(±2000) calories; at high pressures the activation energy is 24,700 calories. These discrepancies between the experimental results and Theory I indicate that this form of the general theory is inadequate for this reaction.

The second form of the general theory is based on the assumption that the critical energy must be localized in some one degree of freedom (Theory II) or in some one bond, which involves two degrees of freedom (Theory III). Kassel[14] has already compared the actual behavior of nitrogen pentoxide with the behavior to be expected from Theory III. We have inserted in Fig. 2 the theoretical curve given by the quantum form of Theory III, using 15 as the number of oscillators in the molecule, 22 as the number of quanta necessary to furnish the critical energy, and 26×10^{-8} cm. as the diameter of the molecule (a considerably larger value than kinetic theory considerations would allow). Even if we disregard the divergence between this theoretical curve and the experimental results below 0.005 mm., where the possible evidence of surface effects makes our results less significant, nevertheless there is a definite discrepancy in the region between 0.06 and 0.02 mm., where the results are more reliable, and where agreement between the different workers is reasonably good. Better agreement at the high pressure end of the curve could be obtained by assuming a larger diameter for the molecule, but this is already unreasonably large.

This reaction has always presented the severest test for the theories of unimolecular reaction. Theory III has given a reasonable interpretation of several other unimolecular reactions, but it is apparent from the present summary of results at low pressures that there is a definite conflict between any reasonable deductions from Theory III and the best existing results on the decomposition of nitrogen pentoxide.

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[14] Ref. 3g, p. 191.

Summary

1. The rate of thermal decomposition of nitrogen pentoxide has been measured in a 22-liter flask at temperatures of 35, 45, 55 and 65°, and at pressures ranging from 0.05 mm. to less than 0.001 mm.

2. Over this pressure range the reaction undergoes a transition from a first order to a second order mechanism. Deviation from a first order reaction becomes apparent around 0.05 mm. pressure, and at 0.001 mm. the reaction is apparently of the order 1.8.

3. The effect on the reaction of the glass walls has been observed by comparing the present results with previous results obtained in a 1.5-liter flask in which the ratio of surface to volume is 2.5 times greater. The surface appears to have no effect down to pressures around 0.005 mm.; below this pressure the surface appears to retard the reaction slightly.

4. The data have been compared with two of the existing theories of unimolecular reaction and differences that seem difficult to reconcile have been pointed out.

ANN ARBOR, MICH. RECEIVED DECEMBER 15, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Reduction of Silver Salts with Hydroxylamine

BY M. L. NICHOLS

Introduction

In their investigation of the photographic process, Sheppard and Mees studied the method of alkaline development. They state that[1] "the concentration of the alkali has a direct and controlling influence both on the composition of the solution and on the development." They also say that[1] "so long as we are ignorant of the quantitative relation between reducer oxidized and silver halide reduced, as also of the former's oxidation product, the survey of development can only be tentative and approximate."

In order to determine this relationship they studied the action of hydroxylamine on silver bromide in the presence of sodium hydroxide, on ammoniacal silver nitrate, and on silver nitrate in the presence of sodium sulfite and sodium hydroxide. In all these experiments they determined the grams of silver obtained per gram molecule of hydroxylamine used and formulated the

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[1] Sheppard and Mees, "Investigations on the Theory of the Photographic Process," Longmans, Green and Co., London, 1907, p. 140.

reaction occurring from these data. They found that when an excess of hydroxylamine acts on silver bromide in the presence of sodium hydroxide the results show that the reaction

$$2NH_2OH + 2AgBr = 2Ag + N_2 + 2HBr + 2H_2O$$

is nearly approached until the dilution of the hydroxylamine becomes very considerable. At great dilution of the hydroxylamine the reaction is probably

$$2NH_2OH + 4AgBr = 4Ag + N_2O + 4HBr + H_2O$$

When hydroxylamine acts upon an excess of ammoniacal silver nitrate the reaction

$$2NH_2OH + 2Ag_2O = 4Ag + N_2O + 3H_2O$$

is approached and it is evident that the addition of the reducer to ammoniacal silver nitrate may lead to a different reaction from that with silver bromide. In the case of the action of hydroxylamine on silver nitrate in the presence of sodium sulfite and sodium hydroxide they found the same reaction occurring as with ammoniacal silver nitrate.

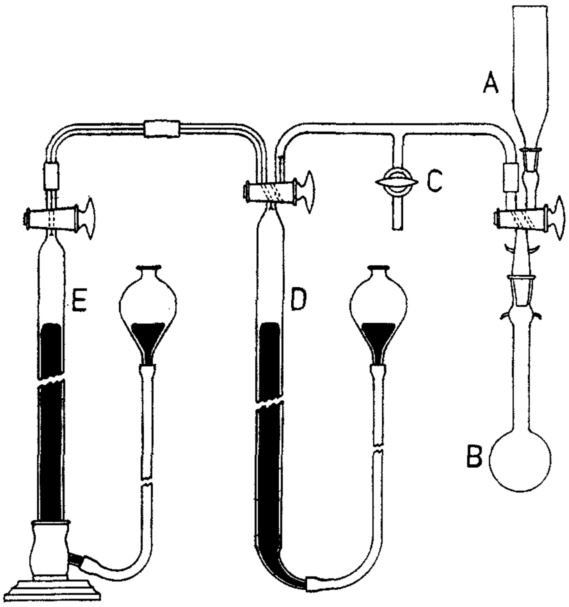

Fig. 1.

They give[2] the following explanation of the action of hydroxylamine on silver salts. "The reducing action of hydroxylamine, when set free from its salts, is greatly intensified by alkali. This is due to its being an amphoteric electrolyte, forming both hydrogen and hydroxyl ions, hence acting as a base in the presence of acids, its salts being considerably hydrolyzed, while with strong bases it acts as a very weak acid. The two stages in which the oxidation of hydroxylamine may take place can be considered as arising from its function as a dibasic acid. Thus at moderate dilutions we have from the equilibrium $NH_2OH + NaOH \rightleftharpoons NH_2ONa + H_2O$ the ion NH_2O^- which reacts with silver ions according to the equation

$$2NH_2O^- + 2Ag^+ = 2Ag + N_2 + 2H_2O$$

"At greater dilutions the ionization of the second hydrogen atom becomes appreciable, and from the equilibrium $NH_2ONa + NaOH \rightleftharpoons NHONa_2 + H_2O$ we have the ion $NHO^=$, reacting according to the equation

$$2NHO^= + 4Ag^+ = 4Ag + N_2O + H_2O$$

"The coupling of the discharged ions NH_2O and NHO in the manner condensed above appears to offer a satisfactory explanation of the reactions of hydroxylamine with copper and silver salts, its behavior being the same with both."

Since in all these experiments Sheppard and Mees made no determinations of the volumes and composition of the gaseous products obtained, it seemed desirable to make such a study to determine if the gases evolved agreed with the formulated reactions.

Experimental

The hydroxylamine hydrochloride used was prepared in the same manner as that of Sheppard and Mees by recrystallization of Kahlbaum pure material from hot 98% alcohol containing a drop of platinic chloride solution. The crystals were then dried *in vacuo* over sulfuric acid and a solution prepared containing 0.702 g. of hydroxylamine hydrochloride in 50 ml. of solution. Exactly normal solutions of silver nitrate, potassium bromide and sodium hydroxide and a saturated solution of sodium sulfite were also prepared.

The experiments were carried out in the apparatus shown in the accompanying figure. The silver bromide or silver nitrate together with the sodium hydroxide or the ammonium hydroxide and sodium sulfite, when they were used, was placed in the bulb B which had a capacity of about 150 ml. This was attached to the rest of the apparatus by the ground glass slip-joint, being held securely by rubber bands fastened over the projecting hooks. The apparatus was then evacuated, most of the air being removed through stopcock C with a water suction pump, the rest by using buret D as a pump. During the evacuation, the bulb was shaken vigorously and the pumping was continued until all of the uncondensable gas was removed. This condition was indicated by a sharp click as the mercury struck the lower side of the stopcock on D, when the pressure in the buret was brought to atmospheric.

Fifty ml. of the hydroxylamine hydrochloride solution was introduced into A and this was run slowly into B, care being taken not to admit any air. Bulb B was then shaken vigorously and the reaction allowed to go to completion. The gas evolved was pumped out completely with buret D and transferred to buret E. In the experiments made at a higher temperature, bulb B was immersed, after evacua-

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[2] Sheppard and Mees, *op. cit.*, p. 146.

tion, in boiling water until the contents started to boil and then the hydroxylamine hydrochloride solution was run in. When the reaction had gone to completion, bulb B was cooled to room temperature by immersing it in cold water and the gas was pumped out.

Any air which might have leaked into the evacuated apparatus during the experiment was determined by treating the evolved gases with alkaline pyrogallol to remove oxygen. The volume of gas obtained was corrected for the volume of air equivalent to the volume of oxygen determined. In the case of the experiments using ammoniacal silver nitrate solution the ammonia was first removed with dilute sulfuric acid. In the experiments with sodium sulfite the evolved gas was treated with sodium hydroxide solution but no oxides of sulfur were found. The amount of nitrous oxide in the evolved gas was determined by measuring the decrease in volume that occurred when the gas mixture was burned with an excess of hydrogen over a red-hot platinum spiral in a slow combustion pipet. The incombustible residue after the burning of the nitrous oxide was considered to be nitrogen.

TABLE I

THE REDUCTION OF SILVER BROMIDE WITH HYDROXYLAMINE IN THE PRESENCE OF SODIUM HYDROXIDE

N $AgNO_3$, ml.	AgBr, g.	Ag formed, g.	*N* NaOH, ml.	H_2O, ml.	NH_2OH, ml.	Temp.	Gas, ml.	N_2O, %	N_2, %	Gas as N_2, ml.	Calcd. vol. N_2, ml.	Yield, %
10			50	..	50	Room	71.73	41.4	58.6	101.43	112.02	90.6
10			50	..	50	Room	72.83	40.6	59.4	101.40	112.02	90.5
5	0.8969		50	..	50	Room	34.06	40.5	59.5	47.85	53.5	89.4
5			50	..	50	Hot	33.85	54.6	45.4	50.33	56.01	93.4
5			50	..	50	Hot	33.25	52.9	47.1	50.84	56.01	91.4
5	.9232	0.5325	25	25	50	Room	40.25	26.4	73.6	50.85	55.07	92.4
5	.9310	.5397	25	25	50	Room	41.68	25.3	74.7	50.47	55.54	90.9
5	.9079	.5306	25	25	50	Hot	37.45	33.0	67.0	49.83	54.16	92.0
5	.9183	.5265	25	25	50	Hot	37.09	32.4	67.6	49.19	54.78	89.8
5	.9221	.5348	25	25	50	Room	41.19	25.2	74.8	51.53	55.01	93.7
							1.61	100	..	54.75		99.6[a]
5	.9190	.5383	25	25	50	Room	41.37	24.8	75.2	51.63	54.82	94.2
							1.17	100	..	53.97		98.4[a]

[a] In these experiments after the gas was pumped out completely, 10 ml. of 6 *N* sulfuric acid was added and the liberated gas pumped out.

In the first experiments with silver bromide it was precipitated by mixing equal volumes of silver nitrate and potassium bromide, filtered through a sintered glass Jena filter, washed and transferred moist to bulb B. In the later experiments the silver bromide was dried in the crucible and the actual weight transferred to bulb B was determined. The reduced silver in bulb B after the experiment was also filtered off and the amount determined.

The results obtained are given in the tables. The volumes of gas given are those at 0°, 760 mm. and dry. In all the experiments except one, 50 ml. of a hydroxylamine hydrochloride solution containing 0.702 g. of $NH_2OH \cdot HCl$ was used. An excess of hydroxylamine was always present except in the one experiment with ammoniacal silver nitrate. Since Sheppard and Mees have shown that under the conditions of these experiments the catalytic decomposition of hydroxylamine is negligible, the theoretical volume of nitrogen is calculated from the weight of silver salt used in all cases except this one where it is calculated from the weight of hydroxylamine hydrochloride. The volume of gas as nitrogen is calculated on the basis of the equations of Sheppard and Mees where the reduction to nitrogen gives twice as many volumes of gas as the reduction to nitrous oxide.

Discussion

In the reduction of silver bromide by hydroxylamine, the results in Table I show that under the conditions of these experiments the gaseous product is always a mixture of nitrous oxide and nitrogen. As the concentration of the alkali is lowered the percentage of nitrous oxide becomes less and as the temperature is raised the percentage of nitrous oxide is increased.

TABLE II

THE REDUCTION OF AMMONIACAL SILVER NITRATE WITH HYDROXYLAMINE

Concd. NH_4OH, 15 ml.; room temp., N_2O, none; N_2, 100%

N $AgNO_3$, ml.	H_2O, ml.	Satd. Na_2SO_3, ml.	NH_2OH, ml.	Gas, ml.	Calcd. vol. N_2, ml.	Yield, %
5	30	..	50	54.88	56.01	98.0
5	30	..	50	55.19	56.01	98.6
15	20	..	10+ 40 ml. H_2O	21.85	22.63	96.5
5	5	25	50	51.85	56.01	92.6

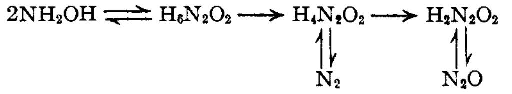
TABLE III

THE REDUCTION OF ALKALINE SILVER NITRATE WITH HYDROXYLAMINE IN THE PRESENCE OF SODIUM SULFITE

N $AgNO_3$, 5 ml.; *N* NaOH, 15 ml.; H_2O, 5 ml.; satd. Na_2SO_3, 25 ml.; NH_2OH, 50 ml.; room temp.

Gas, ml.	N_2O, %	N_2, %	Gas as N_2, ml.	Calcd. vol. of N_2, ml.	Yield, %
15.72	31.2	68.8	20.61	56.01	36.9
15.58	31.3	68.7	20.46	56.01	36.5

If the oxidation of hydroxylamine proceeds in the reverse order of the steps believed to occur in its formation by the reduction[3] of nitric acid, then the process can be represented as



$$\begin{tikzcd}
2NH_2OH \arrow[r, shift left] & H_6N_2O_2 \arrow[l, shift left] \arrow[r] & H_4N_2O_2 \arrow[r] \arrow[d, shift left] & H_2N_2O_2 \arrow[d, shift left] \\
& & N_2 \arrow[u, shift left] & N_2O \arrow[u, shift left]
\end{tikzcd}$$

This indicates that the nitrous oxide can come only from the decomposition of the hyponitrite and its formation may be represented by the reactions

$$2Ag_2O + 2NH_2OH = 4Ag + H_2N_2O_2 + 2H_2O$$
$$H_2N_2O_2 = N_2O + H_2O$$

The nitrogen may result either from the decomposition of the intermediate oxidation product or from a reaction[4] between the hyponitrite formed and hydroxylamine.

$$H_2N_2O_2 + 2NH_2OH = 2N_2 + 4H_2O$$

The formation of the nitrogen may then be represented as occurring either as

$$Ag_2O + 2NH_2OH = 2Ag + H_4N_2O_2 + H_2O$$
$$H_4N_2O_2 = N_2 + 2H_2O$$

or

$$2Ag_2O + 2NH_2OH = 4Ag + H_2N_2O_2 + 2H_2O$$
$$H_2N_2O_2 + 2NH_2OH = 2N_2 + 4H_2O$$

with the volume of nitrogen obtained from a given amount of silver bromide being the same by either process.

It is also known[5] that the hyponitrite is stabilized by alkali as "Divers observed that aqueous solutions of alkali hyponitrites decompose slowly into nitrous oxide and alkali hydroxide—gradually in the cold, rapidly when heated. Alkali hydroxides impede the decomposition and, if in concentration solution, stop it. The neutralization of the alkali by carbon dioxide hastens the decomposition; but this is not due to the decomposition of the hyponitrite by the carbon dioxide."

Since a high concentration of alkali stabilizes the hyponitrite and also yields a higher percentage of nitrous oxide, such a condition must favor the oxidation of the hydroxylamine to the hyponitrite stage instead of the intermediate stage which would decompose giving nitrogen. This is in agreement with the results of Sheppard and Mees, who found that the reducing action of hydroxylamine is greatly intensified by alkali. The stabilization of the hyponitrite must also retard its reaction with the hydroxylamine and allow it to decompose slowly into nitrous oxide and alkali hydroxide. Such must be the case since a higher alkali concentration gives an increased percentage of nitrous oxide. This is also shown by the last two experiments where, after the reaction had gone to completion and the gas was pumped off, the solution was acidified and pure nitrous oxide was obtained. When the temperature was raised with the same concentration of alkali, the decomposition of the hyponitrite formed into nitrous oxide occurs still more readily and a resulting increase in the percentage of nitrous oxide is obtained.

When ammoniacal silver nitrate is used with either an excess of silver salt or of hydroxylamine, pure nitrogen is obtained (Table II) and no nitrous oxide as claimed by Sheppard and Mees. Since ammonium hyponitrite is very unstable, the oxidation to this stage would not be favored and a decomposition of the intermediate oxidation product ($H_4N_2O_2$) into nitrogen is obtained. The preceding experiments show that decreasing the concentration of sodium hydroxide increases the percentage of nitrogen and when a very weak base such as ammonium hydroxide is used, only pure nitrogen is obtained.

When hydroxylamine acts upon silver nitrate, in the presence of sodium hydroxide and sodium sulfite, pure nitrous oxide is not obtained but a mixture of nitrous oxide and nitrogen (Table III). When the mixture of silver nitrate and alkali is treated with sodium sulfite, the precipitated silver oxide dissolves, giving a clear solution. This solution then gives a precipitate of silver on treatment with hydroxylamine. The percentage of nitrous oxide in the mixture is similar to that obtained with silver bromide with a comparable alkali concentration.

The low results in this case for the volume of gas as nitrogen indicate that this is not a simple reduction by hydroxylamine, as stated by Sheppard and Mees, but that we are probably dealing with a coupled or induced reaction similar to the reaction between hydroquinone and silver bromide in the presence of sodium sulfite.[6] If the sulfite also reacts with the silver oxide or soluble silver salt according to the reaction

$$Ag_2O + Na_2SO_3 = 2Ag + Na_2SO_4$$

the volume of gas obtained will be reduced by an amount proportional to the amount of silver salt reduced by the sulfite and an equivalent amount of sulfate should be formed.

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(3) Joss, *J. Phys. Chem.*, **30**, 1270 (1926).

(4) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1928, Vol. VIII, p. 289.

(5) Mellor, Ref. 4, p. 411.

(6) Gordon, *J. Phys. Chem.*, **17**, 47 (1913).

In order to prove the above, the following experiments were made: 5 ml. of the normal silver nitrate solution was treated in bulb B (Fig. 1) with 10 ml. of normal sodium hydroxide. The precipitated silver oxide was washed by decantation, to free it from nitrate, and 10 ml. of *N* sodium hydroxide and sufficient saturated sodium sulfite solution to dissolve it (15 ml.) were added. The bulb B was attached to the apparatus, evacuated with shaking and allowed to stand. The silver was then precipitated with hydrochloric acid, the silver chloride filtered off and the filtrate boiled with hydrochloric acid until the sulfur dioxide was expelled. The sulfate content was determined as barium sulfate. The solution treated in this manner, to determine the amount of oxidation by the air or direct reduction of the silver salt, showed an increase of 0.0397 g. of barium sulfate over the amount obtained (0.3800 g.) from 15 ml. of the untreated sulfite solution. Another experiment was made in the same manner except that after the apparatus was evacuated, 50 ml. of the hydroxylamine solution was added and allowed to react. After filtering off the precipitated silver, the solution was boiled with hydrochloric acid and the sulfate determined. This showed an increase of 0.3744 g. of barium sulfate over the amount in the original sulfite solution or an increase of 0.3374 g. due to the induced reaction.

If the previously mentioned reaction occurs, then 57.4% of the silver nitrate is reduced by the sodium sulfite. In the previous experiments (Table III) a yield of 36.7% of nitrogen was obtained, which together with the above gives a total of 94.1%, similar to that obtained in the other experiments. These results indicate that the silver salt is reduced by both the hydroxylamine and the sodium sulfite due to a coupled or induced reaction. The last experiment in Table II indicates that with ammoniacal silver nitrate no induced reaction occurs or, at least, only a very small amount of the reduction is due to sodium sulfite.

Summary

1. The gaseous products of the action of hydroxylamine on silver salts were determined.

2. Silver bromide in the presence of sodium hydroxide gives a mixture of nitrous oxide and nitrogen.

3. Ammoniacal silver nitrate gives pure nitrogen.

4. Alkaline silver nitrate in the presence of sodium sulfite gives a mixture of nitrous oxide and nitrogen.

5. When hydroxylamine reacts with alkaline silver nitrate in the presence of sodium sulfite, a coupled or induced reaction occurs.

6. The composition of the gaseous products varies with the strength of the alkali and the temperature.

ITHACA, N. Y. RECEIVED DECEMBER 18, 1933

[CONTRIBUTION FROM THE SANDERS LABORATORY OF CHEMISTRY, VASSAR COLLEGE]

The Adsorption of Hydrogen by Copper Poisoned with Cyanogen

BY CARROLL W. GRIFFIN

Several years ago Pease[1] found that at 0° both the adsorption of hydrogen and of ethylene on copper and the catalytic activity of the metal toward an ethylene–hydrogen mixture suffered a marked decrease either by heating the copper to moderately high temperature or by poisoning it with a small quantity of mercury. Especially in the low-pressure region was the decrease in adsorption great and at the time it appeared that a correlation existed between catalytic activity and the strong or low-pressure adsorption of the reactants. Later Pease and Stewart[2] revealed that the catalytic activity of a copper catalyst was much reduced for the hydrogenation of ethylene by poisoning the catalyst with a minute quantity of carbon monoxide. With this poison, however, adsorption measurements[3] showed that a trace of carbon monoxide on the copper causes a low-pressure increase which gives way to a high-pressure decrease in the adsorption of both hydrogen and ethylene at 0 and at 20°. This result was interpreted by supposing the sorption of the gases to comprise two or more processes one of which was thought to be solution.

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[1] Pease, THIS JOURNAL, **45**, 2296 (1923).

[2] Pease and Stewart, *ibid.*, **47**, 1235 (1925).

[3] Griffin, *ibid.*, **49**, 2136 (1927).