

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

PHOTOCHEMICAL STUDIES. XIV. THE DECOMPOSITION OF NITROUS OXIDE SENSITIZED BY MERCURY VAPOR

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The reactions of nitrous oxide have been the subject of numerous recent publications,¹ while its Raman spectrum² and its infra-red³ and ultraviolet⁴ absorption spectra have also been studied. Various suggestions have been made as to the structure of the nitrous oxide molecule.^{1,5} The direct photochemical decomposition⁶ and the decompositions initiated by alpha particles⁷ and cathode rays⁸ have also been investigated. Taylor and Marshall⁹ studied the behavior of nitrous oxide in the presence of excited mercury, both with and without added hydrogen. Finally, the rate of thermal decomposition has been thoroughly investigated so that a more or less satisfactory explanation of the homogeneous thermal reaction is possible.¹⁰

It would not be within the scope of the present article to review the literature of nitrous oxide critically and we shall confine ourselves to a detailed mention of only those works which are intimately related to the present problem. The study of the decomposition of nitrous oxide initiated by excited mercury atoms should be of more than passing interest because of the possibility of at least two different primary steps and because the interaction of excited mercury with all of the gases, with perhaps one exception, which may be formed during the reaction has already been the subject of previous investigation.

I. Experimental

The nitrous oxide used in the present experiments was a commercial product. It was bubbled slowly through concentrated potassium hydroxide, dried by standing over phosphorus pentoxide and purified finally by fractional distillation with liquid air, only the middle fraction being retained for use. It was stored in a system free from stopcocks and wax joints. The reaction vessel was of fused quartz sealed to the line

¹ Cf. W. A. Noyes, Sr., *THIS JOURNAL*, 50, 2902 (1928); 53, 2137 (1931).

² See Kohlrausch, "Der Smekal-Raman Effekt," Julius Springer, Berlin, 1931, pp. 126, 180.

³ Plyler and Barker, *Phys. Rev.*, 38, 1827 (1931); see also Bailey and Cassie, *ibid.*, 39, 534 (1932).

⁴ Wulf and Melvin, *ibid.*, 39, 180 (1932).

⁵ Cf. Pauling, *THIS JOURNAL*, 53, 1386 (1931); see also Bailey and Cassie, Ref. 3.

⁶ Macdonald, *J. Chem. Soc.*, 1 (1928).

⁷ Wourtsel, *Le Radium*, 11, 289 (1919).

⁸ Gedye, *J. Chem. Soc.*, 3016 (1931).

⁹ Taylor and Marshall, *J. Phys. Chem.*, 29, 1140 (1925).

¹⁰ For review see Kassel, "The Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., Inc., New York, 1932, pp. 227-31; Musgrave and Hinshelwood, *Proc. Roy. Soc. (London)*, A135, 23 (1932).

by a graded seal. In the later part of the work two nearly identical reaction systems were used in such a way that variations in the intensity of the mercury arc lamp could be ascertained by using one as a control.

The vapor pressure of mercury in the reaction vessel was maintained constant by separating the vessel from the rest of the system by a trap immersed in an ice-water bath. The pressures were read on a McLeod gage. During the runs both the total pressure and the pressure of the residual gas after condensation with liquid air were measured. The latter pressures were corrected for the cooling of the trap by a constant factor obtained by filling the system with air.

Both the reaction vessel and the lamp were placed under water. In the early runs it became apparent that the light intensity was so high that the rate of reaction seemed to be determined by the rate of diffusion of mercury into the illuminated zone. For the major portion of the work Corex glass screens were placed between the reaction vessel and the lamp.

In certain experiments nitric oxide was added. This gas was prepared by the method previously described.¹¹

II. Results

(a) **The Absorption Spectrum of Nitrous Oxide.**—The absorption spectrum of nitrous oxide has been studied by Leifson¹² and by Wulf and Melvin.⁴ Neither of these authors found any banded absorption but only a continuum extending to wave lengths as long as 2300 Å. Wulf and Melvin⁴ found, moreover, that nitric oxide bands appeared after exposure of the nitrous oxide to radiation from the hydrogen discharge tube, thus agreeing with Macdonald⁶ that nitric oxide is one of the products of photochemical decomposition. It was not proved, however, that the nitric oxide was formed by the primary process although Wulf and Melvin consider this to be probable.

In the present work the absorption spectrum of nitrous oxide was photographed in a tube 3.6 meters in length at a pressure of one atmosphere. No bands could be located and the continuous absorption was found to begin at about 2250 Å., in good agreement with Wulf and Melvin.

These observations raise the question as to whether the present experiments deal with direct or sensitized decomposition of nitrous oxide. The pressures were, however, very low and Corex glass transmits very little radiation which would be absorbed directly by the gas. In addition, immersion of the trap in a carbon dioxide-ether mixture to reduce the vapor pressure of mercury to a low figure practically stopped the reaction. We feel justified in stating that the direct photochemical reaction is not of importance in these experiments.

(b) **The Interpretation of the Pressure Measurements.**—The following gases may possibly result from the decomposition of nitrous oxide: N₂, NO, O₂, NO₂, N₂O₃.¹³ The last named would not be of importance in these experiments.

¹¹ Noyes, *THIS JOURNAL*, 53, 514 (1931).

¹² Leifson, *Astrophys. J.*, 63, 73 (1926).

¹³ Melvin and Wulf, *Phys. Rev.*, 38, 2294 (1931).

At the pressures used nitrogen, nitric oxide and oxygen should remain in the gaseous state at liquid air temperatures, whereas nitrogen dioxide and undecomposed nitrous oxide should condense to give negligible pressures. The reaction between nitric oxide and oxygen is of the third order¹⁴ and should be exceedingly slow under the conditions of these experiments. Nitrogen dioxide might have been formed, however, when the pressure of gas uncondensed by liquid air was measured. Nitrogen dioxide reacts with liquid mercury⁸ according to the equation $6\text{NO}_2 + 2\text{Hg} = 2\text{Hg}(\text{NO}_3)_2 + \text{N}_2$. As will be shown later the total reaction in the present experiments may be written $\text{Hg} + \text{N}_2\text{O} = \text{HgO} + \text{N}_2$ so that very little if any nitrogen dioxide has been formed as an intermediate. Its presence is, therefore, ignored. Oxygen reacts rapidly with excited mercury with the eventual production of mercuric oxide.¹⁵ This gas could not be present to any appreciable extent as the results will be shown to indicate.

With the above facts in mind the total pressure during a run will be represented by the expression

$$P_t = P_{\text{NO}} + P_{\text{N}_2\text{O}} + P_{\text{N}_2} \quad (1)$$

Nitric oxide has a vapor pressure large enough so that it would not be condensed by liquid air at the low pressures prevailing in these experiments.¹¹ When mixtures of nitrous and nitric oxides were studied it became evident that condensation of the nitrous oxide removed a considerable portion of the nitric oxide from the gas phase. In fact some of the results indicated the existence of a definite compound $\text{NO} \cdot \text{N}_2\text{O}$ (or N_3O_2) stable at liquid air temperatures. Definite proof of the existence of this compound could not be obtained, but the results showed that approximately one molecule of nitric oxide is removed from the gas phase per molecule of nitrous oxide condensed. The extent of the removal will depend somewhat on conditions. The pressure of the gas uncondensed by liquid air will be given by

$$P_t = P_{\text{N}_2} + (1 - x)P_{\text{NO}} \quad (2)$$

where x is the fraction of the nitric oxide removed from the gas phase. When the nitrous oxide is present in large excess, x may be taken equal to unity.

If we consider part of the reaction to have proceeded according to the equation $\text{Hg} + \text{N}_2\text{O} = \text{N}_2 + \text{HgO}$ and the rest according to $\text{N}_2\text{O} = \text{NO} + \frac{1}{2}\text{N}_2$, we may obviously write

$$P_{\text{NO}} = 2(P_t - P_i) \quad (3)$$

¹⁴ See Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, London, 1926, p. 110.

¹⁵ Dickinson and Sherrill, *Proc. Nat. Acad. Sci.*, **12**, 175 (1926); Noyes, *This Journal*, **49**, 3100 (1927); Leipunsky and Sagulin, *Z. physik. Chem.*, **B1**, 362 (1928); **B3**, 215 (1929); Noyes, *ibid.*, **B2**, 445 (1929).

where P_i is the initial pressure of nitrous oxide. When the nitrous oxide is in excess we may write

$$P_{N_2O} = 2P_i - P_t - P_f \quad (4)$$

When the nitric oxide is in excess

$$P_{N_2O} = 1/2(P_t - P_f) \quad (5)$$

(c) **The Change of Pressure during Reaction.**—Figure 1 shows typical curves of total pressure and pressure of gas uncondensed by liquid air as a function of time. It will be noticed that the curves both pass through maxima and at the end of the run they become identical. The final pressure indicated on both curves is equal to the initial pressure of nitrous oxide within experimental error. This was always found to be true for reactions which were allowed to proceed to completion.

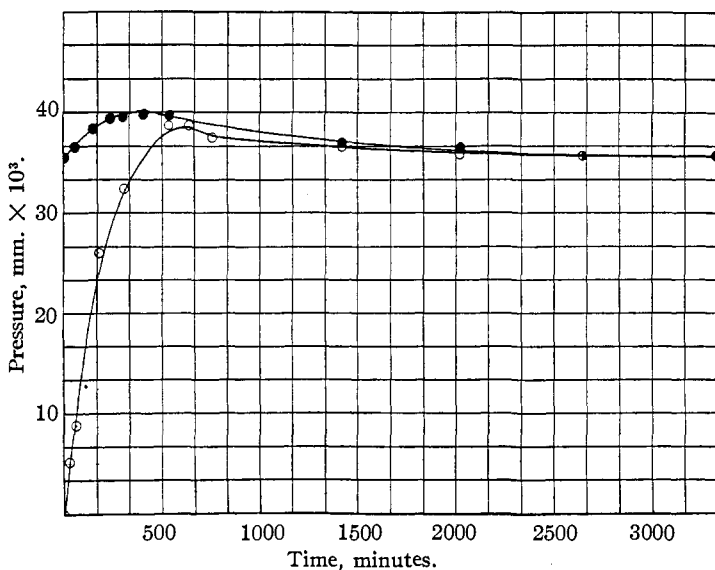


Fig. 1.—Lower curve, gas uncondensed by liquid air; upper curve, total gas.

These facts may be interpreted in the following manner. (1) The total net reaction is represented by the equation $Hg + N_2O = HgO + N_2$. (2) Nitric oxide is formed either by a primary or secondary reaction and reacts eventually with excited mercury to give mercuric oxide and nitrogen.¹¹ Side reactions leading to other final products must be relatively unimportant.

(d) **The Effect of Addition of Nitric Oxide.**—When nitric oxide was added to the nitrous oxide so that pressures of the two gases were both large, the total pressure decreased quite rapidly, thus indicating that nitric oxide was being decomposed more rapidly than it was being formed. When

the nitrous oxide was greatly in excess, this was still found to be the case, the pressure increase at the beginning being very slight or negligible followed by a fairly rapid decrease. Figure 2 shows variation of nitrous oxide pressure and of nitric oxide pressure in a system consisting initially of a mixture of the two gases.

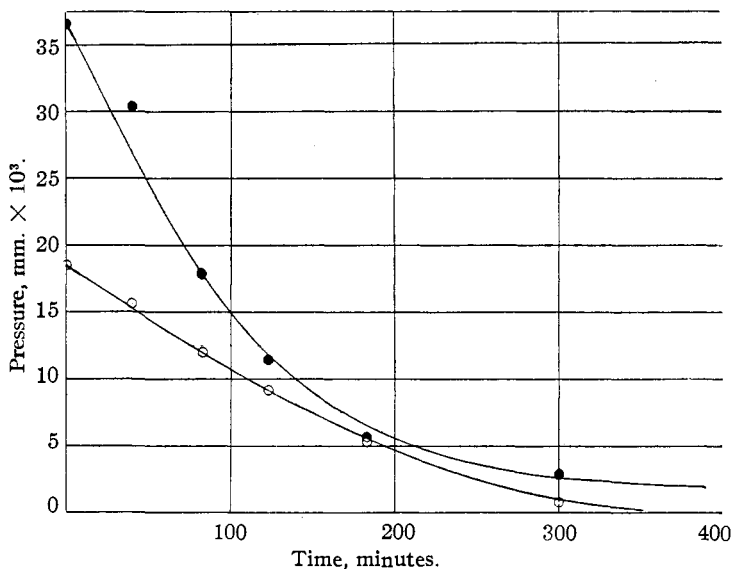


Fig. 2.—Upper curve, nitric oxide; lower curve, nitrous oxide.

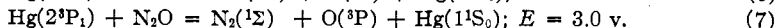
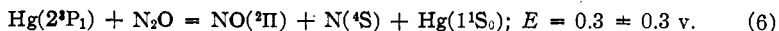
(e) **The Relative Rates of Reaction of Nitrous and Nitric Oxides.**—The rate of decomposition of nitric oxide is markedly affected by impurities, particularly oxygen and nitrous oxide. When carefully purified nitrous and nitric oxides were compared, it was found that the initial rate of reaction of the former was about twenty times that of the latter at the same pressures.

(f) **Variation of Reaction Rate with Light Intensity.**—Only a qualitative study of the variation of reaction rate with light intensity was made. As stated above the rate without a Corex filter was so rapid that it may have been determined by the rate of diffusion of mercury vapor into the illuminated zone. This was further verified by a study of the rate of reaction as a function of the initial pressure of nitrous oxide. The transmission of Corex was determined and it is safe to say that the rate is at least approximately proportional to the light intensity.

(g) **The Quenching of Mercury Vapor Fluorescence by Nitrous Oxide.**—Only a qualitative study of the quenching of mercury fluorescence by nitrous oxide was made. The method has been described previously.¹¹ The results did indicate a very high degree of quenching and a very large probable cross section.

III. Discussion of Results

(a) **The Primary Process.**—The possible primary actions of excited mercury on nitrous oxide may be represented by the equations¹⁶



Electronic excitation of either the nitrogen or nitric oxide molecules would be impossible, although either might separate with a certain amount of vibration energy.¹⁷ Certain higher levels of the nitrogen and oxygen atoms might be of importance. For nitrogen all doublet and quartet levels seem to be too high. For oxygen the ¹D level at 1.9 volts might be formed.⁸

Two principles may be used as guides for the prediction of the most probable primary step, although neither of them is applicable in a simple way to systems as complex as the one under consideration: (1) the principle of conservation of spin angular momentum.¹⁸ Reaction (7) or the corresponding reaction involving formation of a ¹D oxygen atom, would best obey the requirements of this principle. The change in electron spin of the mercury atom would, apparently, favor the formation of ³P oxygen atoms. It seems more necessary, however, for both fragments to have the same spin. (2) Kallmann and London¹⁹ and Rice²⁰ have shown that good resonance is essential to a high probability of energy transfer in collisions of the second kind. Thus equation (6) would be more probable than equation (7) unless in the latter case either the nitrogen molecule or the oxygen atom were in a high energy level.

The molecule of nitrous oxide is linear³ and unsymmetrical.^{1,3} It may have the structure N=N=O or be resonating, according to Pauling, between the structures N—N≡O and N≡N—O. Its electron structure is probably similar to that of carbon dioxide, which, according to Mulliken,²¹ is $\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\pi^4$, corresponding to a ¹Σ state for a diatomic molecule. A definite prediction as to the nature of the upper electron state is difficult,

¹⁶ The energies of dissociation of nitrogen [Birge, *Phys. Rev.*, **34**, 1062 (1929); Tate and Lozier, *ibid.*, **39**, 262 (1932)] and oxygen [Herzberg, *Z. physik. Chem.*, **B10**, 189 (1930)] were taken as 8.7 and 5.1 electron volts, respectively. The heats of formation of nitrous oxide [Ramsperger and Waddington, *Proc. Nat. Acad. Sci.*, **17**, 104 (1931)] and nitric oxide [Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 560] correspond to 0.74 and 0.94 electron volt.

¹⁷ For example, if the nitrogen molecules were formed in the tenth vibration level, nearly perfect resonance would be found. See "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. V, p. 415, for the data concerning vibration levels of nitrogen.

¹⁸ Wigner, *Nachr. Götting. Ges.*, 375 (1927); see Bates, *THIS JOURNAL*, **54**, 569 (1932), for a discussion of the applicability of this principle to systems involving excited mercury.

¹⁹ Kallmann and London, *Z. physik. Chem.*, **B2**, 207 (1929).

²⁰ Rice, *Proc. Nat. Acad. Sci.*, **17**, 34 (1931).

²¹ Mulliken, *Phys. Rev.*, **40**, 60 (1932).

although repulsion seems to exist between the dissociation products at all distances since no bands are observed even at high pressures with long lengths of path. From this one would expect a dissociation into a ^1D oxygen atom and a normal nitrogen molecule to be most probable. It is not improbable that a shift of one of the π bonding electrons by the absorption of radiation would produce a change of this type.

Farkas, Haber and Harteck²² find that nitrous oxide photosensitizes the hydrogen-oxygen reaction in the far ultraviolet. While these results may be interpreted in several different manners, these authors believe the reaction chains to be started by the initial production of oxygen atoms.

The evidence to be presented is somewhat inconclusive as to the nature of the primary step. If a chain is to be propagated, as seems necessary to explain the results of Macdonald,⁴ it must be by reactions of the type $\text{O} + \text{N}_2\text{O} = \text{O}_2 + \text{N}_2$ (or 2NO) or $\text{N} + \text{N}_2\text{O} = \text{NO} + \text{N}_2$, unless a nitrogen molecule in a high vibration state is considered to be effective in this respect. Musgrave and Hinshelwood¹⁰ use the reaction $\text{O} + \text{N}_2\text{O} = 2\text{NO}$ in interpreting the decomposition of nitrous oxide thermally at relatively low pressures.

Since one molecule of nitric oxide is not formed for each molecule of nitrous oxide decomposing even at the beginning of a run, the first step can hardly be (6) followed by $\text{N} + \text{N}_2\text{O} = \text{NO} + \text{N}_2$, unless some exceedingly probable reaction begins to use up nitric oxide immediately.

The behavior of mixtures of nitrous and nitric oxides indicates that nitric oxide is used up quite rapidly. Although nitric oxide alone decomposes with about one-twentieth the rate for pure nitrous oxide, in mixtures of the two gases its rate of disappearance is the larger of the two. This may be due partially to the fact that excited nitric oxide molecules¹¹ react more readily with nitrous oxide than with nitric oxide molecules and it may be due to reactions of the type $\text{N} + \text{NO} = \text{N}_2 + \text{O}$ or $\text{O} + \text{NO} = \text{O}_2 + \text{N}$. Even if the low recent value for the heat of dissociation of nitrogen (8.4 v.¹⁶) is assumed, the second of these reactions is endoenergetic to the extent of more than half a volt. It seems probable, therefore, that either ^1D oxygen atoms or nitrogen atoms are formed during the primary process. The data herein presented may be explained by assuming that both reactions take place simultaneously, but the data may best be interpreted by assuming the ^1D oxygen atoms.²³ Calculation of the probable energy of activation for a reaction of the type $\text{O} + \text{NO} = \text{O}_2 + \text{N}$, although subject to several uncertainties, indicates quite a low value.²⁴ This reaction does, however, violate the electron spin conservation rule.

²² Farkas, Haber and Harteck. *Z. Elektrochem.*, **36**, 711 (1930).

²³ Herzberg [*Z. physik. Chem.*, **B17**, 68 (1932)] has recently come to the conclusion that probably $^1\Sigma$ nitrogen molecules and ^1D oxygen atoms are produced by direct optical dissociation.

²⁴ Cf. Eyring and Polanyi, *Z. physik. Chem.*, **B12**, 279 (1931).

Some experiments were performed in which oxygen was added to the nitrous oxide. Here the results indicate that oxygen catalyzes the reaction $2\text{N}_2\text{O} = 2\text{NO} + \text{N}_2$, in addition to forming mercuric oxide,²⁵ and that when the gases were cooled in the liquid-air trap, nitrogen dioxide was formed from the union of nitric oxide and oxygen. Plausible mechanisms for this process may be advanced, but it seems probable that oxygen atoms (probably in excited levels) do react with nitrous oxide to form nitric oxide. For reasons given above nitrogen dioxide is probably not formed in appreciable quantity in the absence of added oxygen.

(b) **The Rate of Decomposition of Nitrous Oxide.**—The pressure of excited mercury atoms in the steady state will be

$$P_{\text{Hg}^{\circ}} = k_1 I / (k_2 P_{\text{N}_2\text{O}} + k_3 + f(P_x)) \quad (8)$$

where $k_1 I$ is the rate of increase of pressure of excited mercury atoms due to absorption of radiation of intensity I , k_2 is the constant for the bimolecular reaction between excited mercury atoms and nitrous oxide molecules, k_3 is the constant in the equation for the unimolecular rate of decay of excited mercury atoms by fluorescence and $f(P_x)$ is a term depending on the rate of quenching of mercury atoms by gases other than nitrous oxide. The rate of decomposition of nitrous oxide will be given by the equation

$$-dP_{\text{N}_2\text{O}}/dt = M k_2 P_{\text{Hg}^{\circ}} P_{\text{N}_2\text{O}} \quad (9)$$

in the absence of disturbing secondary reactions. M is the number of nitrous oxide molecules decomposing per molecule activated by collisions of the second kind with excited mercury. Equation (10) may be integrated if M is assumed to be constant and $f(P_x)$ is either known or assumed to be small compared to the other terms in the denominator of equation (8).

At the start of a run $f(P_x)$ is zero and other disturbing factors should be a minimum, so that by studying the initial rates of reaction at a series of pressures k_2/k_3 may be calculated. This ratio shows a fair degree of constancy from quite low pressures to pressures of several millimeters. The average value is 4.67×10^{-3} , if the unit of pressure is taken as 10^{-3} mm. Since k_3 is 9.7×10^8 sec.⁻¹, k_2 may be calculated. $1/k_2$ will be the mean time between collisions between excited mercury atoms and nitrous oxide molecules at a pressure of 10^{-3} mm. Using the familiar expressions of kinetic theory the value of σ^2 , the square of the sum of the radii of the nitrous oxide molecule and the excited mercury atom may be calculated. The average value is found to be about 100×10^{-16} sq. cm. This value may be compared with those found by Zemansky²⁶ and by Bates¹⁸ for other molecules by a study of their quenching of the fluorescence of mercury

²⁵ Cf. Dickinson and Sherrill, *Proc. Nat. Acad. Sci.*, **12**, 175 (1926); Noyes, THIS JOURNAL, **49**, 3100 (1927); Leipunsky and Sagulin, *Z. physik. Chem.*, **B1**, 362 (1928); **B3**, 215 (1929); Noyes, *ibid.*, **B2**, 445 (1929).

²⁶ Zemansky, *Phys. Rev.*, **31**, 812 (1928); **36**, 219, 919 (1930).

vapor. Suffice to say that this value is exceedingly large and agrees with the qualitative results presented above on the extent of quenching.

Integration of equation (9) gives

$$K_1(P_{N_2O} - P'_{N_2O}) + K_2 \log_e(P_{N_2O}/P'_{N_2O}) = t' - t \quad (10)$$

if $f(P_x)$ is ignored. $K_1 = 1/Mk_1I$; $K_2 = k_3/Mk_1k_2I$. Thus $K_1/K_2 = k_2/k_3$. Equation (10) is found to be of the right general form to fit the data, as is shown in Fig. 3, where the smooth curve is calculated with arbitrary values of K_1 and K_2 . The ratio of K_1 to K_2 calculated from a given run is much larger than k_2/k_3 found above and the introduction of a term corresponding to $f(P_x)$ only makes matters worse. The deviation is of such a nature that the logarithmic term is actually of less importance than theory would predict.

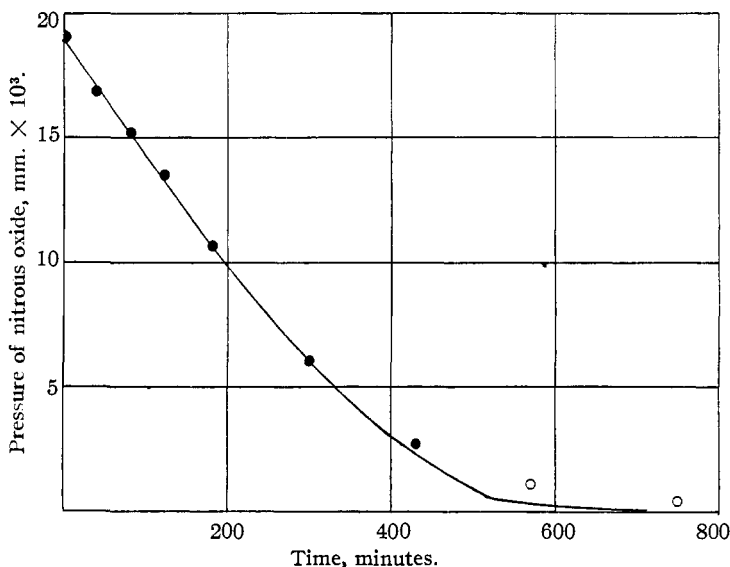


Fig. 3.

One is forced to one of two conclusions: (1) the effective cross section of the nitrous oxide molecule may be much larger than found above; (2) the products of the reaction may be instrumental in bringing about decomposition of nitrous oxide molecules. The former conclusion is entirely unreasonable, whereas the latter would involve a term accounting for a species of autocatalysis. This is to be expected in view of the behavior of mixtures of nitrous and nitric oxides. Previous work indicated that a nitric oxide molecule in a high rotation-vibration state may be produced upon collision with excited mercury atoms.¹¹ Even though Bates¹⁸ has shown nitric oxide to quench strongly the fluorescence of mercury, this gas does not have much inhibiting action on the decomposition of nitrous oxide. It may be,

therefore, that the excited nitric oxide molecules react readily with nitrous oxide. Inclusion of these postulates makes it possible to arrive at an exact rate equation, but since undeterminable constants would at the same time be introduced, the result would have little theoretical significance. The qualitative conclusion here given is, however, further made reasonable by the facts in the following section.

(c) **The Variation of Total Pressure with Time.**—It is well known that there is no appreciable thermal reaction between nitrous and nitric oxides at room temperature. Experiment showed also no noticeable reaction at 100 or at 200°, thus indicating that activation of these molecules to the first few vibration levels is insufficient to produce reaction between them. We may, therefore, neglect both the thermal reaction between these gases and reaction between nitrous oxide molecules and molecules of nitric oxide which have been raised to the second vibration level through quenching 2^3P_1 mercury atoms to the 2^3P_0 state.

At the beginning of the run one finds between 0.3 and 0.5 molecule of nitric oxide to be formed for each molecule of nitrous oxide disappearing. If the equation found by Macdonald⁶ for the direct reaction is identical with that followed by the sensitized reaction, the ratio should be 0.5.

At the point of maximum total pressure the rate of formation of nitric oxide should be equal to its rate of disappearance. If no disturbing influence intervenes, one could calculate, from the ratio P_{NO}/P_{N_2O} at this point, the ratios of the constants for the bimolecular reactions between these gases and excited mercury. The average value of P_{NO}/P_{N_2O} at the maximum is between three and four, although it shows some variation from run to run, and this may be compared with the fact that pure nitrous oxide decomposes about twenty times as rapidly as pure nitric oxide. Since all of the nitrous oxide does not decompose to give nitric oxide, this ratio should be actually between six and ten. On the other hand, when the reaction is nearly complete and the nitrous oxide has practically disappeared, the final pressure changes are very close to what one would predict for pure nitric oxide. This is further evidence that these gases influence each other during reaction.

(d) **Conclusions.**—The course of the reaction between excited mercury and nitrous oxide may be described as follows. (1) Either an excited oxygen atom and a nitrogen molecule or a normal nitrogen atom and a nitric oxide molecule are produced in the primary step. (2) The excited oxygen atom reacts with a nitrous oxide molecule to produce nitric oxide or the nitrogen atom reacts with nitrous oxide to produce nitrogen and nitric oxide. Both of the steps under (1) and (2) may take place simultaneously, but the initial formation of oxygen atoms seems probable. (3) Nitric oxide is used up either by collision with oxygen or with nitrogen atoms. (4) Nitric oxide molecules activated by collision with excited

mercury atoms react with nitrous oxide molecules. (5) Since the final equation of the complete reaction is $\text{Hg} + \text{N}_2\text{O} = \text{HgO} + \text{N}_2$, either ozone or excited oxygen molecules finally react with the mercury to produce mercuric oxide. This is considered to be a relatively fast reaction. The possibility of nitrogen dioxide is not considered to be of importance due to the fact that the final nitrogen pressure in long runs is equal to the initial nitrous oxide pressure. Some reaction of the type $\text{NO}_2 + \text{Hg} = \text{HgO} + \text{NO}$ may, however, take place in the gas phase. With nitric oxide and oxygen present, nitrogen dioxide would result when the gases are cooled in the liquid-air trap.

Summary

1. The total reaction between excited mercury and nitrous oxide may be represented by the equation $\text{Hg} + \text{N}_2\text{O} = \text{HgO} + \text{N}_2$.

2. Definite decision as to the nature of the initial step is not possible, although certain conclusions are drawn. The effects of adding oxygen and nitric oxide make identification of some steps possible.

3. As ascertained from reaction rate experiments the effective cross section of the nitrous oxide molecule as regards its interaction with excited mercury is very large.

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THE RAMAN SPECTRUM OF GERMANIUM TETRACHLORIDE

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The Raman spectrum of germanium tetrachloride was obtained by the method described in the next paper of this series. The frequencies of the Raman lines are given in Table I.

Considerable work, both experimental and theoretical, has been done upon the problem of the vibrational frequencies of molecules of the type

TABLE I
THE RAMAN LINES OF GERMANIUM TETRACHLORIDE

Raman	Raman lines, exciting lines and displacements in cm.^{-1}				
	Excit.	D	Raman	Excit.	D
22487 (1)	22938	451	23112 (5)	22938	174
22544 (10)	22938	394	23337 (6)	22938	399
22595 (1)	22995	400	24309 (6)	24705	396
22768 (6)	22938	170	24535 (2)	24705	171
22808 (6)	22938	130	24571 (2)	24705	134
23070 (5)	22938	132			

SUMMARY OF DISPLACEMENTS IN ORDER OF INTENSITY

397 (10), 132 (6), 171 (6), 451 (or 508) (1)