determination of the standard potential, E_0.

3. The results indicate a maximum in the ionization constant which occurs at 15°.

4. Log K does not vary linearly with the reciprocal of the dielectric constant.

5. The plot of log K versus the mole fraction of dioxane at a given temperature is nearly linear.

Numerical equations expressing this linear relationship have been constructed and a table of deviations compiled from which K may be evaluated in all solvents containing 0 to 82% dioxane and at 5° intervals from 0 to 50° with an accuracy comparable to the experimental error.
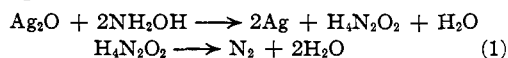

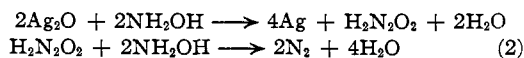# The Reduction of Silver Ions by Hydroxylamine

BY T. H. JAMES

Hydroxylamine appeared to be ideally suited for use in a continuation of the investigation of the reduction of silver ions by developing agents.[1]

The reaction rate can be followed by two independent methods, i. e., optical determination of silver, as previously described, and measurement of nitrogen evolution. The reaction has been subjected to analytical study.[2] Further, it was found that this reaction supplied a transition between the relatively simple kinetics of the hydroquinone reduction and the complicated behavior encountered in a study of the reduction by p-phenylenediamine.

Nichols showed that ammoniacal silver nitrate reacts with hydroxylamine to give pure nitrogen. Strongly alkaline silver nitrate–sodium sulfite solution, on the other hand, yields a mixture of nitrogen and nitrous oxide, but the amount of nitrous oxide produced decreases with decreasing alkalinity. For the production of nitrogen, Nichols postulates the alternative mechanisms

$$Ag_2O + 2NH_2OH \longrightarrow 2Ag + H_4N_2O_2 + H_2O$$
$$H_4N_2O_2 \longrightarrow N_2 + 2H_2O \qquad (1)$$

or

$$2Ag_2O + 2NH_2OH \longrightarrow 4Ag + H_2N_2O_2 + 2H_2O$$
$$H_2N_2O_2 + 2NH_2OH \longrightarrow 2N_2 + 4H_2O \qquad (2)$$

Nitrous oxide, when formed, is considered to arise from the decomposition of hyponitrous acid. Sheppard and Mees showed that the rate of reaction between silver ions and hydroxylamine is accelerated by the addition of alkali, and they concluded that the active species is the ion NH_2O^-. They further observed a catalysis by finely divided silver.

Under the conditions employed in the present investigation, only nitrogen was obtained as reaction product, and this was invariably in the theoretical amount. All measurements were made at $20 \pm 0.02°$, and a solution volume of 75 ml. was employed. The reactions were carried out in total darkness, or under a no. 1 Wratten safelight.

Materials and Procedure

Hydroxylamine Sulfate.—Eastman Kodak Company preparation recrystallized and dried in vacuum, m. p. 172°.

Colloidal Gold.—Phosphorus reduction[3] failed to show the Tyndall cone.

Salts.—General Chemical Company reagent grade. The reaction mixture was prepared in two parts, one containing the silver nitrate and buffer solution, the other containing the hydroxylamine, 2 ml. of 5% gum arabic solution, and, in general, 2 ml. of gold sol. The solutions were freed from oxygen by means of a stream of pure nitrogen, allowed to attain the temperature of the thermostat, and mixed rapidly at time 0. When nitrogen evolution was employed to follow the reaction course, the apparatus previously employed in the measurement of autoxidation rates[4] was used. The reaction chamber was filled with nitrogen and the buret with water at thermostat temperature. The shaking rate employed was adequate to prevent supersaturation of the reaction mixture with nitrogen. When silver determinations were made, a special apparatus was employed which permitted removal of samples at suitable intervals without allowing air to enter the reaction vessel. The solution was stirred by pure nitrogen throughout the course of reaction.

The reduction of silver ions by hydroxylamine is catalyzed by colloidal gold, and more strongly by colloidal silver. Beyond a nitrogen evolution of 0.08–0.10 ml., a plot of $V^{1/3}$ against t yields a straight line for about one-fourth of the entire reaction. This method of the treatment of the

(1) T. H. James, THIS JOURNAL, **61**, 648 (1939).

(2) S. E. Sheppard and C. E. K. Mees, "Investigations of the Theory of the Photographic Process," Longmans, Green and Company, New York, 1907, 141 pp.; M. L. Nichols, THIS JOURNAL, **56**, 841 (1934).

(3) H. B. Weiser, "Inorganic Colloid Chemistry," J. Wiley and Sons, Inc., New York, N. Y., Vol. I, 1933, p. 38.

(4) T. H. James and A. Weissberger, THIS JOURNAL, **59**, 2040 (1937).

data is based upon the rate equation derived in the previous paper.[1] The extension downward of this straight line cuts the t-axis at fairly large values of t when the reaction mixture is nucleated with gold sol. As will appear subsequently, the gold-catalyzed reaction is slower than the silver-catalyzed reaction and involves some difference in mechanism. As the reaction proceeds, however, the gold particles become coated with silver, and the reaction goes over into that of the silver-catalyzed reduction. In the following, the rates of the silver-catalyzed reaction are expressed in terms of the slope of the $V^{1/3}$–t straight-line plots, where the volumes are at 20° and 760 mm. As a measure of the preliminary reaction or reactions, the reciprocal of the time, T, required to yield a nitrogen volume of 0.08 ml. (determined from the straight-line intersection) is employed. Time is expressed in minutes.

Parallel determinations of optical density and nitrogen evolution were made under several sets of conditions, and found to yield identical results within experimental error. This is illustrated for one set of data in Fig. 1. In the construction of this figure, the density and volume units were adjusted to give the same maximum value. These results establish the practical identity of the two methods of following the reaction. Further, they show that, if nitrogen evolution is the result of a subsequent reaction, as suggested by Equations
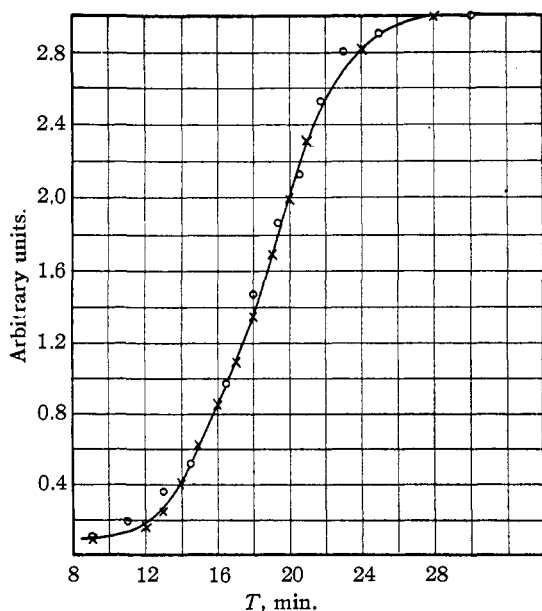
1 and 2, the reaction must be very rapid in comparison with the reduction of the silver ions.

The variation of reaction rate with pH is given in Table I. A plot of log R against pH

TABLE I
VARIATION OF RATE WITH pH

0.2 M sodium acetate, 25 ml.; 1.0 M acetic acid, x ml.; AgNO$_3$, 0.50 mmole.; hydroxylamine sulfate, 2.0 mmole.; gum arabic, 0.133%.

pH	R	$2 + \log R$	T	Log $(100/T)$
3.70	0.0254	0.405	44.0	0.36
3.89	.0603	.780	19.0	.72
4.16	.170	1.23	5.4	1.27
4.44	.485	1.680	1.5	1.82

(Fig. 2) yields a curve which, at the lower pH values, has a slope of nearly 2.0. At pH 4.4 the slope has dropped to 1.4. On the other hand, a plot of log $(100/T)$ against pH yields a straight line of slope approximately 2.0.
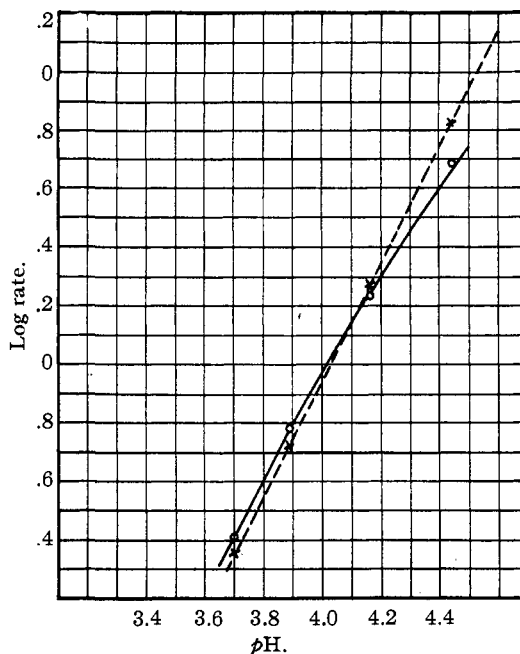

Fig. 2.—Variation of rate with pH; ○, R, silver-catalyzed; ×, $100/T$ preliminary.

The variation of the rate with hydroxylamine concentration for several pH values is given in Table II. A log–log plot of the data for the silver-catalyzed reaction is given in Fig. 3. The variation of the rate with silver-ion concentration at pH 4.16 is given in Table III. A log–log plot of the data is given in Fig. 4.

The Reaction in the Presence of Sodium Sulfite.—In order to extend the investigation of the hydroxylamine silver-ion reaction into the

Fig. 1.—Reduction of silver ions by hydroxylamine: ○, silver; ×, N$_2$ volume.

TABLE II

AgNO₃, 0.50 mmole.   Au 2.00 ml.

Hydroxyl-amine sulfate, mmole.	R	pH	R, corr. pH 4.16	T	Log (100/T)
0.50	0.068	4.22	0.058	21.4	0.56[a]
1.00	.121	4.20	.105	11.0	.88[a]
2.00	.170	4.16	.170	5.4	1.27[a]
4.00	.209	4.09	.275	3.5	1.60[a]
1.00	.021	3.82		55.0	0.26
2.00	.042	3.82		29.0	.54
4.00	.073	3.82		13.0	.89

AgNO₃, 0.30 mmole.; Na₂SO₃, 10.0 mmole.

1.00	0.179	8.54		5.2	1.28
2.00	.228	8.54		2.9	1.54
4.00	.265	8.54		1.4	1.85

[a] Values corrected to pH 4.16.

Fig. 4.—Dependence of rate upon silver ion concentration at pH 4.16: O, R, slope 0.64; ×, 100/T slope 0.66.

evidence was obtained of complications resulting from reduction of silver ion by the sulfite. Once more, nitrogen was evolved in the theoretical amount. In most of the work, sulfite was present in considerable excess, and in calculations of the silver-ion concentration it was assumed that Ag(SO₃)₂$^{\equiv}$ was the only complex ion present. The dissociation constant of this ion was taken as 3×10^{-9}. This rough figure is adequate for calculations of relative concentrations.

The variation of reaction rate with concentration of silver ion and of excess sodium sulfite is given in Tables IV and V. A plot of log R against log C gives an acceptable straight line of slope about 0.53 in the case of silver-ion variation, and of slope about 1.08 in the case of excess sulfite-ion variation.
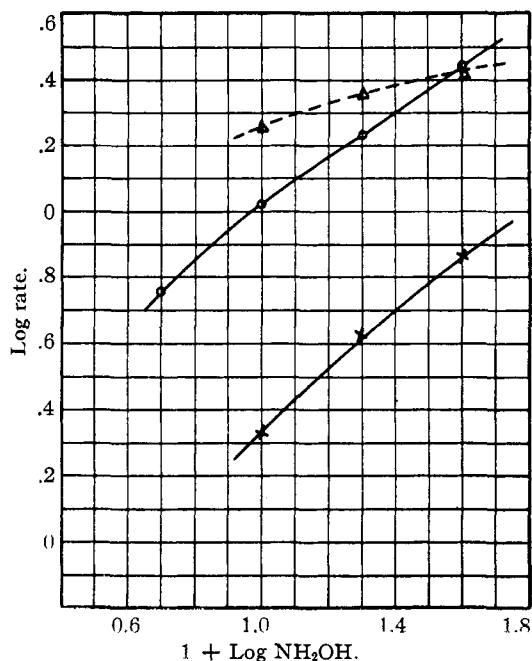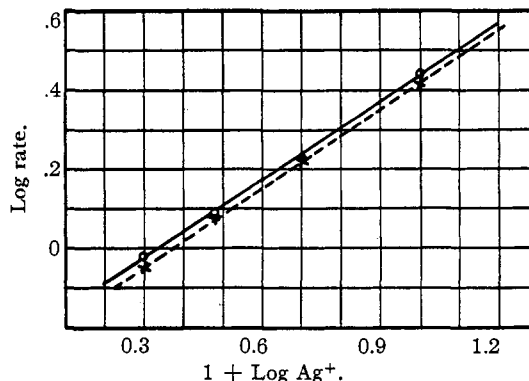

Fig. 3.—Variation of rate with [NH₂OH]: ×, pH 3.82 slope 0.95; O, pH ~4.16 slope 0.75; △, pH 8.54 slope 0.3.

TABLE III

Hydroxylamine sulfate, 2.00 mmole.; pH 4.16; gum arabic, 0.133%; gold sol, 2.00 ml.

AgNO₃, mmole.	R	T
0.20	0.096	11.2
.30	0.123	8.3
.50	1.69	6.0
1.00	0.275	3.9

alkaline region, sodium sulfite was employed to reduce the silver-ion concentration to a sufficiently small value to permit measurement of the reaction rate. Under the conditions employed, no

TABLE IV

VARIATION OF RATE WITH SILVER-ION CONCENTRATION

Hydroxylamine sulfate, 1 mmole.; gum arabic, 0.133%; gold sol, 2.00 ml.; pH 8.54 (borate buffer).

AgNO₃	Na₂SO₃	Excess SO₃⁻	[Ag⁺]	R	T
0.20	10.0	9.6	4.88×10^{-10}	0.144	6.8
.30	10.0	9.4	7.63	.179	5.2
.50	10.0	9.0	13.7	.245	2.75
1.00	10.0	8.0	35.1	.387	0.90

TABLE V

VARIATION OF RATE WITH SODIUM SULFITE

AgNO₃, 0.30 mmole.; hydroxylamine sulfate, 1.0 mmole.; pH 8.54.

Na₂SO₃	Excess SO₃⁻	R
10.0	9.4	0.179
5.0	4.4	.409
3.0	2.4	.796
2.4	1.8	1.06

The salt effect on the silver-catalyzed reaction is negligible, as shown by the data in Table VI.

Similar results were obtained at pH 8.54 in the presence of sodium sulfite.

KNO₃, g.	pH	R	R pH 4.16	T	100/T pH 4.16
0.00	4.16	0.170	0.170	6.0	16.7
.50	4.13	.156	.174	9.5	12.0
1.00	4.10	.135	.170	11.4	11.6

An increase in gum arabic concentration resulted in a decrease in the reaction rate, but it was not proportional to the concentration. Thus, at pH 4.16, R equalled 0.169 for a solution containing 0.133% gum arabic. When the percentage was increased fivefold to 0.665, R only dropped to 0.100.

Discussion

The kinetics of the reduction of silver ion by hydroxylamine show some interesting departures from those of the hydroquinone reduction. In the case of hydroquinone, a direct proportionality was observed between the reaction rate and the concentration of the reducing agent. This is approximately true for hydroxylamine at pH 3.8 but, as the pH increases, the dependence upon the concentration of reducing agent falls off, until at pH 8.54 the rate depends upon about the 0.3 power of the concentration. No indication of similar behavior was obtained with hydroquinone. The dependence of the rate upon the solution pH follows a similar course and, in the region 3.7–4.4, the dependence upon the power of the hydroxyl-ion concentration is almost exactly double that of the hydroxylamine concentration. These results indicate clearly that the active form of the reducing agent is the ion NH_2O^-. They indicate further that the hydroxylamine *is adsorbed to the silver by means of the amino group.* At low pH the hydroxylamine exists chiefly as NH_3OH^+, which presumably is not adsorbed. The concentration of NH_2OH is very small, and this accounts for the power of nearly unity. As the pH increases, the concentration of the free amine increases and the power of the concentration in the Freundlich isotherm representing the adsorption decreases. At pH 8.54 the hydroxylamine exists almost completely as free amine, and fairly strong adsorption is indicated. Adsorption involving the $-O^-$ end of the molecule is rendered doubtful by the failure of hydroquinone to show any evidence of adsorption.

The dependence of the rate upon the silver-ion concentration almost exactly parallels that found previously in the study of the reaction with hydroquinone. At pH 4.16 a power of 0.64 was obtained for hydroxylamine as compared with 0.66 for hydroquinone at pH 5.74; and at pH 8.54, a power of 0.53 was obtained for hydroxylamine as compared with 0.55 for hydroquinone at pH 8.9. Further, the dependence of the rate upon the $SO_3^=$ concentration observed at pH 8.54 shows that a reaction between hydroxylamine and the silver sulfite complex does not encroach measurably upon the reaction with silver ion.

In contrast to the hydroquinone–silver-ion reaction, it was possible in the present case to obtain a measure of a preliminary reaction in the gold-nucleated solutions. This preliminary reaction may be either the homogeneous reduction or the gold-catalyzed reduction. Presumably, it is largely the latter, at least in the acid solutions. If we take as a measure of the rate of this preliminary reaction the reciprocal of the T values given in Tables I to III, no evidence of adsorption of hydroxylamine is obtained, either in the acid region or at pH 8.54. The rate in the pH range 3.7–4.4 varied almost exactly as the square of the hydroxyl-ion concentration and as the first power of the hydroxylamine concentration. Once more, however, a dependence upon approximately the two-thirds power of the silver-ion concentration appeared. In addition to the results recorded previously, the real existence of this preliminary reaction received confirmation from the fact that when a freshly prepared nuclear silver sol was employed in place of the gold, only the silver-catalyzed reaction could be detected.

Summary

1. The reaction between silver ion and hydroxylamine is catalyzed by colloidal gold and colloidal silver. The rate of formation of silver was shown to equal the rate of evolution of nitrogen.

2. The reaction in gold-nucleated solution can be resolved into two parts, the silver-catalyzed reaction and a preliminary reaction which is probably gold-catalyzed.

3. Both reactions involve the ion NH_2O^- as the active reducing agent. The kinetics suggest that the ion is adsorbed to silver by way of the amino group in the silver-catalyzed reaction. No adsorption of hydroxylamine is indicated for

the preliminary reaction. Silver ion adsorption is indicated for both reactions. The reactions were studied over the pH range 3.7–8.5.

4. The catalyzed reduction of silver ion by hydroxylamine may be expressed by the equation

$Ag^+ + NH_2O^- \longrightarrow Ag + N + H_2O$. The NH_2O radical, if it is formed, decomposes at a rate rapid in comparison with the reduction process.

ROCHESTER, NEW YORK   RECEIVED JUNE 26, 1939

The Relative Rates of Alcoholysis of Certain Aralkyl p-Nitrobenzoates

BY LAURENCE F. KING

Previous investigations on the alcoholysis of esters, chiefly those of aliphatic alcohols, indicate that the nature of the functional alcoholic groups involved, and the amount of branching of the carbon chain of the alkyl rather than its length, are the chief factors determining both the relative velocity with which replacement of alkyl radicals occurs[1] and the extent to which reaction will proceed until equilibrium is attained.[2] Tertiary alkyls are less reactive than secondary, which in turn are less reactive than primary. The replacement values of straight-chain groups, derived from both types of measurement, are generally of the same order of magnitude no matter what the length of the carbon chain, and are greater than those of more centralized radicals. These generalizations are in disagreement with the observations of Bellet[3] on rates of replacement of certain aromatic alkyls.

The present paper constitutes a method for measuring the velocities with which esters of aromatic alcohols react in a faintly alkaline medium with aliphatic alcohols of low molecular weight. In order to eliminate the necessity for the customary fractional distillation of the reaction mixture, methanol and ethanol were chosen as the solvent alcohols; separation could then be effected quantitatively at room temperature and analysis made by a methoxyl or ethoxyl determination. Rates of reaction of the readily purified solid esters with the sodium alkoxide in a large excess of the alcohol were studied, absolute ether being used as a diluent in most cases.

Pseudo first-order velocity coefficients decrease markedly but regularly with the progress of the reaction; the existence of side reactions is indicated whether the medium is methanol, ethanol

or diluted with ether. Kremann[4] has shown that hydrolysis of the ester may be a relatively important factor, and in confirmation of this we observed that the rates of methanolysis of phenyl and benzyl p-nitrobenzoates are influenced to an abnormally high degree by slight variations in the concentration of alkali and water in the solvent. Hydrolysis is not the only disturbing side reaction, however, since the K-values in ethanol exhibit no greater constancy than those in methanol; in the latter case the concentrations of alkali and water are much higher than in the former. Assumptions of other than a simple first-order reaction lead to no greater constancy of K. In order to relate, more or less quantitatively, the reactivities of the ester alkyl groups, the first-order coefficients were averaged for the same reaction interval (15–40% ester conversion) and the benzyl radical was assigned a value of 100 (see Table I). The limits of accuracy shown are an indication only of the "fading" of the K-values and not of errors of measurement. The presence of anhydrous ether is apparently of little consequence as far as relative rates are concerned: for groups (1) and (2) the ratio K_1/K_1 is approximately equal to K_2/K_2. The peroxide content of the ether is not a determining factor, identical re-

TABLE I

RELATIVE REACTIVITY OF ARALKYL GROUPS (R) IN ALCOHOLYSIS OF p-NITROBENZOATES

R	K_1 (CH$_3$OH)	K_2 (CH$_3$OH– ether)	K_3 (C$_2$H$_5$OH– ether)
(1) Benzyl	100[a] ± 22	100 ± 16	100 ± 6
(2) 2-Ph-ethyl	37 ± 3	36 ± 6	30 ± 4
(3) 2-Ph-propyl		18 ± 3	16 ± 2
(4) 3-Ph-propyl		10 ± 1	16 ± 1
(5) 1-Ph-propyl		6 ± 1	6.0 ± 0.7
(6) 1-Ph-ethyl		5.0 ± 0.2	16 ± 1
(7) 2-Ph-isopropyl		1.0 ± 0.2	1.0 ± 0.07
(8) 1-Ph-isopropyl		0.0	0.0

[a] K_1 for phenyl considerably >100.

(1) Pfannl, Monatsh., 31, 301 (1910); 32, 509 (1911).

(2) (a) Fehlandt and Adkins, THIS JOURNAL, 57, 193 (1935); (b) Hatch and Adkins, ibid., 59, 1694 (1937).

(3) Bellet, Compt. rend., 193, 1020 (1931); 194, 1655 (1932).

(4) Kremann, Monatsh., 26, 783 (1905); 29, 23 (1908).