[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF STANFORD UNIVERSITY]

The Photolysis of Hydroxylamine[1]

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The photolyses of ammonia, hydrazine, water and hydrogen peroxide have been studied with care, and while many questions yet remain concerning the mechanisms of these reactions, the experimental evidence suggests that amino or hydroxyl radicals are produced as intermediates in all of them, and that the secondary processes consist largely of reactions of these radicals. The work here reported indicates that this is true also of hydroxylamine, and provides added support for some of the specific reactions of amino and hydroxyl radicals which have already been postulated.

Materials.—Hydroxylamine was prepared by the method of Hurd and Brownstein.[2] After removing all traces of solvent retained from the preparation, the solid hydroxylamine was purified by sublimation *in vacuo*. The hydroxylamine reservoir was kept evacuated and at dry-ice temperature at all times except when withdrawing samples. The melting range of one sample thus prepared was determined to be 31.8–32.8°, in good agreement with reported data.

The ammonia used was stored over sodium to remove water. All traces of air were removed by alternately warming the ammonia to atmospheric pressure and then freezing the ammonia with liquid air and evacuating.

Oxygen and hydrogen samples were taken from commercial tanks in a manner which prevented contamination by air. The purity of new samples was always determined by combustion before use in analysis, and if impurities were present, a different sample was collected.

The hydrogen peroxide used at one point was prepared by concentrating a 30% commercial aqueous solution from about 30 cc. to 3 cc. by distillation *in vacuo* at room temperature. The purity of this product was estimated to be well over 90%.

Ultraviolet Absorption Spectrum of Hydroxylamine.—The literature reveals no spectrochemical data for hydroxylamine other than the results of the determination of the infrared spectrum of aqueous solutions[3] and the infrared and Raman spectra of solid hydroxylamine hydrochloride and its aqueous solutions.[3,4]

To determine its ultraviolet absorption spectrum, a 150-cm. focal length quartz prism spectrograph and an Allen–Franklin type hydrogen discharge tube[5] were employed. A slit width of 0.001" was used. The absorption cell was made of fused silica, 3.5 cm. in diameter and 134.7 cm. long. It was connected to a hydroxylamine reservoir and a diamyl phthalate differential manometer by interchangeable ground joints. The entire absorption system was capable of being highly evacuated. Eastman Kodak Co. No. 33 photographic plates coated with a thin film of transil oil were used for recording the light transmitted. After each exposure, the absorption tube and reservoir (at dry-ice temperature) were evacuated. If such a procedure was not followed, the diffuse ammonia bands and the characteristic bands and fine structure of nitric oxide at 2269, 2260 and 2154 Å. appeared. These products apparently arise from the thermal decomposition of hydroxylamine, especially after long standing at the higher hydroxylamine pressures.

Figure 1 shows a microphotometer tracing of spectrograms taken at different hydroxylamine pressures. It is evident that in this region only continuous absorption is observed. For the length of cell used here, "complete" absorption sets in at about 2140 Å., at 3.02 mm. and about 2015 Å. at 0.15 mm., but at the higher pressure, some absorption takes place at wave lengths as long as 2350 Å. It is evident that the measurements were taken to the limit of the transmission of silica. Photographic plate characteristics were not obtained, and hence absorption coefficients have not been calculated.

Apparatus and Method.—The reaction system is shown in Fig. 2. The fused silica reaction cell, M, was connected to the rest of the system by a silica-to-Pyrex graded seal. The cell was cylindrical in shape, 10 cm. long and 3.0 cm. in diameter, with plane windows at either end. The hydroxylamine reservoir was at R. The amount of hydroxylamine added to the system was measured on the wide-bore mercury manometer, J, by means of a cathetometer. T_1 was a small freeze-out trap where first liquid air and then dry-ice was used to effect a partial separation of the products. The products obtained in each fraction were collected in a gas cup at Z by means of the atmospheric Toepler pump, W. The system was evacuated between runs through f_5.

The light source consisted of a spark discharge between two rapidly rotating zinc disks with a 5 mm. gap which could be accurately maintained and reproduced. A potential difference of 11,000 volts was supplied. The variation in light intensity with this apparatus was never more than 1 or 2%. The effective wave lengths were chiefly the 2025, 2062, 2100 and 2138 Å. lines of zinc.

The crystal quartz lens, L, was arranged to give a convergent beam of ultraviolet light through M with the ultraviolet focus somewhere past N. The volume effectively illuminated was a conical section of average cross section 150 mm.^{2} and volume 15 cc. Proper shielding of the cell and leads from stray radiation was provided.

An ammonia actinometer was used to measure the amount of light absorbed by the hydroxylamine. The actinometer cell, N, was 11 mm. deep and of slightly larger diameter than the reaction cell. At first it was sealed directly to the rear window of M with de Khotinsky cement, but the cement reacted slowly with ammonia and for most of the runs a crystal quartz window sealed to N with paraffin was used. With this arrangement N was about 1 mm. from the rear window of M. In use, N was first evacuated through f_1 and f_6, then with f_6 closed and f_7 open the ammonia reservoir P was warmed and N filled to 600 mm. Hg pressure, which in a cell of 11 mm. depth may be taken as completely absorbing for the wave lengths concerned.

After irradiation, the undecomposed ammonia in N was frozen out in T_2 with liquid air. The hydrogen and nitrogen resulting from irradiation were passed through f_1, collected in a gas cup, and their volume measured with a microburet.

To calculate the number of quanta of light absorbed, let *A* be the volume (cu. mm., corrected to S. T. P.) of hydrogen and nitrogen produced in M when filled with ammonia at 600 mm., *B* the volume of hydrogen and nitrogen formed in N with M empty, and *C* the volume of hydrogen and nitrogen formed in N with hydroxylamine in M. Then, using Wiig's value[6] of 0.18 for Φ_{NH_3} at this pressure and recognizing the fact that the volume of hydrogen and nitrogen

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[2] Hurd and Brownstein, THIS JOURNAL, **47**, 67 (1925).

[3] Freymann, Freymann and Rumpf, *J. phys. radium*, **7**, 30 (1936).

[4] Ananthrakrishman, *Nature*, **138**, 803 (1936); Edsall, *J. Chem. Phys.*, **5**, 225 (1937); Heintz, *Arch. phys. biol.*, **14**, 131 (1937).

[5] Allen and Franklin, *J. Opt. Soc. Am.*, **29**, 453 (1939).

[6] Wiig, THIS JOURNAL, **57**, 1559 (1935); **59**, 827 (1937).

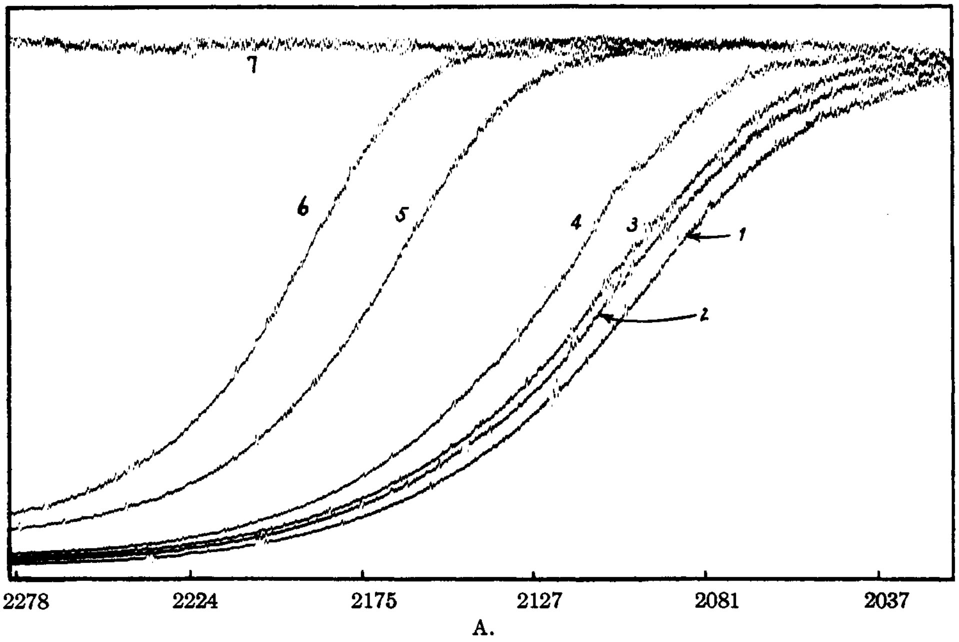

Fig. 1.—Microphotometer tracing of absorption spectrograms of hydroxylamine at different pressures. Exposure time is 20 minutes; light absorbing path is 134.7 cm.

Tracing	1	2	3	4	5	6
Hydroxylamine pressure, mm.	0.00	0.15	0.38	0.76	1.51	4.02

7 Background; corresponding to complete absorption

formed is twice the volume of ammonia decomposed, the number of quanta absorbed by hydroxylamine is

$$q = \frac{6.02 \times 10^{23}}{2.24 \times 10^{7}} \times \frac{1}{2\Phi_{NH_3}} \times \left(1 - \frac{C}{B}\right)A = \frac{7.47 \times 10^{16}(B - C)A}{B}$$

Parameter *A* remained nearly constant over a long period of time and did not often have to be redetermined. *B* tended to decrease over a period of time, but not regularly, and it was necessary to determine it daily. The measurement of *C* was a part of each run.

Variations in light intensity were accomplished by reducing the intensity with varying thicknesses of 0.001" cellophane. It was shown that the cellophane did not measurably change the spectral distribution of the light effective in the decomposition.

In carrying out a run, the system was first evacuated, and ammonia added to N to a pressure of 600 mm. The ammonia was then frozen in T_2 with liquid air and the hydroxylamine frozen in R with dry-ice while the entire system was re-evacuated. Then with f_1 and f_2 closed, T_2 and R were allowed to warm to room temperature. Hydroxylamine was allowed to sublime into M to the desired pressure as measured on J. This was done slowly to

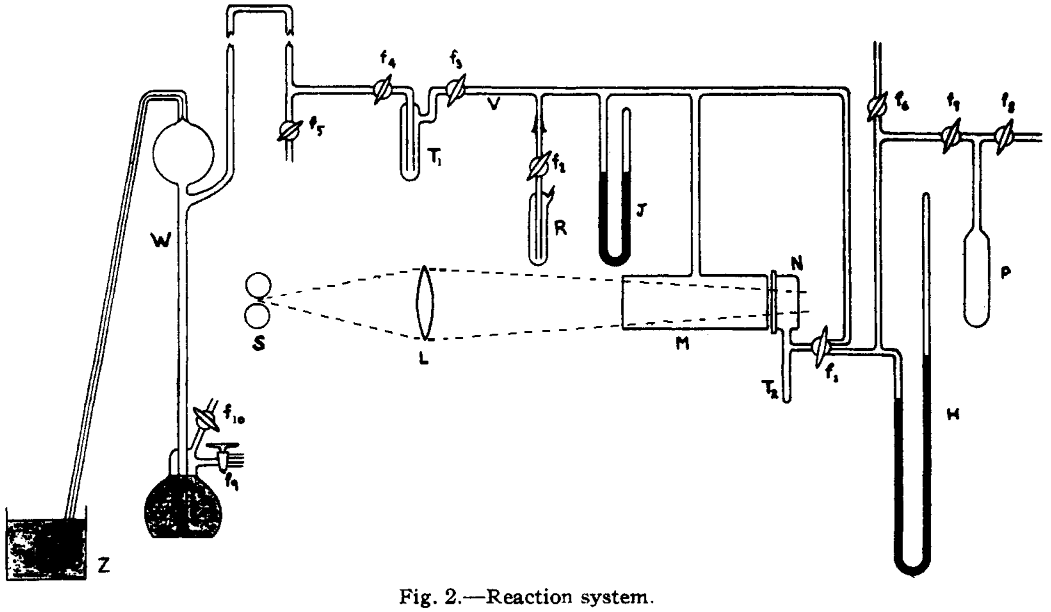

Fig. 2.—Reaction system.

TABLE I

THE PHOTOLYSIS

Av. NH_2OH press., mm.	Expt. time, min.	Runs	Light intensity, quanta/sq. mm. × sec.	Approx. percentage photolyzed	Av. amount of products, in moles, $\times 10^7$					dH_2/dt, obs., moles/cc. × sec.	Ω, einsteins absorbed	Φ_{H_2}	Φ_{NH_2OH}[f]
					H_2	N_2	NO	N_2O	NH_3				
1.0	1	5	3.12×10^{13}	6.6	1.11	1.09	0.00	0.56	0.14	12.3×10^{-11}	1.26×10^{-7}	0.88	2.19
1.0	2	13	3.12×10^{13}	12.0	1.93	1.91	.08	0.88[a]	.03[a]	10.7×10^{-11}	2.13×10^{-7}	.90	2.34[e]
1.0	3	5	3.12×10^{13}	17.9	2.91	2.80	.08	1.20	.01	10.8×10^{-11}	4.64×10^{-7}	.63	1.60
1.0	4	5	3.12×10^{13}	24.7	4.04	3.76	.10	1.75	.12	11.2×10^{-11}	6.93×10^{-7}	.58	1.48
1.0	5	9	3.12×10^{13}	29.2	4.40	4.99	.12	1.90[b]	.73[b]	9.8×10^{-11}	7.99×10^{-7}	.55	1.52[b]
2.0	2	4	3.12×10^{13}		4.07	3.44	.00	3.42	2.87	22.6×10^{-11}	4.98×10^{-7}	.82	
2.1	5	10	3.12×10^{13}		7.79	9.35	.14	...	...	17.3×10^{-11}	12.23×10^{-7}	.64	
3.1	2	4	3.12×10^{13}		4.04	6.49	.06	8.74	13.45	22.5×10^{-11}	5.59×10^{-7}	.72	
3.1	5	5	3.12×10^{13}		10.45	15.52	.12	9.83[c]	19.51[c]	23.2×10^{-11}	18.50×10^{-7}	.57	
3.2	10	4	3.12×10^{13}		19.87	27.57	.08	12.63[d]	26.53[d]	22.1×10^{-11}	36.64×10^{-7}	.54	
3.9	5	11	3.12×10^{13}		10.87	16.86	.47	16.35[e]	33.68[e]	24.2×10^{-11}	18.97×10^{-7}	.57	
3.7	10	1	3.12×10^{13}		20.90	28.30	.14	...	...	23.2×10^{-11}	38.78×10^{-7}	.55	
1.0	8.80	2	0.71×10^{13}	7.1	0.99	1.18	.00	0.54	0.21	1.25×10^{-11}	2.19×10^{-7}	.45	1.35
1.0	17.6	1	0.71×10^{13}	13.6	2.00	2.31	.00	.86	.00	1.26×10^{-11}	5.19×10^{-7}	.39	1.09
1.0	5	3	1.25×10^{13}	9.2	1.41	1.54	.00	.71	.00	3.13×10^{-11}	2.49×10^{-7}	.57	1.53
1.0	3.11	3	1.91×10^{13}	9.3	1.51	1.47	.00	.72	.17	5.41×10^{-11}	2.34×10^{-7}	.64	1.65

[a] Based on 8 runs. [b] Based on 1 run. [c] Based on 2 runs. [d] Based on 3 runs. [e] Based on 6 runs. [f] Assuming formation of no N_2H_4.

TABLE II

THE THERMAL REACTION

Av. NH_2OH, press., mm.	Runs	Av. amount of products, in moles, $\times 10^7$					H_2/N_2, av.		NH_3/N_2O, av.	
		H_2	N_2	NO	N_2O	NH_3	Photo + thermal	Thermal	Photo + thermal	Therma
1.0[b]	4				~ 0.25	~ 0	0.996	...	0.067	~ 0
2.1	3	0.09	1.09	0.01	3.02	2.69	.971	0.083	0.81	0.89
3.3	5	.08	1.72	.79	8.14	16.39	.673	.047	1.85	2.01
3.8	5	.13	2.95	1.24	11.34	22.12	.653	.044	2.06	1.95
3.4[a]	7	.15	2.86	0.93	18.08	27.90		.053		1.54

[a] Pyrex vessel. Values corrected for differing vessel sizes. [b] The combined vol. of H_2, N_2 and NO was only 0.25 cu. mm. at S. T. P. at this pressure, and was insufficient for analysis.

minimize thermal decomposition. After filling, f_2 was closed and dry-ice restored around R. After irradiation liquid air was placed around T_1 and the products noncondensable at that temperature were transferred to a gas cup at Z. Liquid air was again placed around T_2 and with liquid air still around T_1, the hydrogen and nitrogen formed in the actinometer were removed from the system to a second gas cup. This volume was measured, but the gas was not retained for analysis. Material condensed in T_2 was vaporized and refrozen to remove trapped gas. Finally, with f_1 closed, dry-ice was placed around T_1 and the gases non-condensable at this temperature were removed to a third gas cup.

In the thermal runs, exactly the same procedure was followed except that no actinometric measurements were made. The times required for filling the cell were about fifteen, twenty-two and thirty minutes for pressures of 1, 2, and 3–4 mm., and for a given pressure the length of time required for filling the cell was very nearly the same for all runs, both thermal and photolytic.

Identification and Determination of Products.—The micro methods devised by Blacet, Leighton and coworkers[7] were used for identification and analysis of the gaseous reaction products. The fraction not condensed at liquid air temperature was found to consist of hydrogen and nitrogen, usually with small amounts of nitric oxide. The dry-ice fraction was found to consist only of nitrous oxide and ammonia. These mixtures were analyzed by methods which have been described separately.[8]

In addition to the above products, the formation of both water and hydrazine was qualitatively demonstrated. Water was detected by first removing the undecomposed hydroxylamine, then passing the remaining gas over magnesium metal at 300°. Hydrazine was identified by the method of Curtius and Schrader,[9] *viz.*, the reduction of auric ion in 9 *M* sulfuric acid. The test for hydrazine was much stronger when the photolysis was carried out in a flowing system, by distilling hydroxylamine from one flask to another through an illuminated section of silica tubing. Slight tests were obtained with samples of hydroxylamine which had stood a long time, indicating that some hydrazine may also be formed in the thermal decomposition.

Quantitative Results.—Table I shows the results of the investigation of the photolysis of hydroxylamine for varying pressures, light intensities, and exposure times. Temperatures were 27 ± 3°. Table II compares the thermal decomposition of hydroxylamine in Pyrex and silica vessels for different pressures, and at 27 ± 1°. The thermal decomposition products represent the amounts obtained in times closely approximating those used for photolyses at the same pressure. It is evident that the amount of thermal decomposition is seriously large at pressures above 1 mm. It was not reproducible from run to run, and on this account accurate corrections could not be made either on the basis of alternate light and dark runs in the same vessel or simultaneous light and dark runs in separate vessels. It is evident by comparison with the photolytic experiments that at all pressures the amount of hydrogen produced in the thermal decomposition is negligible

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[7] Blacet and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 266 (1931); Blacet and Volman, *ibid.*, **9**, 44 (1937); Blacet, Sellers and Blaedel, *ibid.*, **12**, 356 (1940).

[8] Smith and Leighton, *ibid.*, **14**, 758 (1942).

[9] Curtius and Schrader, *J. prakt. Chem.*, **58**, 311 (1894).

compared to the amount produced on irradiation. Hence the yield of hydrogen is useful as an index of the extent of photolysis, and the rate of hydrogen formation and the Φ_{H_2} have been calculated for all runs.

A lower limit for the amount of hydroxylamine decomposed by light can be obtained from the nitrogen content of the measured products corrected for the thermal contribution, a correction which can be closely approximated only at 1 mm. pressure. The values of Φ_{NH_2OH} in Table I were estimated in this way. The true values will be higher by the amount of nitrogen in other nitrogenous products, such as hydrazine, which were not measured.

The decrease in hydrogen–nitrogen ratio with increasing hydroxylamine pressure is due to the increase in thermal decomposition with pressure. Approximate corrections for the amount of thermal reaction indicate a hydrogen–nitrogen ratio of nearly unity for the photolysis alone.

Since nitric oxide comprises about 31% of the liquid air fraction of the thermal decomposition, but only a very small percentage of the same fraction of the combined thermal and photolytic products, it seems likely that nitric oxide is formed only in the thermal reaction.

Any quantitative statement regarding the amounts of nitrous oxide or ammonia formed in the photolysis is impossible because of the magnitude of the contribution of the thermal decomposition and its erratic character. Except for a 1-mm. pressure of hydroxylamine, one can say only that the dry-ice fraction obtained from a photolysis is on the average only slightly larger than the dry-ice fraction from the thermal reaction at the same pressure and that the ammonia-nitrous oxide ratio is about the same in both cases and increases markedly with pressure.

At constant light intensity and for a given period of irradiation, the observed rate of hydrogen formation increases with increasing hydroxylamine pressure. From the per cent. of light absorbed at each pressure it is possible to calculate the rate of hydrogen formation for equal amounts of light absorbed. When this is done it is found that the rate actually decreases with increasing pressure (Fig. 3).

At constant pressure and for equal amounts of incident light (obtained by properly adjusting the irradiation time), the rate of hydrogen formation increases very markedly with increasing light intensity. If one plots $I_a^{3/2}$ *vs.* the rate of hydrogen formation, a straight line is obtained (Fig. 4), while Φ_{H_2} increases with the $I_a^{1/2}$. I_a is the rate of light absorption, in einsteins/cc. sec.

The figures given in Table I for Φ_{NH_2OH} are based on the nitrogen content of the measured decomposition products, corrected for the thermal contribution. Due to the increase in thermal reaction with pressure the values could be closely estimated only at 1 mm., and since some hydrazine is known to be found, they are only a lower limit. Φ_{NH_2OH} also increases with increasing light intensity, and, as with Φ_{H_2}, the drop in Φ_{NH_2OH} with increasing exposure time may be attributed to absorption by products.

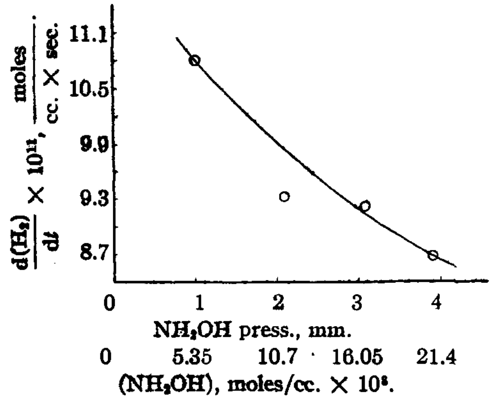

Fig. 3.—Rate of hydrogen formation at room temperature (27 ± 3°) *vs.* hydroxylamine pressure at constant light intensity and for a given amount of light absorbed. Points are experimental, but curve is calculated from the equation $\frac{d(H_2)}{dt} = \frac{5.74 \times 10^{-14}}{[2.3 \times 10^{-7} + (NH_2OH)]^{1/2}}$.

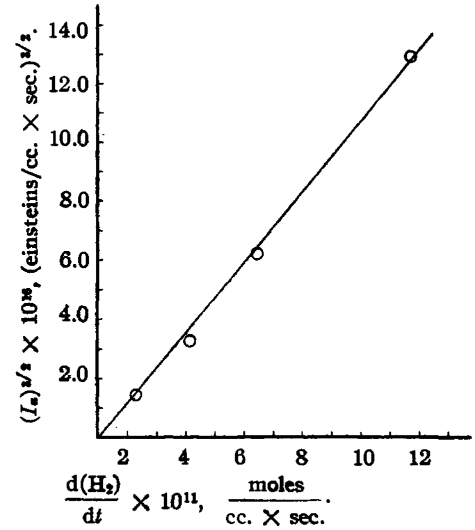

Fig. 4.—Rate of hydrogen formation *vs.* $(Ia)^{3/2}$, for hydroxylamine pressure of 1 mm. and equal amounts of light absorbed at each intensity.

Discussion

Thermal Reaction.—Little evidence is available upon which to base any mechanism for the thermal decomposition. It is evident that wall surfaces play an important part in the process. Hofmann and Kroll[10] postulated the formation of the mono- and diamides of nitrous acid as intermediates in the thermal decomposition of hydroxylamine hydrochloride in solutions and in the solid state. Reactions may be written involving

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[10] Hofmann and Kroll, *Ber.*, **57**, 937 (1924).

these radicals and leading to the observed products,[11] but there is no evidence to support them.

Photochemical Reaction.—A reaction mechanism which qualitatively explains all the photochemical data accumulated is given here. It consists of a primary splitting into amino and hydroxyl radicals, followed by at least four secondary reactions, namely

$$
\begin{array}{lll}
\phi I_a & NH_2OH + h\nu \longrightarrow NH_2 + OH & (6) \\
k_1 & NH_2 + OH + NH_2OH \longrightarrow N_2 + H_2 + 2H_2O & (7) \\
k_2 & OH + NH_2OH \longrightarrow H_2O_2 + NH_2 & (8) \\
k_3 & NH_2 + NH_2 + M \longrightarrow N_2H_4 + M & (9) \\
 & 2H_2O_2 + 2NH_2OH \longrightarrow N_2O + 5H_2O & (10)
\end{array}
$$

Assuming a steady state concentration of the intermediates, NH_2 and OH, the rate of hydrogen formation becomes

$$\mathrm{d}(H_2)/\mathrm{d}t = k_1(NH_2)(OH)(NH_2OH) = k_1k_3(M)(NH_2)^3/k_2 \quad (11)$$

The amino radical concentration may be obtained as the solution of the equation

$$(NH_2)^3 + \frac{k_2}{k_1}(NH_2)^2 - \frac{k_2\phi I_a}{k_1k_3(M)} = 0 \quad (12)$$

The solution is greatly simplified if it is assumed that $k_2/k_1 \gg (NH_2)$ (*vide infra*). With this assumption

$$(NH_2) = \sqrt{\phi I_a/k_3(M)} \quad (13)$$

and by substitution of this value in (11), one obtains

$$\frac{\mathrm{d}(H_2)}{\mathrm{d}t} = \frac{k_1(\phi I_a)^{3/2}}{k_2k_3^{1/2}(M)^{1/2}} \quad (14)$$

Since the reactant is a dilute gas and no fluorescence was observed, it is probable that ϕ is unity.

The third body, M, required for the stabilization of the hydrazine molecule formed in (9) may be hydroxylamine, the wall or any of the products of the thermal reaction. That hydroxylamine may be partly responsible is indicated by the fact that the rate of hydrogen formation increases to some extent with decreasing hydroxylamine pressure. That it is not wholly responsible is suggested by the fact that this dependence is to a much smaller degree than the $^1/_2$ power of the hydroxylamine pressure, as would be expected from the derived rate expression if hydroxylamine replaced M. Considering the nature of amine radicals and of hydrazine itself, and the low pressures used in the experiments, it is conceivable that the walls play a role in the stabilization. Hence it should be possible to divide M into two parts, M = (W + N), where W represents the part played by the walls and N the concentration of hydroxylamine. If either W or N were greatly predominating, (M) would depend only on the one which predominated, but since it depends on both, W and N must be of the same order of magnitude. Figure 3 may be exactly reproduced by the equation

$$\frac{\mathrm{d}(H_2)}{\mathrm{d}t} = \frac{5.74 \times 10^{-14}}{[2.3 \times 10^{-7} + (NH_2OH)]^{1/2}} \quad (15)$$

where (NH_2OH) is expressed in moles per cc., and the rate is expressed in moles per cc. per sec. The dependence of W on hydroxylamine pressure is neglected here because of the short pressure range (4 mm.) studied. Similarly, equation (14) may be modified to give

$$\frac{\mathrm{d}(H_2)}{\mathrm{d}t} = \frac{k_1(I_a)^{3/2}}{k_2k_3^{1/2}[2.3 \times 10^{-7} + (NH_2OH)]^{1/2}} \quad (16)$$

also

$$\Phi_{H_2} = \frac{\mathrm{d}(H_2)/\mathrm{d}t}{I_a} = \frac{k_1(I_a)^{1/2}}{k_2k_3^{1/2}[2.3 \times 10^{-7} + (NH_2OH)]^{1/2}} \quad (17)$$

It is evident from (17) that the slope of Φ_{H_2} *vs.* $(I_a)^{1/2}$ will yield some information regarding the rate constants. For a pressure of 1 mm., it is found that

$$\text{slope} = 1.19 \times 10^{-5} = k_2k_3^{1/2}(2.8 \times 10^{-7})^{1/2}/k_1$$

and

$$\frac{k_2}{k_1} = \frac{2.24 \times 10^{-2}}{k_3^{1/2}}$$

If k_3 is assumed to be of the same order of magnitude as rate constants for atomic recombination, *i. e.*, about 10^{15} (moles/cc.)$^{-2}$ sec.$^{-1}$, then $k_2/k_1 \sim 10^{-9}$.

Several arguments may be applied which lead one to the conclusion that the stationary amino radical concentration cannot be greater than 10^{-12} mole per cc. Now if $k_3 = 10^{15}$ and $(NH_2) < 10^{-12}$ mole per cc., then in equation (12) the cubic term, $(NH_2)^3$, is less than 1/1000 as large as $(k_2/k_1)(NH_2)^2$, and the original assumption in which the cubic term is neglected is valid.

If one assumes the pre-exponential factor values of 10^{14} (moles/cc.)$^{-1}$ sec.$^{-1}$ and 10^{15} (moles/cc.)$^{-2}$ sec.$^{-1}$ for the second and third order reactions (8) and (7), respectively, and if $k_2/k_1 = 10^{-9}$, it may be calculated from the Arrhenius equation that at 27° the activation energy of step (8) is about 11 kcal. greater than for step (7).

In addition to accounting for the observed products, it is seen that this mechanism accounts for the dependence of the rate of hydrogen formation on the 3/2 power of the light intensity. It is true that only a few cases have been reported in which increasing the light intensity leads to an increasing quantum yield, yet some of the most recent mechanisms proposed for the photolysis of ammonia[11a,12,13] yield ane xpression in which the

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[11] Hofmann and Kroll's reactions are

$$
\begin{array}{ll}
NH_2OH + NH_2OH \longrightarrow NH_2NHOH + H_2O & (1) \\
NH_2NHOH + NH_2OH \longrightarrow (NH_2)_2NOH + H_2O & (2)
\end{array}
$$

and to account for the majority of the observed products they suggested that the diamide acid decomposes to give nitrogen, ammonia and water. Further possibilities are

$$
\begin{array}{lll}
 & \nearrow N_2O + 2NH_3 + H_2O & (3) \\
2NH_2NHOH & & \\
 & \searrow N_2 + N_2H_4 + 2H_2O & (4) \\
2(NH_2)_2NOH \longrightarrow & 2NO + 2NH_3 + N_2H_4 & (5)
\end{array}
$$

[11a] Mund and van Tiggelen, *Bull. soc. chim. Belg.*, **46**, 104 (1937).

[12] Mund, Brenard and Kaertkemeyer, *ibid.*, **46**, 211 (1937).

[13] Taylor, *J. Phys. Chem.*, **42**, 783 (1938).

quantum yield of ammonia decomposition increases with the cube root of the light intensity. Mund, Brenard and Kaertkemeyer[12] have pointed out that experiments performed by them, by Wiig and by Ogg, Leighton and Bergstrom are in accord with this relation.

The requirement that hydrogen and nitrogen should be formed in approximately equal amounts is satisfied by step (7).

Step (10) was shown to take place by mixing hydrogen peroxide and hydroxylamine vapors. The dry-ice fraction resulting from this mixture was shown to contain only nitrous oxide. The quantities of nitrous oxide thus obtained were much larger than resulted at any time from the simple thermal decomposition of hydroxylamine. It is postulated that this reaction could account for the small amount of nitrous oxide observed in the photolysis. It is probable that the reaction is not fourth order as shown, but takes place in a series of simple bimolecular collisions, quite possibly involving the intermediates postulated in the thermal decomposition of hydroxylamine [equations (1) and (2)]. It is unlikely that hydrogen peroxide remains as a final product in the photolysis, but it is possible that some of it decomposes to form water and oxygen. This is not obviated by the fact that no oxygen was ever observed, since any formed in this manner would react with nitric oxide formed in the thermal decomposition to produce nitrogen dioxide. This in turn would either be frozen out or would react with ammonia formed in the thermal decomposition. Nitrous oxide, if it is formed directly in the photolysis, might appear as the result of reaction (10), while ammonia might result from the decomposition of hydrazine.

The requirement that Φ_{NH_2OH} should increase with increasing light intensity is also satisfied, and values of greater than 2 are permitted by the proposed mechanism. The decrease in Φ_{NH_2OH} with exposure time already has been partially explained.

Other possibilities for the primary step should be noted. The two most probable ones require breaking either an N–H bond or an O–H bond. All other possibilities require the breaking of more than one bond. It may be calculated that at least 67 kcal. would be necessary to break the N–O bond in step (6). This is some 40 kcal. less than that required for the O–H or N–H bonds. So though 67 kcal. is a lower limit to step (6), it is in all probability more likely from an energetic standpoint than are the other two. The fact that no structure whatever was observed in the absorption spectrum, and that no fluorescence could be observed, is evidence against the formation of an activated complex or excited hydroxylamine molecule which by secondary reactions is caused to decompose.

It should be noted that step (8) might be replaced by

$$NH_2 + NH_2OH \longrightarrow N_2H_4 + OH \qquad (18)$$

and (9) by

$$OH + OH + M \longrightarrow H_2O_2 + M \qquad (19)$$

Such a replacement in no way alters either the form of the rate expression for hydrogen formation or the amounts of hydrogen peroxide or hydrazine and their rate of formation. However, (9) seems more likely than (19) because there is some evidence that the latter does not readily take place.

Summary

1. The ultraviolet absorption spectrum of hydroxylamine vapor is found to be experimentally continuous from its onset at about 2350 Å. down to at least 2000 Å.

2. Absorption in this region results in photolysis, the chief products being hydrogen, nitrogen and water. Some hydrazine is also produced, the amount increasing in a flow system. The chief products of the thermal decomposition at room temperature are nitrogen, nitric oxide, nitrous oxide, water and ammonia. Small amounts of nitrous oxide and ammonia may also result directly from the photolysis.

3. For equal amounts of light absorbed, the rate of hydrogen formation decreases with increasing hydroxylamine pressure, and increases with the 3/2 power of the incident light intensity.

4. A mechanism involving amino and hydroxyl radicals is found to fit the experimental data.

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