
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 64

APRIL 6, 1942

NUMBER 4

[COMMUNICATION 835 FROM THE KODAK RESEARCH LABORATORIES]

Effect of Catalysis upon the Oxidation Products of Hydroxylamine

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Several analytical investigations have been made of the oxidation of hydroxylamine.¹⁻⁸ Most of the oxidizing agents employed yield a mixture of oxidation products, and some reactions are complicated further by catalytic decomposition of the hydroxylamine.⁶ Ferric oxide, however, used in acid solution yields quantitatively nitrous oxide^{1,3}; cupric hydroxide in caustic solution yields no nitrogen and 95-96% nitrous oxide.¹ There is no autocatalysis in the oxidation by ferric salts,⁹ and none was observed in the present work with cupric hydroxide. On the other hand, silver salts and mercurous chloride in acid or neutral solution yield 99% or more nitrogen.¹⁰ A strong autocatalysis by the metal product was observed in these reactions. However, it was known that silver salts under some conditions oxidize hydroxylamine to a mixture of nitrogen and nitrous oxide.⁸ The same phenomenon has been found in work with mercurous nitrate. The present study is concerned with the conditions which favor the formation of each product.

(1) G. V. Knorre and K. Arndt, *Ber.*, **33**, 30 (1900).

(2) M. Adams and E. Overman, *THIS JOURNAL*, **31**, 637 (1909).

(3) W. C. Bray, M. E. Simpson and A. A. MacKenzie, *ibid.*, **41**, 1363 (1919).

(4) A. Benrath and K. Ruland, *Z. anorg. allgem. Chem.*, **114**, 267 (1920).

(5) A. Kurtenacker and R. Neusser, *ibid.*, **131**, 27 (1923).

(6) A. Kurtenacker and F. Wengefeld, *ibid.*, **140**, 301 (1924); **141**, 119 (1924).

(7) F. Raschig, "Schwefel- und Stickstoffstudien," 1924, p. 163ff.

(8) M. L. Nichols, *THIS JOURNAL*, **56**, 841 (1934).

(9) A. D. Mitchell, *J. Chem. Soc.*, 336 (1926).

(10) T. H. James, *THIS JOURNAL*, **61**, 2379 (1939); **62**, 536 (1940); **63**, 1601 (1941).

Experimental

Procedure.—The method followed in the kinetic experiments was essentially the same as that previously employed.¹⁰ The composition of the gaseous reaction product was calculated, in general, from the measured total volume of gas produced by the reaction. In each experiment the completion of the reaction was confirmed analytically. Control analyses of the gaseous product obtained from oxidation of hydroxylamine by silver salts were in satisfactory accord with the calculated values. Hydroxylamine was always present in at least fourfold excess and a total solution volume of 50 milliliters was employed. The mercurous nitrate solutions used were free of mercuric salt, and their strength was determined by oxidation to the mercuric state, followed by thiocyanate titration.

Oxidation by Mercurous Salts.—At pH 4.0 the reaction between hydroxylamine and mercurous nitrate follows an auto-accelerating course, the mercury formed acting as a catalyst. If colloidal silver is added to the reaction mixture during the initial slow stage, the reaction rate increases sharply, as illustrated by Curve 1, Fig. 1. In this experiment, the gas obtained as reaction product contained 98% nitrogen. As the pH increases, the rate of the initial reaction increases markedly. At pH 4.85, reaction is rapid and proceeds without induction period (see Curve 2, Fig. 1). Addition of colloidal mercury or colloidal silver increases the reaction rate and greatly alters the composition of the gaseous product. The increase in nitrogen content accompanying the increase in the amount of catalyst used is shown in Table I. The mercury sol employed was unstable and of much smaller specific surface than the silver sol. When catalyst was added, reaction was carried out in the presence of 20 mg. of gelatin.

The nitrogen yield was finally increased to 98% by the addition of solid mercurous nitrate crystals to a hydroxylamine solution containing 5 ml. of silver sol. Mercurous chloride reduced under conditions described in a previous paper¹⁰ produced substantially 100% nitrogen in the pH range 5.7-6.3. The mercury produced by this reaction re-

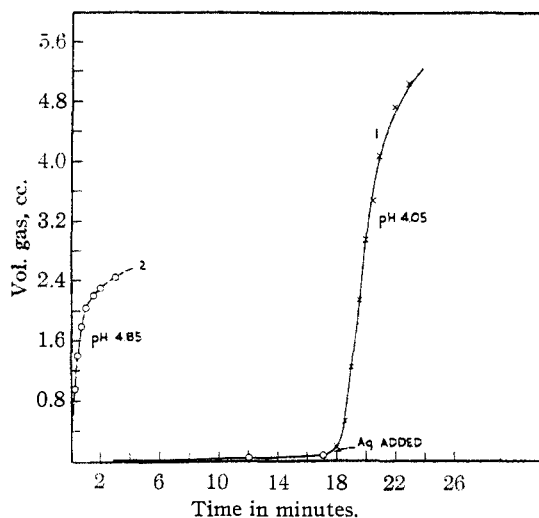


Fig. 1.—Oxidation of NH_2OH by $\text{Hg}_2(\text{NO}_3)_2$.

mained in a finely divided state at the end of the experiment, in contrast to the globular mercury obtained by the reduction of the nitrate in the absence of added catalyst.

TABLE I

OXIDATION OF HYDROXYLAMINE BY MERCUROUS NITRATE
 NH_2OH , 0.04 M; $\text{Hg}_2(\text{NO}_3)_2$, 0.005 M; temp. 20°

Catalyst added	Amount added, ml.	N ₂ , %	N ₂ O, %
None	..	13	87
Hg	5.0	27	73
0.07% Ag	0.1	30	70
.07% Ag	2.0	51	49
.07% Ag	10.0	63	34

Oxidation by Silver Salts.—Nitrous oxide was obtained as a product of the reaction between silver salts and hydroxylamine only in the alkaline region. Attempts to suppress the silver catalysis by the use of poisons were unsuccessful. Strongly adsorbed materials, such as gelatin and polyvinyl alcohol, which decreased the activity of added powdered silver catalyst, promoted the formation of silver sols of high specific surface.¹¹ Other poisons tried, including several thiols, formed complexes with silver ions and thus interfered with the reaction.

In alkaline solution, the composition of the gaseous product depended both upon pH and upon the salt employed. The data obtained under various conditions are summarized in Table II. The striking increase in the yield of nitrogen with the increase in catalyst obtained in the mercurous nitrate reaction could not be duplicated for the silver salts in strongly alkaline solution, but a significant effect was obtained by the exposure of silver chloride and silver bromide to actinic light. The action of the light resulted in the formation of a large number of silver nuclei which served as centers of propagation of the catalyzed reaction.^{11a} Table III shows the increase in nitrogen obtained by the exposure.

(11) Even though polyvinyl alcohol is strongly adsorbed, the stable silver sol has greater catalytic activity than the powder. Cf. results by Rampino, Kavanagh, Wyckoff and Nord on palladium catalysts (THIS JOURNAL, 63, 2749, footnote (1941)).

(11a) T. H. James, THIS JOURNAL, 62, 1649 (1940).

TABLE II

REDUCTION OF SILVER SALTS BY HYDROXYLAMINE

Ag salt	Max. $[\text{Ag}^+]$ (solution)	pH	N ₂ , %
AgCl	3.8×10^{-10}	7.2	100
		10.3	63
		12.7	5
AgCNS	1.2×10^{-11}	12.7	21
AgBr	6.3×10^{-12}	10.3	100
		12.7	65
$\text{Ag}(\text{S}_2\text{O}_8)^{2-}$	2.1×10^{-14}	12.7	89
AgI	9.7×10^{-16}	12.7	91

TABLE III

REACTION PRODUCTS FROM EXPOSED AND UNEXPOSED PRECIPITATES

Ag salt	Condition	pH	N ₂ , %
AgCl	Unexposed	10.3	63
	Exposed	10.3	84
AgBr	Unexposed	12.7	65
	Exposed	12.7	72
AgCNS	Unexposed	10.2	74
	Exposed	10.2	75

Only the thiocyanate, which is relatively insensitive to light, showed no significant effect.

Reduction of Silver Thiosulfate Complex.—Silver thiosulfate complex, with a dissociation constant of 4.2×10^{-14} at 25°,¹² yields such a low concentration of silver ions that catalysis involving adsorption of silver ions to silver should not play a significant part in the reaction with hydroxylamine.¹³ Since, however, a marked silver catalysis was observed, the kinetics of the reaction were examined.

Reaction was carried out in 0.06 N sodium hydroxide solution in the presence of 20 mg. of gelatin and 2.0 ml. of gold sol per 50 ml. of the reaction mixture. The rather high gelatin concentration and high reaction velocities were necessary to minimize coagulation of the silver sol formed in the reaction. The effects of variation of total silver salt, sodium thiosulfate concentration and hydroxylamine concentration are given in Table IV. S_m is the maximum slope of the reaction curve, and t is the time required for the evolution of the first 0.10 ml. of gas. R represents the slope of the initial straight-line portion of the curve obtained by plotting the cube root of the volume of gas evolved against the reaction time.¹⁰ A logarithmic plot of the data on the variation of rate with hydroxylamine is given in Fig. 2.

Discussion

In the reduction of silver nitrate by hydroxylamine,¹⁰ the R and S_m values served as measures of the rate of the silver-catalyzed reaction. This reaction involved adsorption of both silver ions and hydroxylamine ions. The $1/t$ values, on the other hand, measured the rate of a preliminary reaction which was evidently gold-catalyzed, since the kinetics indicated adsorption of silver ions but not of hydroxylamine. In the reduction of silver thiosulfate complex, the R and S_m rates

(12) M. Randall and J. O. Halford, *ibid.*, 52, 178 (1930).

(13) T. H. James, *ibid.*, 62, 3411 (1940).

TABLE IV

VARIATION OF THE REACTION RATE WITH VARYING CONCENTRATION OF REACTANT AT 20°

Na ₂ S ₂ O ₃ , 0.12 M; NH ₂ OH, 0.04 M			AgNO ₃ , 0.01 M; NH ₂ OH, 0.04 M				AgNO ₃ , 0.01 M; Na ₂ S ₂ O ₃ , 0.12 M				
AgNO ₃ , M	t, min.	R	Na ₂ S ₂ O ₃ , M	Initial (Ag ⁺) × 10 ¹⁴	t, min.	S _m	NH ₂ OH, M	t, min.	R	S _m	N ₂ , %
0.020	0.65	0.452	0.120	4.2	1.15	1.65	0.080	0.55	0.340	2.70	79.7
.010	1.20	.232	.080	10.75	0.75	1.88	.040	1.15	.232	1.65	80.0
.006	2.15	.142	.060	26.2	.40	2.3	.020	2.10	.180	1.11	81.4
.004	3.5	.090	.050	46.7	.24	2.8	.010	4.00	.140	0.59	83.1

again measure the silver-catalyzed reaction. The S_m data are in accord with the equation

$$S_m = \{K_1[Ag^+] + K'[Ag(S_2O_3)_2^{=}]\}[NH_2O^-]^{0.66} \quad (1)$$

This expression indicates adsorption of hydroxylamine to silver, but gives no evidence for the adsorption of either silver ions or the undissociated complex. Both silver ions and undissociated complex participate in the reaction, and extrapolation of the data in Table IV to zero silver-ion concentration gives 1.6 as the rate of reaction of the undissociated complex. A similar expression is obtained for the R rates, which apply to the early stages of the catalyzed reaction. The fractional power of the hydroxylamine concentration in this case is 0.42.

The 1/t rates are given by the equation

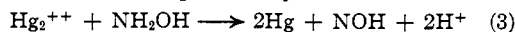
$$1/t = \{K_2[Ag^+] + K'[Ag(S_2O_3)_2^{=}]\}[NH_2O^-] \quad (2)$$

No absorption is indicated, and the kinetics may be taken as those of the uncatalyzed reaction. Extrapolation to zero silver-ion concentration gives the value 0.25 for the rate of reaction of the undissociated complex under the conditions employed. The gold catalysis which assisted in the reduction of silver nitrate is absent, probably because of the low concentration of silver ions involved.

The catalyst markedly favors the formation of nitrogen in the oxidation of hydroxylamine by mercurous nitrate. Yields of as low as 13% nitrogen were obtained in the absence of added catalyst, and considerable variation in yield was observed upon changing the method of mixing of the component solutions. Addition of catalyst progressively increased the nitrogen yield. When conditions were such that the rate of the uncatalyzed reaction was comparatively very small, the product was almost wholly nitrogen.

The uncatalyzed reduction of silver salts by hydroxylamine in acid or neutral solution occurs at a rate inconsequential in comparison with that of the silver-catalyzed reaction. The product is substantially pure nitrogen. The greater prevalence of the uncatalyzed reaction in the reduction of mercurous nitrate may be due in a large part to

the tendency of the reduced metal to coagulate to globules, thus greatly reducing the available catalyst surface. The possibility that the reaction



may occur in a single bimolecular step must also be considered.

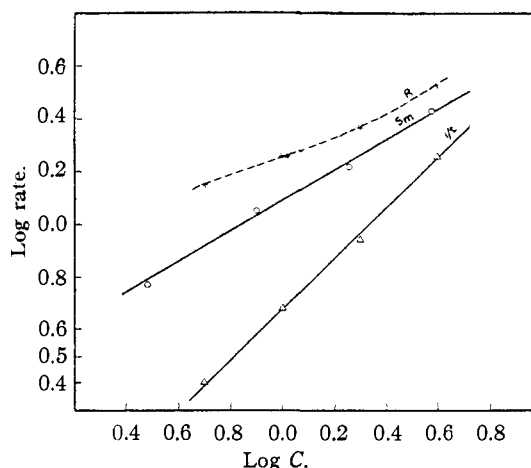


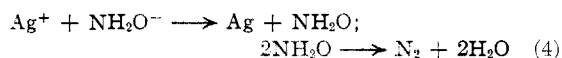
Fig. 2.—Variation of rate with NH₂OH concentration.

In moderately to strongly alkaline solutions, the oxidation product varies markedly with the nature of the silver salt employed. Most of the reactions which yield substantial quantities of nitrous oxide are too rapid for kinetic study, but it is significant that the conditions which kinetically should favor the uncatalyzed reactions are the ones which experimentally favor the formation of nitrous oxide. This is further substantiated by Nichols' observation that an increase in the reaction temperature increases the nitrous oxide yield.⁸

In no case was 100% nitrogen obtained by reaction in 0.06 N sodium hydroxide. The reduction of silver thiosulfate complex yields as high as 89% nitrogen in the absence of gelatin, and from 79.7 to 83.1% under the conditions specified in Table IV. The nitrogen yield increases with decreasing hydroxylamine concentration, as would be expected. However, it would be necessary to assume that the uncatalyzed reaction accounted for about one-fifth of the total reaction product

under the latter conditions if the catalyzed reaction yielded pure nitrogen. This assumption is untenable. It will be noted, however, that the mechanism of the catalysis in this reaction is different from the more usual one which involves adsorption of the metal ions. There is no evidence that the catalyzed reaction involving primarily adsorption of silver ions yields any nitrous oxide.

It was suggested previously that deformation of the adsorbed ions permits the simple removal of the electron from the hydroxylamine ion, thus



In the absence of catalyst, on the other hand, formation of the nitrosyl radical may occur,⁵ as in Eq. 3. The work of Baudisch¹⁴ supplies good evidence for the formation of this radical in the oxidation of hydroxylamine by cupric ion. The nitrosyl radical would yield only nitrous oxide on decomposition. Some nitrogen could be formed in the uncatalyzed reaction by the action of the nitrosyl radical on hydroxylamine.⁵

(14) O. Baudisch, *Naturwiss.*, **27**, 768 (1939); *Science*, **92**, 336 (1940).

Summary

1. Mercurous nitrate, under proper conditions, oxidizes hydroxylamine without an induction period and produces chiefly nitrous oxide. Addition of colloidal mercury or silver catalyst produces a progressive increase in nitrogen yield. The product of the catalyzed reaction is predominantly nitrogen.

2. The product of the oxidation of hydroxylamine by silver salts in strongly alkaline solution varies markedly with the nature of the salt and reaction conditions. Nitrogen yields ranging from 5 to 90% were obtained at pH 12.7.

3. The catalyzed reduction of silver thiosulfate complex involves adsorption of hydroxylamine to silver, but not adsorption of silver ions or complex. Kinetic data on the initial uncatalyzed reaction were obtained.

4. The evidence indicates that the metal-catalyzed oxidation of hydroxylamine by mercurous and silver salts yields wholly or predominantly nitrogen. The uncatalyzed reaction yields chiefly nitrous oxide.

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RECEIVED NOVEMBER 17, 1941

[CONTRIBUTION FROM COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Molecular Weights of Hydrogenolysis Products from a Pittsburgh Seam Bituminous Coal

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Treatment of a Pittsburgh seam bituminous coal with hydrogen at elevated pressures and at temperatures of 350–425°, in the presence of an oxide catalyst, such as copper chromium oxide, results in degradation to a series of condensed cyclic structures of varying complexity, incompletely saturated and containing some 80% of the carbon and an important fraction of the oxygen, nitrogen, and sulfur of the original coal. The extent of degradation can be measured roughly by the solubility of the reaction products in specific types of solvents. Phenols, and in general compounds of high internal pressure, are "good" solvents and the greater part of the coal becomes soluble in such a solvent after relatively short reaction times but, as is to be expected, the products recovered from such solutions are still highly complex. To obtain complete solubility in a hydro-

carbon solvent of low internal pressure such as pentane, it is necessary to continue the reaction for a longer time or to work at a higher temperature.

The present investigation deals with the molecular weights of fractions obtained by solvent precipitation and vacuum distillation from the hydrogenolysis products of a Pittsburgh seam coal. The coal was subjected to intermittent treatment with hydrogen at 350° and extraction with cyclohexane, until further treatment failed to yield significant amounts of material soluble in this solvent. The cyclohexane was distilled off on the water-bath through a column and the remaining viscous residue was subjected to fractionation as indicated below. Molecular weight determinations of the fractions were made cryoscopically in catechol and in diphenyl and ebullioscopically in benzene.