It is impossible, however, to assume that nitric oxide molecules with a vibrational quantum number of 1 are appreciably more reactive than those with $v = 0$. Otherwise reaction would take place at room temperature and would have a very high temperature coefficient. There must, therefore, be some other process involved.

The 26th vibration level of nitric oxide lies 4.90 volts above the zero level and the 24th is found at 4.61 volts.⁸⁶ In optical absorption the forma-

⁸⁵ See Ref. 9, p. 3212.

⁸⁶ See Ref. 33. This value is calculated by means of the formula $\bar{\nu} = v(\omega'' - \omega''x''v)$, where $\bar{\nu}$ is the vibrational energy in cm.^{-1} and v is the vibrational quantum number. ω'' and $\omega''x''$ are constants, 1888.31 and 13.88, respectively. It is recognized that use of

tion of such high levels would be an exceedingly rare occurrence. One might expect their formation by collision of the second kind with 2^3P_1 (4.863 v.) and 2^3P_0 (4.645 v.) mercury atoms to be improbable in the absence of some special resonance effect. The first excited electron level of nitric oxide lies 5.45 volts above the normal and differs from 4.863 volts by an amount probably too large to be of importance in such an effect. However, 5.45 volts is only 5.22, 4.99 and 4.77 volts above the first, second and third vibration levels, respectively. One might expect, therefore, that molecules in vibration levels higher than the zero level would have some possibility of being excited to vibration levels as high as the 26th or 27th. Thus 4.81 volts will raise the first vibration level to the 27th and this differs by only 0.05 volt from the energy 2^3P_1 mercury atoms may give up. Calculations concerning this type of collision may only be made by approximate methods, but is it possible that the paramagnetic characters of the two bodies entering into the collision might be a determining factor in the type of resonance effect obtained?

There are two arguments against the mechanism represented by Equation 5. (1) Mercuric oxide is not deposited in the reaction vessel in the zone of illumination. (2) No bands could be detected which might be ascribed to either HgO or HgN molecules. This last argument should be given little weight since bands, if emitted, might lie in the infra-red. In the absence of a radiative process, such an exoenergetic mechanism would be improbable. Equation 5 would, however, satisfy the rate equations obtained.

Reaction 7 would seem to be excluded by the fact that only the first power of the nitric oxide pressure occurs in the rate equation. Other information concerning this mechanism is lacking.

It seems probable, therefore, that the mechanism is correctly represented by Equation 6. In order for this to be true, the life of NO° must be appreciably longer than the average time between collisions even at low pressures. From what is known of the life of molecules in high vibration states, this would not be unexpected.

It can now be shown that the rate of activation of nitric oxide should be given by the equation

$$+ d(NO^\circ)/dt = c_1c_2Ip/(c_1c_2p + c_3) \quad (8)$$

(NO°) = total number of activated molecules

I = number of quanta of resonance radiation absorbed per second

p = pressure of nitric oxide in millimeters

c_1 = number of collisions per second per excited mercury atom at 1 mm. pressure

c_2 = fraction of these collisions which lead to activation

$c_3 = 9.7 \cdot 10^8$ = constant for fluorescent decay of excited mercury

this formula for such high values of v is approximate, for higher powers of v should undoubtedly be included.

Comparison of the rate obtained at low pressures with the one obtained at 24 mm. shows that $c_1c_2 = 5 \cdot 10^6$. Equation 8 satisfies all of the requirements of the data presented above, for at low pressures c_1c_2p will be small compared to c_3 .

It is impossible to calculate c_1 and c_2 separately without introducing special assumptions. If $c_2 = 1$, the radius of the nitric oxide molecule is found to exceed the kinetic theory radius by a small amount if the radius of the excited mercury atom is taken equal to the kinetic theory radius of the normal mercury atom. If nitric oxide molecules in vibration levels above the lowest are alone capable of reacting, their effective radius would be found to be much larger.

Equation 8 with the values of the various constants determined from reaction rate data gives lower values for the quenching of the fluorescence of mercury vapor than those found experimentally. Thus quenching should be 51% at 2 mm. and 75% at 6 mm. as compared to 72 and 85% found experimentally. One would not expect precise agreement, however, due to the difference in optical arrangement between the reaction system and that used for the study of fluorescence, as well as on account of certain factors mentioned by Zemansky.³⁰ This is partial evidence that part of the quenching occurs by a process which does not lead to chemical reaction, presumably through the production of 2^3P_0 atoms.

Summary

1. The rate of pressure decrease in a system consisting of mercury vapor and nitric oxide illuminated with the resonance radiation of mercury has been studied.
2. The quenching of the fluorescence of mercury vapor by nitric oxide has been studied. It is probably to be ascribed to two processes.
3. Various mechanisms for the activation process are discussed. Probably a nitric oxide molecule in a high vibration state of the normal electron level is produced by collisions of the second kind.

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