kins and Wormall[18] were able to introduce 60–70% of the theoretical amount of phenyl isocyanate (based upon a reaction with lysine). Clutton, Harington, Mead and Yuill[19,20] found the glucose content of their preparation of O-β-glucosido-N-carbobenzyloxy-tyrosyl serum albumin to be 11.5%. Gurin and Clarke[21] demonstrated that the ε-amino groups of gelatin reacted with benzenesulfochloride at *p*H 10 to 11 by the isolation of ε-monobenzenesulfonyl-*d*-lysine upon hydrolysis of the conjugate.

**Acknowledgments.**—The authors wish to thank the International Cancer Research Foundation for the grant supporting the research. They wish to express their appreciation of the advice and encouragement given by Professor L. F. Fieser. Thanks are also due to Professor E. J. Cohn and Dr. T. L. McMeekin of the Harvard Medical School for valuable suggestions regarding the preparation of the proteins and to Lyon Southworth for micro Kjeldahl determinations.

## Summary

Conjugated proteins containing the 1,2-benzanthryl radical as the prosthetic group have been prepared in a condition suitable for studies of their possible carcinogenic and serological properties. Coupling was effected by interaction of the protein with the hydrocarbon isocyanate in an aqueous dioxane medium. By ultraviolet spectrophotometry, it has been possible to establish the fact that true conjugation has occurred and to determine the degree of conjugation. Purified samples of 1,2-benzanthryl-10-carbamido horse serum albumin contain approximately twelve hydrocarbon residues per molecule, while the best samples of 1,2-benzanthryl-3-carbamido horse serum albumin contain eighteen hydrocarbon prosthetic groups per molecule.

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[18] Hopkins and Wormall, *Biochem. J.*, **27**, 740 (1933).

[19] Clutton, Harington and Mead, *ibid.*, **31**, 764 (1937).

[20] Clutton, Harington and Yuill, *ibid.*, **32**, 1111 (1938).

[21] Gurin and Clarke, *J. Biol. Chem.*, **107**, 395 (1934).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

# Photochemical Studies. XXXII. The Photochemical Reaction between Nitrous Oxide and Hydrogen

BY J. WILLIAM ZABOR[1] AND W. ALBERT NOYES, JR.

The photochemical decomposition of nitrous oxide gas has been studied for the general wave length region 1800–2000 Å.[2] Two mechanisms were proposed, either one of which would provide an adequate explanation for the data. In the first the primary process

$$N_2O + h\nu = N_2 + O \tag{1}$$

was presumed to be followed by the secondary reactions

$$O + N_2O = 2NO \tag{2}$$

and

$$O + O(+M) = O_2(+M) \tag{3}$$

The products are known to be[2,3,4] NO, $N_2$ and $O_2$. If the sole primary process is assumed to be reaction (1), the production of nitric oxide can only be obtained through reaction (2).

The second mechanism assumes that both primary process (1) and primary process (4)

$$N_2O + h\nu = NO + N \tag{4}$$

occur simultaneously. In order to obtain the correct quantum yields of products, it is necessary to assume further that these primary processes are followed by (3) plus (5) and (6)

$$N + N_2O = NO + N_2 \tag{5}$$

$$N + N(+M) = N_2(+M) \tag{6}$$

If this second mechanism is correct, the two primary processes must take place to approximately equal extents and (6) is relatively unimportant compared to (5).

A decision between these two mechanisms can be based on several types of investigation. The production of nitric oxide in the first mechanism would result from a reaction of oxygen atoms with nitrous oxide molecules. In a later investigation[5] an attempt was made to prove that this reaction

[1] Fellow for 1938–39 and for 1939–40 of the Sherman Clarke Fund in Research Chemistry of the University of Rochester.

[2] Noyes, *J. Chem. Phys.*, **5**, 807 (1937).

[3] Wulf and Melvin, *Phys. Rev.*, **39**, 180 (1932).

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

[5] Henriques, Duncan and Noyes, *J. Chem. Phys.*, **6**, 518 (1938)

takes place by obtaining oxygen atoms from the photochemical decomposition of nitrogen dioxide. While other reactions involving oxygen atoms seem to have quite low activation energies, it was demonstrated that the activation energy of (2) is probably more than 14,000 cal. and that this reaction would probably be unimportant compared to the recombination of oxygen atoms on the walls. From this rather negative result it seemed necessary to conclude that the first mechanism is not so probable as the second.

If the second mechanism is correct, the nitrogen atoms produced from the primary process might be detected under certain conditions by the formation of ammonia if hydrogen is added to the system. The present investigation has been undertaken with this in mind and offers further proof that in the photochemical decomposition of nitrous oxide both primary processes must occur.

The spectrum of nitrous oxide seems to be continuous from 1768–2068 Å.[6] At high pressures and at long path lengths absorption is observed to considerably longer wave lengths.[7] The products of dissociation by either primary process (1) or primary process (4) may be in ground states or in low lying excited states. The relationship of the spectra to the modes of dissociation has been discussed by Sponer and Bonner as well as in earlier articles.[2] No evidence, either spectroscopic or photochemical, indicates clearly the levels in which the products would be formed.

## I. Experimental Procedure and Results

Nitrous oxide was prepared by the method described in previous articles.[2,5,8] In experiments in which nitric oxide was added, this gas was prepared by the method of Johnston and Giauque.[9] Hydrogen from a cylinder was passed through a palladium diaphragm for purification.

The light source consisted of a condensed discharge between rotating aluminum disks. The main group of aluminum lines lying between about 1850 and 2000 Å, was isolated by the method of focal isolation. Since no other radiation from this source could be absorbed by the nitrous oxide, the complete elimination of longer wave lengths seemed unnecessary.

The quantum yields are referred to the hydrogen bromide actinometer, which was used in the same manner as that described.[2] For each quantum absorbed by hydrogen bromide it is assumed that one molecule of hydrogen is produced. Since mercury is present in the actinometer to react with the bromine, this figure should be very nearly correct.[10]

The determination of the amount of water was performed by first condensing all gases with liquid air and pumping to a high vacuum. This removes hydrogen, nitrogen, oxygen and probably most of the nitric oxide. The condensed gases were distilled with liquid air from one trap to another several times to aid in the removal of occluded gas. Between the two traps was placed a third trap immersed in dry-ice and ether which would condense water but none of the other gases present in the system (except hydrogen peroxide if it were present). Finally the trap containing gases condensed by liquid air was sealed off and the pressure of the water measured after removal of the dry-ice and ether from the middle trap. The pressure of water was measured by a Bourdon glass gage and usually amounted to one or two millimeters.

The main reaction system did not contain either mercury or stopcock grease. Gases entering the reaction system were passed through traps immersed in dry-ice and ether, and the system was sealed off before a run was started. Apiezon N grease was used on stopcocks through which gases were admitted to the line.

When experiments were carried out at higher temperatures, the cell was jacketed with a heating coil so that the temperature could be maintained reasonably constant over quite long periods of time.

The first experiments were performed merely with the object in view of determining whether both ammonia and water, as well as nitric oxide, are formed in a mixture of nitrous oxide and hydrogen when illuminated by radiation from the aluminum spark.

The qualitative detection of ammonia was performed by absorption spectroscopy using the well-known predissociation bands in the general region 2100–2400 Å. The spectrum was recorded with a small Littrow spectrograph, and the wave lengths were obtained from a reference iron arc spectrum; interpolations were made by means of a Hartmann dispersion formula. Table I shows the observed absorption bands compared with the known wave lengths of ammonia absorption as obtained by Duncan[11] and others.[12] Further identification of ammonia was carried out by the use of Nessler reagent, but since the amount of ammonia formed was always small, its exact determination proved to be difficult and in fact impossible.

TABLE I

ABSORPTION BANDS OF AMMONIA OBSERVED AFTER IRRADIATION

| Band centers | Dixon | Duncan | Leifson |
|---|---|---|---|
| 2213 + 2218 | | | 2210.1 |
| 2167 | 2167.3 | 2167.9 | 2166.5 |
| 2162 | 2164.5 | 2164.4 | |
| 2127 | 2126.3 | 2127.2 | 2127.5 |
| 2124 | 2123.6 | 2124.5 | |

The identification of nitric oxide was also performed by absorption spectroscopy and was based on the $\beta$ bands of that substance. These occur in the same general region

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(6) Duncan, *J. Chem. Phys.*, **4**, 638 (1936).

(7) Sponer and Bonner, *ibid.*, **8**, 33 (1940).

(8) Manning and Noyes, THIS JOURNAL, **54**, 3907 (1932).

(9) Johnston and Giauque, *ibid.*, **51**, 3194 (1929); see Noyes, *ibid.*, **53**, 514 (1931).

(10) Leighton and co-workers, private communication.

(11) Duncan, *Phys. Rev.*, **47**, 822 (1935).

(12) Dixon, *ibid.*, **43**, 711 (1933); Leifson, *Astrophys. J.*, **63**, 87 (1926).

of absorption as those of ammonia although the wave lengths are sufficiently different to remove all ambiguity. Semi-quantitative estimates of the amounts of ammonia and of nitric oxide could be made by comparison of the absorption spectra of mixtures containing unknown amounts of these gases with others obtained when the quantities were known.

The positive identification of water was accomplished by compressing the gases condensed by dry-ice and ether in a McLeod gage. These gases always contained a small amount of non-condensable gas in addition to water vapor. Let $D$ be the difference in level in centimeters between the two arms of the McLeod gage and let $H$ be the distance in centimeters from the mercury level to the top of the capillary attached to the bulb. If one of the gases in the bulb is condensable and has a vapor pressure in centimeters of $P_0$ at the temperature of the experiment, then

$$(D - P_0)HF = \text{pressure of non-condensable gas in the system} = P \qquad (7)$$

where $F$ is the factor by which pressures in centimeters are obtained from $H$ and $D$ providing only non-condensable gases are present. By rearrangement of equation (7) to give $D = (P/HF) + P_0$ it is evident that a plot of $D$ *vs.* $1/H$ should give a straight line with slope $P/F$, and with intercept with the axis $P_0$ when $1/H = 0$. Therefore by making a series of readings on the McLeod gage and by constructing such a plot, it is possible to obtain $P_0$, the vapor pressure of the condensable gas, by extrapolation. Figure 1 shows two such plots at temperatures of 24.7° and 26.0°, respectively. From the intercept the vapor pressure of water at the former temperature is found to be approximately 23.2 mm., whereas the correct value is about 23.4. At the latter temperature one obtains 26.4 mm. whereas the experimental value is about 25.2. These vapor pressures are sufficiently close to those of water and sufficiently far removed from those of any other substance which could be formed during the reaction to make it certain that water is the main condensable gas present. A more positive identification of water seemed to be unnecessary.

A series of runs was made to determine qualitatively the change in total pressure during reaction. If the over-all reaction may be written

$$N_2O + H_2 = N_2 + H_2O \qquad (8)$$

there should be no change in total pressure unless some of the water condenses. On the other hand, if some of the fragments from the nitrous oxide do not produce water, there should be a pressure increase as found for pure nitrous oxide.[2] If ammonia is formed, there might be a small pressure decrease. Table II presents some of the results obtained in such runs and indicates that, when hydrogen is present, there is a smaller pressure change than when it is absent. Indeed, several runs show a slight decrease in pressure which is probably due to adsorption of water by the walls rather than to ammonia formation. The results are shown graphically in Fig. 2 where the pressure changes are brought to the same basis by referring to the blanks with no hydrogen and taking 0.1 as the standard $\Delta P$ for pure nitrous oxide.

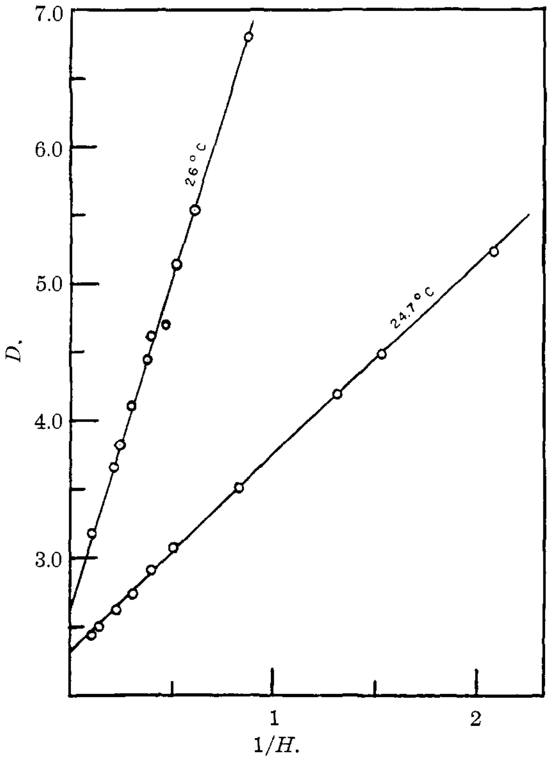

Fig. 1.—Identification of water.

The data may be taken to indicate that when sufficient hydrogen is present, the main course of the reaction may be represented by equation (8) but that when insufficient hydrogen is present, some pressure increase is observed. In run 9 the water from run 8 was left in the vessel so that the walls were saturated at the beginning of the run. During run 9 no pressure decrease was observed beyond experimental error, thus offering presumptive evidence that the pressure decrease in other runs was due to the adsorption of water vapor even though the pressure of water vapor had not attained the vapor pressure of water.

Table II

Change in Total Pressure during Reaction

| Run | $N_2O$ press., cm. | $H_2$ press., cm. | Irradiation, min. | $\Delta P$, cm. | Pressure of $H_2O$ formed, cm. |
|---|---|---|---|---|---|
| 1-a | 4.8 | | 30 | 0.088 | |
| 1-b | 4.8 | 4.8 | 30 | .030 | |
| 2-a | 5.0 | | 45 | .155 | |
| 2-b | 5.1 | 0.5 | 45 | .105 | |
| 3-a | 5.0 | | 45 | .119 | |
| 3-b | 5.0 | 0.9 | 45 | .071 | |
| 4-a | 5.1 | | 45 | .155 | |
| 4-b | 5.1 | 2.0 | 45 | .02 | |
| 5-a | 5.15 | | 30 | .11 | |
| 5-b | 5.9 | 10.6 | 300 | − .038 | 1.0 |
| 6-a | 5.7 | | 15 | .059 | |
| 6-b | 5.88 | 10.4 | 15 | − .011 | 0.102 |
| 6-c | 5.4 | 18.45 | 15 | − .029 | .108 |
| 7 | 2.7 | 11.2 | 20 | − .023 | .092 |
| 8 | 4.8 | 21.3 | 5 | − .0328 | |
| | | | 10 | − .0358 | |
| | | | 20 | − .0323 | |
| | | | 30 | − .0325 | |
| | | | 60 | − .0341 | .232 |
| 9 | 4.3 | 20.0 | 46 | − .003 | |
| 10[a] | 4.67 | 19.46 | 10 | − .0004 | |
| | | | 20 | + .0011 | |
| | | | 30 | .0041 | |
| | | | 40 | .0157 | |
| | | | 50 | .0129 | |
| | | | 60 | .0258 | .58 |

[a] Ammonia (at 0.0874 cm. pressure) was added for this run. The pressure increase is due, perhaps, to some photochemical decomposition of the ammonia.

The next experiments were made for the purpose of determining the products by absorption spectroscopy. The following facts were ascertained: (1) with pure nitrous oxide the bands of nitric oxide appear[3]; (2) if hydrogen is added, the nitric oxide bands are less intense than otherwise; (3) with sufficient hydrogen and after long periods of illumination no nitric oxide bands are observed, but the bands of ammonia are visible; (4) with added nitric oxide (0.15–0.20 mm.), no ammonia bands are observed even after very long exposure, but the nitric oxide bands increase in intensity; (5) when ammonia is added (0.9 mm.), this substance does not seem to be either used up or formed.

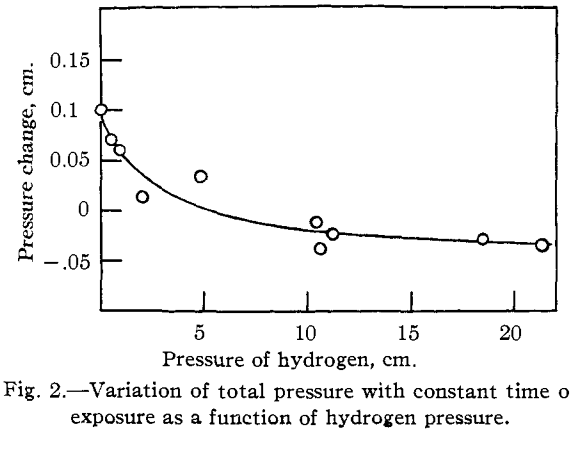

Fig. 2.—Variation of total pressure with constant time of exposure as a function of hydrogen pressure.

The rather strange fact that nitric oxide is not formed when hydrogen is present, unless it is present at the beginning of the experiment, seems at first glance to be mystifying. As data to be presented in the next few paragraphs will indicate, nitric oxide also reduces the quantum yield of water formation. The reaction

$$N + NO = N_2 + O \tag{9}$$

probably would not afford an explanation of the facts since oxygen atoms thereby produced should form water with the same efficiency as those from nitrous oxide. Furthermore, reaction (9) would lead to disappearance of nitric oxide.

The next experiments were performed to obtain the quantum yield of water formation as a function of several variables. These yields were determined by a method quite similar to that previously described.[2] Instead of reproducing all of the details, we will give merely one sample calculation and present the rest of the data by graphs.

By placing hydrogen bromide first in the reaction system and then by placing it in the actinometer system with the reaction cell evacuated, the transmission coefficient of the windows between the reaction vessel and the actinometer was found to be

$$\frac{\text{quanta absorbed in actinometer vessel}}{\text{quanta absorbed in reaction vessel}} = 0.358 \tag{10}$$

This figure may be expected to change when absorbing gas is present because the light is not strictly monochromatic. It was shown, however, that the change was small and, moreover, operated to affect the quantum yields in the opposite direction from errors due to adsorption of water vapor. The error introduced, therefore, is small compared to other errors.

A photronic cell was placed at a distance of about 15 cm. from the spark to intercept radiation which was not monochromatic but which could be used to ascertain fluctuations in light intensity. Current from the photronic cell was measured directly by a galvanometer with a resistance in series. The pressure of hydrogen produced in the actinometer per minute and per unit of light intensity measured by the photronic cell was determined from blank runs with the reaction vessel evacuated. This was found to be

$$dP_{H_2}/dt\ (1/D) = 0.0179\ F \qquad (11)$$

where $D$ is the deflection of the galvanometer and $F$ is the factor which converts the arbitrary units of the McLeod gage into cm. pressure ($F = 2.69 \times 10^{-4}$).

From the deflection of the galvanometer during the run it is now possible to calculate the pressure of hydrogen which would have been produced in the actinometer if the reaction vessel had been evacuated. By subtracting from this the pressure of hydrogen produced in the actinometer during the run and dividing by the factor 0.358 from equation (10), the pressure of hydrogen which would have been produced by the radiation absorbed during the run can be calculated. This can be converted into quanta by multiplying by $K$, the number of molecules per unit pressure per cc. at the temperature of the experiment and by the volume of the actinometer system.

In a sample run the following data were obtained:

(a) Pressure of hydrogen produced (reaction vessel evacuated) = 55.868 $F$
Time of irradiation, sixty minutes
Time of dark reaction, eighty minutes
Galvanometer deflection, 51.4 cm.
Dark reaction correction = 0.00761 $F$ per minute

$$\frac{(55.868 - 0.0076 \times 80)}{60 \times 51.4} F = 0.0181\ F = \text{pressure}$$

of hydrogen formed by photolysis per unit intensity per minute (12)

(b) Pressure of hydrogen (during run), 21.09 $F$
Time of irradiation, one-hundred and twenty minutes.
Time of dark reaction, one hundred and twenty-eight minutes
Galvanometer deflection, 50.4 cm.
$(21.09 - 128 \times 0.00761)\ F = 20.12\ F$ = pressure of hydrogen formed by photolysis (13)
Pressure of water formed, 0.163 cm.

(c) Pressure of hydrogen produced (reaction vessel evacuated) = 56.70 $F$
Time of irradiation, sixty minutes
Time of dark reaction, sixty-five minutes
Galvanometer deflection, 52.8 cm.

$$\frac{(56.70 - 65 \times 0.00761)}{52.80 \times 60} F = 0.0177\ F = \text{pressure}$$

of hydrogen produced by photolysis per unit light intensity per minute (14)

Average of (a) and (c), 0.0179 $F$
Pressure of hydrogen which would have been produced during (b) = $0.0179 \times 120 \times 50.4\ F = 108.26\ F$

$$\text{Quanta absorbed} = \frac{(108.26 - 20.12)F \times 459 \times K}{0.358} = 30.4\ K \qquad (15)$$

where 459 cc. is volume of actinometer system

Number of molecules of water formed = $0.163 \times 189\ K = 30.8\ K$ (16)
where volume of reaction system = 189 cc.
Quantum yield of water formation = $30.8\ K/30.4\ K = 1.01$ (17)

Figure 3 shows the quantum yield of water formation at constant pressure of nitrous oxide (6.3 cm.) as a function of the hydrogen pressure. It is evident that the quantum yield approaches a constant value of about one at sufficiently high pressures.

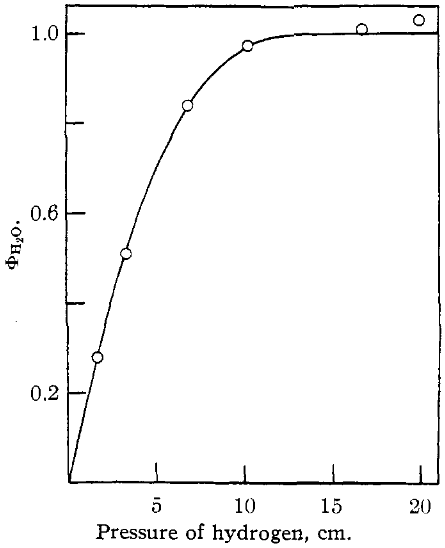

Fig. 3.—Variation of quantum yield of water formation with hydrogen pressure at constant nitrous oxide pressure (6.3 cm.) at 24°.

The effect of nitric oxide on the quantum yield is shown in Fig. 4. Small additions of nitric oxide cause a reduction in the quantum yield, which then passes through a minimum and finally rises above unity. An attempt to reduce the radiation absorbed by nitric oxide through the introduction

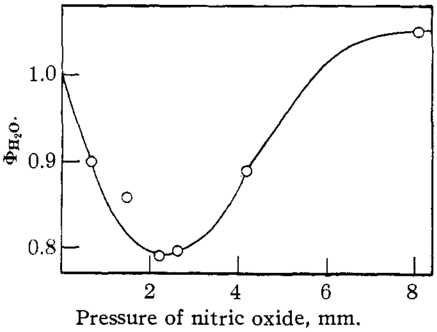

Fig. 4.—Variation of quantum yield of water formation with nitric oxide pressure at constant pressure of nitrous oxide (6.3 cm.) and constant pressure of hydrogen (15 cm.) at 24°.

of a filter of this substance proved to be unsatisfactory. The fraction of the radiation absorbed by the nitric oxide is difficult to calculate because the radiation was not monochromatic and Beer's law was not obeyed by either pure nitrous oxide or by pure nitric oxide.

The quantum yield of water formation when nitric oxide and hydrogen were irradiated without the presence of any nitrous oxide proved to be higher than unity and attained values in the neighborhood of 1.6. Since nitric oxide in this region of the spectrum dissociates into atoms,[13] it seems that both nitrogen atoms and oxygen atoms are capable of leading to water formation, although some combination to $O_2$ and $N_2$ evidently takes place. This fact undoubtedly accounts for the increase beyond unity of the quantum yield when sufficient nitric oxide is present.

The effect of temperature on the quantum yield of water formation at constant nitrous oxide pressure (6.3 cm.) and constant hydrogen pressure (3.44) is shown in Fig. 5. A plot of log $\Phi_{H_2O}$ *vs.* $1/T$ does not give a straight line.

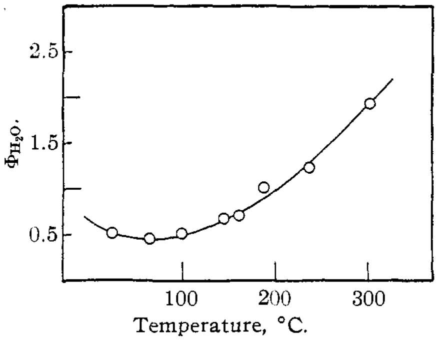

Fig. 5.—Effect of temperature on quantum yield of water formation at constant nitrous oxide pressure (6.3 cm.) and constant hydrogen pressure (3.44 cm.).

## II. Discussion of Results

The fact that ammonia and water are both formed when hydrogen is present with the nitrous oxide makes it appear probable that both primary processes (1) and (4) take place. This was indicated also by previous work.[2,5] Number (1) is necessitated by the fact that oxygen is one of the products when pure nitrous oxide is irradiated, and it seems impossible to account for ammonia formation unless nitrogen atoms are formed.

Even in a simple system such as this the number of secondary reactions is so large that it is very difficult to derive a satisfactory theoretical expression for the quantum yield. The introduction of all individual steps would lead to the inclusion of so many arbitrary constants that their evaluation would be impossible. Moreover, it would be difficult to prove that even the form of the expression presented a unique solution of the problem.

The data presented in this article are, however, compatible with the following mechanism:

$$\begin{aligned}
N_2O + h\nu &= N_2 + O && (18)\\
&= NO + N && (19)\\
O + H_2 &= H_2O && (20)\\
N + H_2 &= NH_2 && (21)\\
NH_2 + H_2 &= NH_3 + H && (22)\\
NH_2 + NO &= N_2 + H_2O && (23)\\
O + O(+M) &= O_2(+M) && (24)\\
N + N(+M) &= N_2(+M) && (25)\\
N + N_2O &= NO + N_2 && (26)\\
N + NO &= N_2 + O && (27)
\end{aligned}$$

In this reaction scheme it is not implied that equations (20), (21) and (23) necessarily take place as single steps.

Oxygen atoms seem always to lead to the production of water when sufficient hydrogen is present.[14] Hydrogen atoms with oxygen seem to lead to hydrogen peroxide. In the present instance water may be formed directly as indicated in equation (20), or it may result from the reactions

$$\begin{aligned}
O + H_2 &= OH + H && (28)\\
OH + H_2 &= H_2O + H && (29)
\end{aligned}$$

These reactions would, if subdivided further, merely complicate the mechanism without necessarily affording any better explanation of the data.

Reactions (18), (19), (20), (21) and (23) would give a quantum yield of unity for water formation. At low hydrogen pressures reactions (24), (25) and (26) would cause the yield to decrease and, indeed, approach zero at zero hydrogen pressure.

Since by the mechanism outlined and from the results in Fig. 4, nitric oxide plays an important role in water formation, the yield may depend on time with low hydrogen pressures where the amount of nitric oxide increases during a run. Thus the real quantum yields in Fig. 3 for low hydrogen pressure might be higher at zero time.

With sufficient nitric oxide present so that absorption by this substance becomes important, one must add the primary process

$$NO + h\nu = N + O \qquad (30)$$

In the absence of nitrous oxide, (30) followed by (20), (21) and (23) would lead to a quantum yield of water formation of 2, and this figure, as shown by the data, is approached.

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[13] Flory and Johnston, This Journal, **57**, 2641 (1935).

[14] See Smith and Napravnik, *ibid.*, **62**, 385 (1940).

The fact that the addition of small amounts of nitric oxide lowers the quantum yield, and the fact that the presence of nitric oxide promotes the further formation of this substance are difficult to explain unless the third bodies (M) in equations (24) and (25) are nitric oxide. The high efficiency of nitric oxide in this connection has no very sound theoretical basis other than that it should combine rather readily with either oxygen atoms or nitrogen atoms. The process of recombination could then be written, following a similar suggestion made by Taylor and Burton[15]

$$N + NO + N = N_2 + NO \qquad (31)$$

Reaction (23) has been assumed to take place by Bamford[16] when ammonia is photochemically decomposed in the presence of nitric oxide.

The fact that the yield of ammonia is always small, about one-fortieth or less the yield of water can be explained partially by reaction (23) and also at low pressures of hydrogen by reactions (25) and (26). The absence of ammonia formation when nitric oxide is added may be due either to (23) or (27) or (31) or all three.

The effect of temperature on the quantum yield is of such a nature that chains must occur at high temperatures. These could be brought about by some such reactions as

$$H + N_2O = OH + N_2 \qquad (32)$$

or

$$H + N_2O = NH + NO \qquad (33)$$

At the pressures used wall recombination of atoms will make long chains unlikely at least until quite high temperatures are reached. The decisive step in this chain reaction seems to differ from that of the reaction at room temperature since a plot of log $\Phi_{H_2O}$ *vs.* $1/T$ is not a straight line. These results on the direct reaction agree with those found by Melville[17] for the mercury sensitized reaction. From equations (28) and (29) two hydrogen atoms are obtained per oxygen atom. If these can react with nitrous oxide by (32) or (33), the possibility of a chain reaction exists. At high temperatures (over 440°) Melville found log $\Phi$ *vs.* $1/T$ for the mercury-sensitized reaction to be a straight line. This indicates that some step such as (32) is decisive in determining the rate at these temperatures.

## Summary

1. It is shown that both water and ammonia are formed when nitrous oxide mixed with hydrogen is irradiated. The yield of ammonia is much smaller than that of water.

2. The quantum yield of water formation increases with the hydrogen pressure and approaches a value of unity at room temperature.

3. When nitric oxide is added, no ammonia is formed.

4. With sufficient hydrogen present no nitric oxide is produced unless this substance has been added initially to the reaction mixture.

5. The addition of nitric oxide first lowers and then increases the quantum yield of water formation.

6. A quantitative explanation of the data cannot be given, but a reaction scheme is presented which accounts qualitatively for the facts.

7. The quantum yield increases with temperature above 100°. The reaction probably changes character as the temperature is raised.

8. It seems necessary to conclude that nitric oxide is effective in aiding the removal of nitrogen atoms, perhaps by acting as an effective third body for their recombination.

ROCHESTER, NEW YORK RECEIVED MAY 2, 1940

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[15] Taylor and Burton, *J. Chem. Phys.*, **7**, 675 (1939).

[16] Bamford, *Trans. Faraday Soc.*, **35**, 568 (1939).

[17] Melville, *Proc. Roy. Soc.* (London), **A146**, 737 (1934).