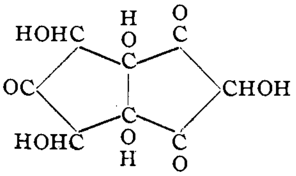
which theoretically would be formed from the reduction of three hydroxyl groups to hydrogen in the compound formed by the condensation of two benzamidine molecules with a hypothetical polymerization product of four molecules of glyoxal to the triketopentahydroxy compound



We have isolated several other highly colored reaction products of benzamidine and glyoxal, but have not yet obtained them pure enough to be certain of their empirical formulas.

Summary

A series of highly colored condensation products of benzamidine and glyoxal has been prepared. In two cases their absorption spectra in neutral and basic solution have been determined and a theory has been proposed to explain their formation. Among these are the following:

1. Glyoxaline red, formerly obtained by the condensation of benzamidine and acetylenedicarboxylic ester.
2. A condensation product between 2 g. moles of benzamidine and 3 g. moles of glyoxal.
3. A condensation product between 4 g. moles of benzamidine and 6 g. moles of glyoxal.
4. A condensation product between 4 g. moles of benzamidine and 7 g. moles of glyoxal.
5. A condensation product between 2 g. moles of benzamidine and 4 g. moles of glyoxal.

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 595]

Argentic Salts in Acid Solution. IV. The Kinetics of the Reduction by Water and the Formation by Ozone of Argentic Silver in Nitric Acid Solution[1]

BY ARTHUR A. NOYES, CHARLES D. CORYELL, FRED STITT AND ALEXANDER KOSSIAKOFF

In a preceding paper[2] of this series there were discussed preliminary results concerning the rate of oxidation by ozone of acid solutions of argentous nitrate, and of the rate of reduction by water of the argentic solutions thus formed. The present article describes in detail the more extensive kinetic study referred to there, as well as further observations on the behavior of argentic solutions toward some reducing agents.

Methods of Analysis

Considerable effort was spent in search of a rapid, accurate method of analysis for argentic silver in nitric acid solutions in the presence of ozone. A series of qualitative experiments revealed several interesting facts briefly summarized here.

The Action of Argentic Nitrate[3] and of Ozone on Certain Reducing Agents.—The following experiments were made with solutions of argentic nitrate or of ozone either 2 or 4 N in nitric acid and initially at 0°.

The following reducing agents reduce both argentic nitrate and ozone completely in a short time: Fe^{++}, $Fe(CN)_6^{\equiv}$ $HAsO_2$, Hg_2^{++}, Mn^{++}. This was shown by the immediate disappearance of the brown-black argentic nitrate color on adding argentic solution to the reducing agent in a glass-stoppered flask, or by the absence of the odor of ozone after adding to the reducing agent a sample of ozone-saturated nitric acid. Argentic nitrate solutions oxidize Mn^{++} to MnO_4^-, but ozone oxidizes it principally to manganese dioxide even with argentous ion present. Tl^+ also reduces both argentic nitrate and ozone, but the reduction of ozone is not complete within a few minutes (with shaking) unless a rather large excess of reagent is used. A ten-fold excess results in complete reduction of ozone in less than two minutes, and in much less time if argentic silver is also present.

The following reducing agents reduce argentic nitrate immediately, but within an hour with occasional shaking do not reduce ozone completely even in the presence of argentous ion, as is shown by the persistence of the ozone odor:

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[1] This investigation was initiated by Professor Noyes, who directed a large part of the experimental work. After his death in June, 1936, the junior authors brought the work to a close and prepared this article for publication. They assume full responsibility for imperfections and wish to acknowledge their great debt to Professor Noyes.

[2] Noyes, Hoard and Pitzer, THIS JOURNAL, **57**, 1221 (1935).

[3] The term "argentic nitrate" is used in this paper to designate argentic silver in nitric acid solution, although no compound $Ag(NO_3)_2$ has yet been isolated.

HCOOH, $H_2C_2O_4$, H_2O_2, H_3PO_3, Cr^{+++}, VO^{++}, Pb^{++}. ClO_3^- is very slowly if at all oxidized by argentic nitrate solutions.

Direct titration of argentic nitrate solutions (2 *N* in nitric acid) using the disappearance of the brown-black color as end-point was found possible with a great number of reagents. In the absence of ozone comparison of such titrations with the thallium method of analysis[4] showed them to be quantitative within experimental error for all cases tested, namely, $H_2C_2O_4$, H_2O_2,[5] and VO^{++}.

Tests made on formic acid, oxalic acid and hydrogen peroxide with argentic solutions containing ozone showed partial reduction of the ozone. VO^{++} is satisfactory for argentic nitrate alone, but reduces a small but appreciable amount of ozone. Pb^{++} seems rapidly to be oxidized to lead dioxide by argentic silver only in the presence of the solid product. The presence of ozone seems to have little effect on Pb^{++} and Cr^{+++}, but it was not shown that no ozone was reduced. Cr^{+++} was found not to be a satisfactory reducing agent for argentic nitrate in 6 *N* nitric acid.

For analyses of samples containing ozone it was finally decided to use a reducing agent which completely and rapidly reduces both argentic silver and ozone, and to analyze for ozone in a separate determination. For this purpose arsenious acid was chosen at the suggestion of Professor E. H. Swift. For analyses in the absence of ozone either arsenious acid or ferrous sulfate was used.

Arsenious Acid Method of Analysis.—The sample was added to an excess of arsenious acid solution, the silver precipitated as chloride, the solution neutralized with sodium hydroxide, made slightly acid with sulfuric acid, sodium bicarbonate added, and the excess arsenious acid titrated with iodine using starch solution as an indicator.

For testing the method the thallium method of analysis was used. This method is known[4] to be precise in the absence of ozone, and further tests comparing it with the standard potassium iodide method for determining ozone showed that Tl^+ also reduces one oxygen atom of ozone quantitatively. Similar tests with arsenious acid showed that it is quantitatively oxidized by ozone in the same manner (see Table I). Comparison values of the oxidizing power of the same argentic solution with ozone present and absent by the thallous and arsenious acid methods of analysis are shown in Table I.

Further tests showed that 0.25 *N* arsenious acid is not oxidized appreciably in one hour by 5 *N* nitric acid solution at room temperature, but is almost completely oxidized by 7.5 *N* nitric acid within that time. Also it was found that the presence of nitrogen dioxide in the nitric acid causes oxidation of the arsenious acid at an appreciable rate for acid concentrations less than 5 *N*.

TABLE I

TESTING THE ARSENIOUS ACID METHOD OF ANALYSIS FOR ARGENTIC NITRATE

Concentrations in milliequivalents per liter

Type of sample	Method of analysis KI	$HAsO_2$	$TlNO_3$
O_3 alone	2.31	2.31	
	2.03 2.05	2.06	
	2.59	2.63 2.60	
Ag^{II} alone		2.37 2.35	2.35
Ag^{II} and O_3		6.61	6.61 6.62

Ferrous Sulfate Method of Analysis.—Samples of argentic solutions were added with stirring to an excess of slightly acid ammonium-free ferrous sulfate, the solutions were diluted, and the excess ferrous ion titrated with standard permanganate within two minutes. If the acidity of the sample was 6 *N* or greater care was taken to have the solutions of ferrous sulfate in sufficient volume of water that the permanganate end-point was permanent, indicating that reduction of nitrate by ferrous ion had not occurred. A comparison of this rapid method with the thallium method of analysis is presented in Table II. Here analyses made on a solution 6 *N* in nitric acid and 1 *f* in total silver at 0° are recorded. The two methods of analysis were alternated because the argentic solution was being reduced by water at an appreciable rate. The two methods are seen to be in satisfactory agreement.

TABLE II

TESTING THE FERROUS SULFATE METHOD OF ANALYSIS FOR ARGENTIC NITRATE

Concentrations in milliequivalents per liter

Time of sampling, min.	(Ag^{II}) by $FeSO_4$	(Ag^{II}) by $TlNO_3$
0	..	45.8
1.8	45.6	..
2.8	..	45.5
4.6	45.1	..
5.5	..	45.3
7.1	45.5	..
8.5	..	44.8

Experimental Methods

Chemically pure nitric acid of commerce was used. Chemically pure silver nitrate was crystallized from water solution by addition of concentrated nitric acid. Ozone was prepared as described in ref. 2. The current in the primary coil of the transformer and the rate of flow of oxygen through the ozonizer were kept constant so that the ozone yield was approximately 8%.

Oxidation Rate and Steady State.—The reaction vessels and thermostat described in ref. 2 were used. The ozone-oxygen mixture was passed through a known quantity of standard nitric acid solution to which the calculated quantity of dry silver nitrate had been added after allowing time for saturation by the gas. By use of the arrangement shown in Fig. 1 samples of from 20 to 35 g. were drawn by

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[4] Noyes, Pitzer and Dunn, THIS JOURNAL, **57**, 1229 (1935).

[5] We are indebted to Mr. Robert Heitz for testing the hydrogen peroxide titration.

suction from reaction vessel A to deliver beneath the surface of the solution of the reducing agent in C. The rate at which the sample was drawn was regulated by stopcock. The flow was stopped by removing the paraffined cork fitting at B, and air was drawn through to ensure complete mixing in the gas phase. The flow of ozone through the bottle was stopped just before drawing a sample and started after an interval of some twenty seconds. A tube containing solid sodium hydroxide was placed in B on removing the cork fitting and delivery tube in order to prevent ozone in the atmosphere from interfering. The delivery tube was dried and cooled before taking each sample. The quantity of sample was determined by weighing tube C.

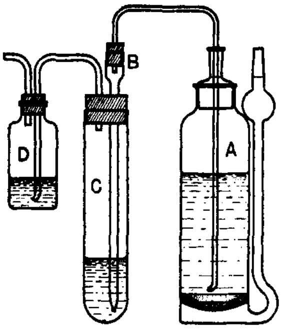

Fig. 1.—Arrangement for drawing samples: A, reaction flask; B, paraffined cork connection; C and D, solutions of reducing agent.

For each point of the rate curve two samples were taken. One yielded the sum of the argentic and ozone concentrations, the other the concentration of ozone in solution. The samples for ozone concentration were taken in the middle of the time intervals between argentic samples. For determining the sum of the argentic and ozone concentrations, C contained excess arsenious acid solution and D buffered neutral potassium iodide solution. For determining the concentration of ozone in solution, C was empty and D was replaced by two large test tubes in series containing buffered neutral potassium iodide. (There was no oxygen error with potassium iodide solution buffered to *p*H 7.1.)

Samples were drawn at intervals until the steady state was reached at which the oxidation and reduction rates were equal.

Reduction Rate.—The following technique was employed for those runs in which the arsenious acid method of analysis was used. Through solutions oxidized to the steady state a swift stream of oxygen cooled to 0° was passed until there was no test for ozone. Then samples were withdrawn by suction as already described and analyzed for total oxidizing power. During the run a slow stream of oxygen was passed through the solution.

For those runs in which the ferrous sulfate method of analysis was used the argentic solutions were prepared by the anodic oxidation of argentous nitrate at a platinum gauze electrode in nitric acid solutions, using an unglazed porcelain cup as cathode compartment. This method of preparation proved itself very serviceable, high concentrations being obtained in fifteen to twenty minutes. By proper cooling any desired temperature could be attained within a few tenths of a degree. At low nitric acid concentrations (2 *N*) at 0° a small amount of ozone was formed and was removed by a stream of air. Care was taken lest high enough concentrations of argentic nitrate be obtained for the precipitation of the emery-like argentic oxynitrate; if this formed the solution was filtered through sintered glass, during which time the reduction reaction lowered the argentic concentration so no more oxynitrate precipitated.

After solutions prepared in the above manner had come to the temperature of the thermostat (0.00 ± 0.05° or 25.00 ± 0.10°), samples were withdrawn by pipet and transferred to flasks containing standard ferrous sulfate solution, the time recorded being that at which the pipet was half drained.

Solutions prepared by electrolysis underwent reduction at the same rate as solutions of the same composition prepared by ozonization, indicating identical products.

The Rate of the Reduction Reaction

The rate of reduction for the over-all reaction

$$4\mathrm{Ag}^{\mathrm{II}} + 2\mathrm{H_2O} = 4\mathrm{Ag}^+ + 4\mathrm{H}^+ + \mathrm{O}_2 \qquad (1)$$

was studied at four nitric acid concentrations at 0° and at three at 25°. Columns 2, 3, and 4 of Tables V and VI indicate the scope of the runs. Those runs designated with the letter a involved the use of the arsenious acid method of analysis; all other runs involved the use of the ferrous sulfate method of analysis.

The Treatment of the Data.—As no simple one-term differential equation seemed to represent the data satisfactorily, large scale plots of $(\mathrm{Ag^{II}})$ against time were carefully drawn,[6] and slopes, $-d(\mathrm{Ag^{II}})/dt$, were measured at various values of $(\mathrm{Ag^{II}})$. In those runs in which the rate changed many fold from start to finish $(\mathrm{Ag^{II}})$ was plotted against $\sqrt{t}$; $-d(\mathrm{Ag^{II}})/dt$ is then the slope of this curve divided by $2\sqrt{t}$. These values of $-d(\mathrm{Ag^{II}})/dt$ were then used in determining the differential equation governing the reaction rate.

The earlier work[2] showed that, at least under certain conditions, the reduction rate of the argentic solutions is second order with respect to the argentic concentration and is dependent on the acidity. In this work it is shown that a reduction reaction fourth order with respect to argentic concentration is superimposed on this second-order reaction. In the following paragraphs there will be discussed the argentic dependence of the reduction rate, the argentous dependence, the separation of the two reactions, the effect of change of nitric acid concentration, the nature of the mechanism, and the effect of temperature.

Argentic Dependence.—Because of the relatively large concentration of nitric acid present the hydrogen ion concentration and the ionic

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(6) The symbol $(\mathrm{Ag^{II}})$ is used to represent the equivalents per liter of oxidizing power due to silver. The oxidized silver is assumed throughout to be essentially bivalent (see the following paper and ref. 4).

strength remained essentially constant throughout any one run. In runs in which the total silver concentration, (ΣAg), was high, the argentous concentration, (Ag^+), changed little during the course of the reduction, hence the rate should be nearly a function of (Ag^{II}) alone.

For a rate equation of the type $-d(Ag^{II})/dt = k(Ag^{II})^n$, the slope of the straight line resulting from plotting log $[-d(Ag^{II})/dt]$ against log (Ag^{II}) is n. Such plots for several runs in the course of which (Ag^+) varied only slightly are shown in Fig. 2. For runs 82 and 83 at 25° and in 9.31 N nitric acid the slope approaches two at low (Ag^{II}), whereas for runs 36a, 37, and 38 at 0° and in 3.34 N nitric acid the slope is nearly four for high (Ag^{II}). In all other runs the slopes for such plots vary within these limits. This suggests that two reduction reactions occur simultaneously, one second order and the other fourth order with respect to (Ag^{II}). The former reaction predominates at high acidity and low (Ag^{II}) at 25°, the latter at low acidity and high (Ag^{II}) at 0°.

Argentous Dependence.—By comparing the rate of reduction at the same (Ag^{II}) for runs at the same (HNO_3) but different (ΣAg), the argentous dependence may be studied independent of the argentic dependence. In Table III there are shown values of $(Ag^+)[-d(Ag^{II})/dt]$ at specified values of (Ag^{II}) for all runs made at 25° in 6.1 N nitric acid. In Table IV all runs made at 0° in 3.3 N nitric acid are similarly treated.

TABLE III

THE EFFECT OF (Ag^+) ON THE REDUCTION RATE AT 25° IN 6.1 N HNO_3

Values of $-10^6(Ag^+)d(Ag^{II})/dt$ tabulated for various values of (Ag^{II}).

Run	(ΣAg)	$10^3(Ag^{II})$: 10	9	8	7	6	5
71	0.0496	6.4	5.1	3.7	2.8	2.02	1.38
72	.0582	6.1	4.7	3.6	2.4	1.85	1.25
73	.106	5.0	3.9	3.1	2.5	1.69	1.19
74	.217	5.6	4.1	3.3			

For inverse first power dependence on (Ag^+) the values in any one column should be the same within experimental error. In both tables the values in any one column vary appreciably and perhaps show a slight downward trend as (Ag^+) is increased, but these variations do not seem significantly large in view of the change in (Ag^+) involved. From Table III, under conditions where the argentic dependence of the rate was found to be nearly second order, it is seen that the rate is approximately inversely proportional to (Ag^+). Under conditions where the argentic dependence was more nearly fourth order (Table IV), the rate is apparently inversely proportional to (Ag^+) also.

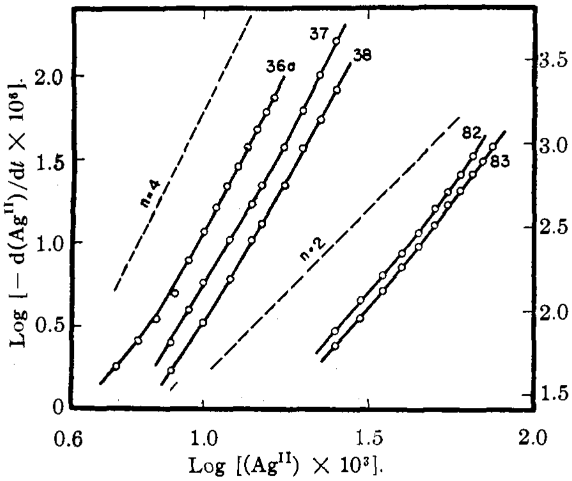

Fig. 2.—Dependence of the reduction rate on (Ag^{II}).

Separation of the Two Reactions.—The above analysis of the dependence of the rate of reduction on (Ag^{II}) and (Ag^+) at constant (HNO_3) leads to the following equation

$$\frac{-d(Ag^{II})}{dt} = k_2\frac{(Ag^{II})^2}{(Ag^+)} + k_4\frac{(Ag^{II})^4}{(Ag^+)} \qquad (2)$$

If equation (2) adequately represents the rate of reaction (1) a plot of $\frac{-d(Ag^{II})}{dt}\,\frac{(Ag^+)}{(Ag^{II})^2}$ against

TABLE IV

THE EFFECT OF (Ag^+) ON THE REDUCTION RATE AT 0° IN 3.3 N HNO_3

Values of $-10^6\,(Ag^+)d(Ag^{II})/dt$ tabulated for various values of (Ag^{II})

Run	(ΣAg)	$10^3(Ag^{II})$: 27.5	25.0	22.5	20.0	17.5	15.0	14.0	12.0	10.0	8.0	6.0
31a	0.0196										0.43	0.158
32	.0245									1.17	.56	.22
33a	.0544								2.05	1.08	.45	.182
34	.0742				11.9	6.7	4.1	2.80	1.68	0.94	.41	.198
35	.0761			18.2	12.3	6.7	4.1	2.92	1.67	.91	.42	.198
36a	.0906							3.10	1.80	.94	.40	.185
37	.174	35	23.8	15.2	9.5	5.8	3.5	2.72	1.70	.95	.41	
38	.273	30	20.1	13.6	9.1	5.6	3.4	2.66	1.57	.84	.45	

$(Ag^{II})^2$ should be a straight line whose slope is k_4 and whose intercept at $(Ag^{II})^2 = 0$ is k_2. In order to show how well equation (2) does represent the experimental data, in Figs. 3 to 9 inclusive there are shown such plots for all the runs. The values thus found for k_2 and k_4 are given in columns 6 and 7 of Tables V and VI.

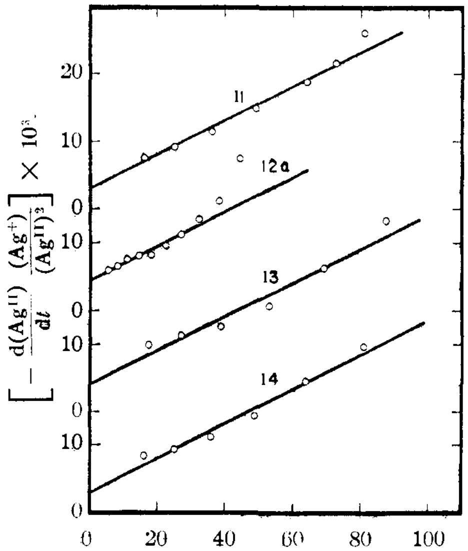

Fig. 3.—Determination of the rate constants k_2 and k_4 at 0°, 1.9 N HNO_3.

TABLE V

REDUCTION RATE EXPERIMENTS AT 0°

Run	(HNO_3), m./l.	(ΣAg), m./l.	Range (Ag^{II}), millim./l.	No. samples	$10^3 k_2$, min.$^{-1}$	k_4, (m./l.)$^{-2}$ min.$^{-1}$
11	1.88	0.0265	10 to 3	8	3.1	250
12a	1.90	.0284	7 to 2	10	4.3	260
13	1.90	.0498	9 to 3	8	4.0	250
14	1.92	.0541	10 to 3	10	3.0	250
				Mean	3.6	255
				Mean deviation	±0.5	± 5
21a	2.69	0.0282	8 to 2	11	3.8	105
22a	2.69	.0564	12 to 4	11	3.4	125
				Mean	3.6	115
				Mean deviation	±0.2	± 10
31a	3.38	0.0196	8 to 3	11	1.3	82
32	3.32	.0245	12 to 2	11	2.7	93
33a	3.38	.0544	13 to 4	20	1.8	88
34	3.39	.0742	22 to 4	12	2.2	68
35	3.39	.0761	25 to 4	13	2.4	68
36a	3.38	.0906	17 to 4	20	3.2	65
37	3.33	.174	34 to 4	13	2.7	55
38	3.33	.273	31 to 6	14	4.0	47
				Mean	2.5	71
				Mean deviation	±0.6	±13
41	6.22	0.0477	31 to 7	22	0.33	5.3
42	6.11	0.0647	41 to 6	19	.43	3.7
				Mean	0.38	4.5
				Mean deviation	± .05	±0.8

TABLE VI

REDUCTION RATE EXPERIMENTS AT 25°

Run	(HNO_3), m./l.	(ΣAg), m./l.	Range (Ag^{II}), millim./l.	No. samples	$10^3 k_2$, min.$^{-1}$	k_4, m./l.$^{-2}$ min.$^{-1}$
51	3.38	0.0922	14 to 2	12	144	850
52	3.36	.151	15 to 2	14	171	820
53	3.36	.176	11 to 2	16	145	1410
54	3.35	.248	18 to 3	12	135	1180
				Mean	149	1070
				Mean deviation	± 11	± 230
61	3.37[a]	0.118	17 to 3	16	97	375
62	3.37[a]	.264	20 to 5	16	106	265
				Mean	102	320
				Mean deviation	± 5	± 55
71	6.13	0.0496	17 to 2	17	50	148
72	6.11	.0582	20 to 2	16	47	142
73	6.14	.106	26 to 1	18	38	119
74	6.14	.217	48 to 7	17	51	99
				Mean	46	127
				Mean deviation	± 4	± 18
81	9.31	0.0783	24 to 1	20	19.2	....
82	9.31	.1902	75 to 7	18	18.8	1.29
83	9.31	.2315	89 to 13	20	19.1	1.46
				Mean	19.0	1.38
				Mean deviation	± 0.2	± 0.09

[a] ($NaNO_3$) = 2.72 m./l.; ionic strength = 6.3.

At a given acid strength at either temperature the values of k_2 fluctuate considerably, but seem to show no systematic trend as the total silver concentration is increased. At 25° the mean deviation for k_2 is on the average about 6% of the mean value, and at 0° about 15% of the mean, the increase corresponding to the smaller contribution of the second-order reaction at the lower temperature.

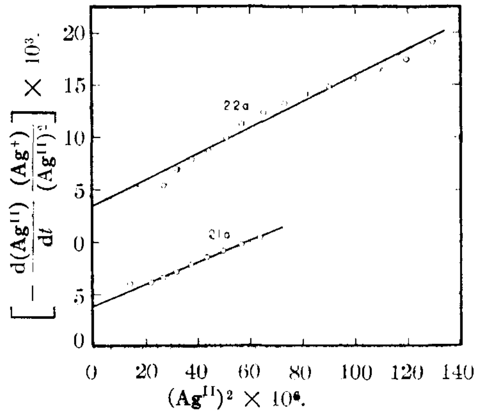

Fig. 4. Determination of the rate constants k_2 and k_4 at 0°, 2.69 N HNO_3.

At a given acid strength at either temperature the values of k_4 also vary considerably and suggest a downward trend as (ΣAg) is increased. However, in the two cases where (ΣAg) changes more than fourfold, the magnitude of this trend does not seem especially large. At 0° the mean deviation for k_4 is on the average about 12% of the mean, and at 25° about 15% of the mean.

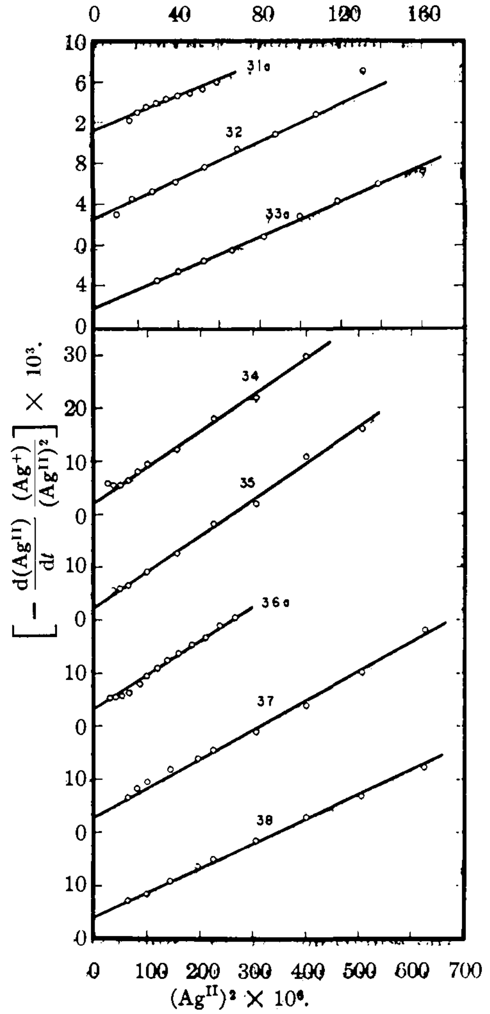

Fig. 5.—Determination of the rate constants k_2 and k_4 at 0°, 3.4 N HNO_3.

Effect of Nitric Acid Concentration.—Due to the complex nature of k_2 and k_4 it is difficult to discuss quantitatively their dependence on various factors. It will be seen later that both are probably functions of nitrate and hydrogen ion concentrations and of certain activity coefficients, as well as of the dielectric constant and the temperature. That increasing (NO_3^-) considerably lowers the values of k_2 and k_4 for a given (HNO_3) at a given temperature is shown by runs 61 and 62 in Table VI.

It is seen from Tables V and VI that k_2 and k_4 both decrease rapidly as the nitric acid concentration is increased. In Fig. 10 there are plotted values of $\log[10^3(k_2)]$ and of $\log k_4$ against $\log\,(HNO_3)$. Each point is plotted with an indication of the uncertainty in the ordinate corresponding to the mean deviation shown in Tables V and VI. The points are connected by straight lines for convenience. The slope of these lines measures approximately the power (n) of the nitric acid concentration to which k is proportional.[7] Lines with $n = -2$ and $n = -4$ are shown for comparison.

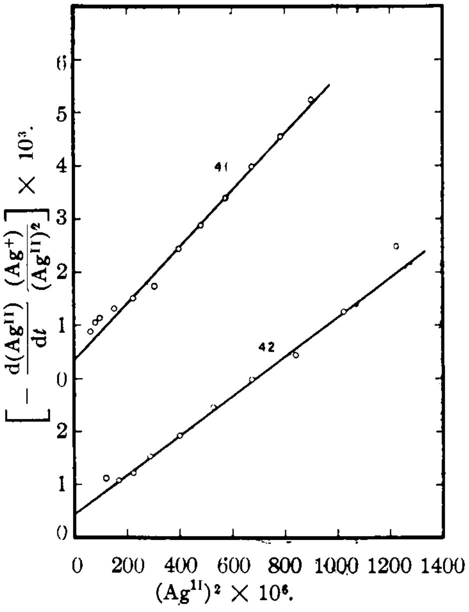

Fig. 6.—Determination of the rate constants k_2 and k_4 at 0°, 6.1 N HNO_3.

At 25°, where k_2 is more accurately determined, it shows approximately inverse square dependence on (HNO_3). At 0° the apparent dependence of k_2 found from Fig. 10 varies from $n = -2$ to -3 in the range $(HNO_3) = 2.7$ to 6.2. The apparent independence of (HNO_3) shown by k_2 below 2.7 N nitric acid at 0° may not be real.

At 0°, where k_4 is more accurately determined, it shows approximately inverse square dependence on (HNO_3) between 1.9 and 3.4 N nitric acid, and approximately inverse fourth power dependence from $(HNO_3) = 3.4$ to 6.1 N. In this latter range at 25° k_4 shows nearly the same dependence as at 0°, but at higher acid strengths it shows much greater inverse dependence on (HNO_3).

Nature of the Mechanism.—In view of the fact that compounds containing trivalent silver may be precipitated from argentic solutions in which the silver exists essentially in the bivalent

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(7) These slopes are not greatly changed by use of activity of nitric acid instead of concentration.

form,[2] the inverse dependence of the reduction rate on (Ag^+) indicates the presence of an equilibrium involving the three positive valence states of silver in solution

$$Ag^{III} + Ag^+ \rightleftharpoons 2Ag^{II} \qquad (3)$$

an equilibrium which lies far to the right.

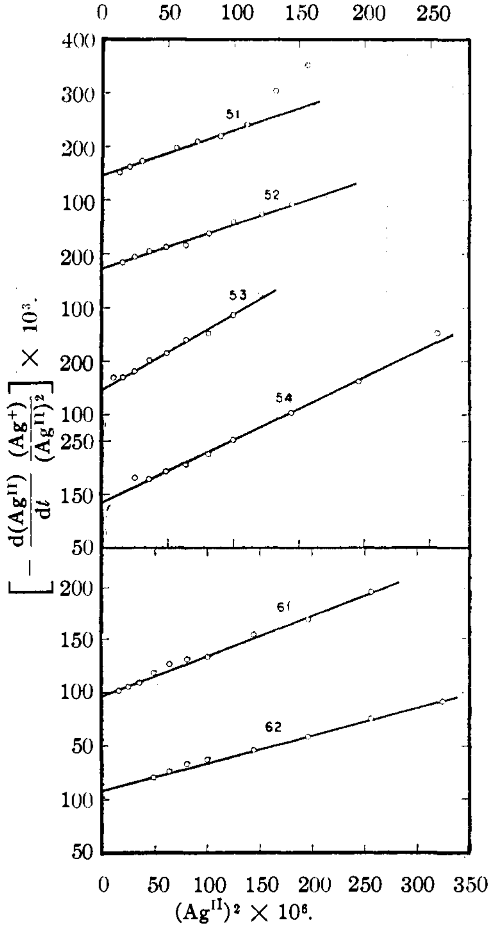

Fig. 7.—Determination of the rate constants k_2 and k_4 at 25°, 3.4 N HNO_3.

The first term of the rate equation (2) then probably results from a pseudo-unimolecular reaction involving one trivalent silver atom, such as

$$Ag^{III} + 2H_2O = Ag^+ + H_2O_2 + 2H^+ \qquad (4)$$

The decrease by two in the valence of silver, as well as the thermodynamic discussion presented earlier,[8] seems to require the formation of a peroxy compound in this rate-controlling step. The peroxide is, of course, immediately oxidized by excess argentic silver

$$H_2O_2 + 2Ag^{II} = 2Ag^+ + 2H^+ + O_2 \qquad (5)$$

The second term of the rate equation (2) probably results from a reaction involving one trivalent and two bivalent silver atoms

$$Ag^{III} + 2Ag^{II} + 2H_2O = 3Ag^+ + O_2 + 4H^+ \qquad (6)$$

In accordance with equation (3) the rate of such a reaction would be proportional to $(Ag^{II})^4/(Ag^+)$. A bimolecular reaction involving two trivalent silver atoms would result in a reduction rate term proportional to $(Ag^{II})^4/(Ag^+)^2$, but the observed dependence of the rate on (Ag^+) eliminates this possibility.

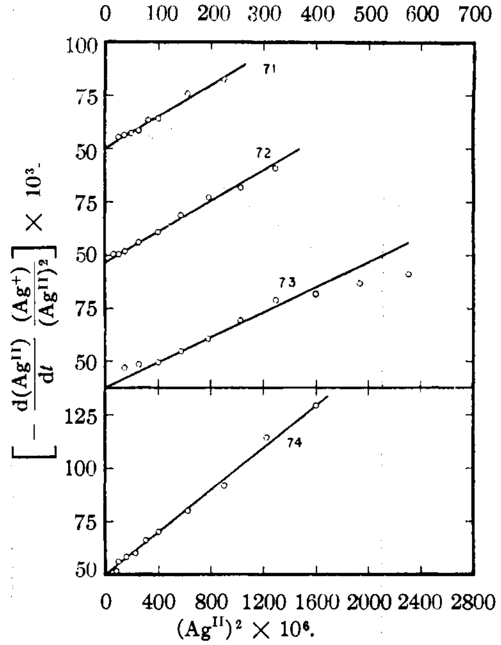

Fig. 8.—Determination of the rate constants k_2 and k_4 at 25°, 6.1 N HNO_3.

In the equations (3), (4), and (6) no attempt has been made to indicate the formulas of the species containing Ag^{II} or Ag^{III}. The kinetics of the oxidation of silver nitrate solutions by ozone (*vide infra*) suggests the existence (perhaps only transitory) of trivalent silver as the ion AgO^+. In the paper following this one it is shown that in 2 to 4 N nitric acid an average of between one and two nitrate groups is associated with each bivalent silver atom in a complex. The high inverse dependence of the rate constants on the nitric acid concentration probably is due in large measure to this effect, which is discussed qualitatively in the following paragraph.

If the Ag^{III} being reduced in equation (4) does not contain nitrate or hydroxide in complex formation and if the preponderant form of Ag^{II} includes from one to two nitrates, the expression for the second-power reduction rate derived

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[8] Noyes and Kossiakoff, THIS JOURNAL, **57**, 1241 (1935).

from equation (4) and the suitable modification of equation (3) would show inverse nitrate dependence of from the second to the fourth power. If the trivalent silver of equation (4) is associated with nitrate in a complex, the inverse nitrate dependence of the second-power rate term will be decreased accordingly; if the form reduced is in a hydroxide complex, an inverse hydrogen ion dependence will be superimposed on the nitrate dependence. Corresponding treatment of complex formation in connection with equations (3) and (6) would lead one to expect an inverse nitric acid dependence of the fourth-power constant. For these complicated reactions where the charges of the molecular species involved are not known, the effect on the constants of changing the ionic strength cannot be predicted at present. However, the observed effect of nitric acid on the rate constants is not inconsistent with what is now known about complexes of bivalent silver.

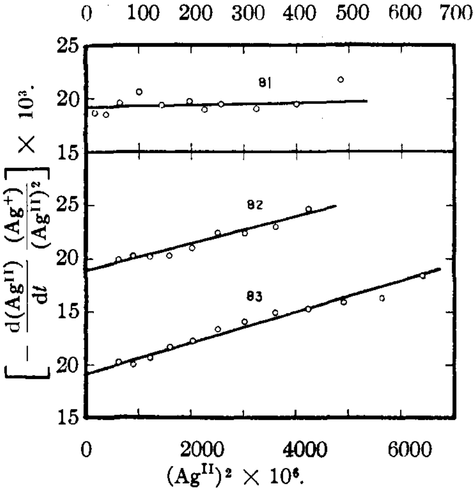

Fig. 9.—Determination of the rate constants k_2 and k_4 at 25°, 9.31 N HNO_3.

Effect of Temperature.—The rate of reduction of a particular argentic nitrate solution has been seen to depend more on the second power of (Ag^{II}) at 25 than at 0°, indicating the greater temperature dependence of the second-order reaction. The critical increment of energy for k_2 calculated from the Arrhenius equation is $Q_2 = 26{,}500 \pm 2000$ cal. in 3.3 N nitric acid and $Q_2 = 31{,}000 \pm 1400$ cal. in 6.1 N nitric acid. (The limits given for Q_2 correspond to calculations based on the upper limit for k_2 at one temperature taken with the lower limit at the other temperature.) Similarly the critical increment for k_4 is calculated to be $Q_4 = 17{,}500 \pm 2500$ cal. in 3.3 N nitric acid and $Q_4 = 21{,}600 \pm 2100$ cal. in 6.1 N nitric acid.

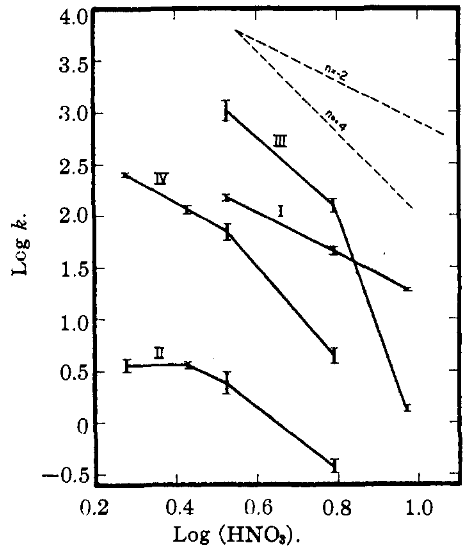

Fig. 10.—Dependence of the rate constants on (HNO_3): I, 10^3 k_2 at 25°; II, 10^3 k_2 at 0°; III, k_4 at 25°; IV, k_4 at 0°.

Despite the uncertainties in Q_2 and Q_4 both seem to increase with increase in nitric acid concentration. This effect, if real, may be due in part to changes in the medium and in part to change in the extent of nitrate complex formation. The fact that Q_2 is larger than commonly found for solution reactions is probably due to an apparent increase of the critical increment of reaction (4) by one or more preceding endothermic reactions, such as the equilibrium (3).

The Rate of the Oxidation Reaction and the Steady State

It was found in the earlier investigation[2] that the initial rate of oxidation by ozone of argentous nitrate in nitric acid solution

$$2Ag^+ + O_3 + 2H^+ = 2Ag^{II} + O_2 + H_2O \quad (7)$$

is directly proportional to the ozone and argentous concentrations and independent of the acid concentration. These results with regard to the argentous and acid concentrations are confirmed in the present work in which this oxidation rate has been studied at 0° over the whole course of the reaction. The effect of ozone concentration on the rate was not studied. For these oxidation rate experiments the arsenious acid method of analysis was used.

In order to test this rate over more than the

TABLE VII

OXIDATION RATE EXPERIMENTS AT 0°

Run	(HNO_3), m./l.	(ΣAg), m./l.	t, min.	(Ag^{II}), millim./l.	(O_3), millim./l.	$\Delta(Ag^{II})/\Delta t$, 10^{-6}(m./l.) min.$^{-1}$	Reduction rate, 10^{-6}(m./l.) min.$^{-1}$	k_0, (m./l.)$^{-1}$ min.$^{-1}$	Mean k_0, (m./l.)$^{-1}$ min.$^{-1}$
1a	1.90	0.0284	0	0					
					1.04	68	..	2.43	
			30	2.03					
					1.00	40	2	1.63	
			60	3.22					
					1.08	36	6	1.59	
			101	4.70					
					1.11	30	22	2.08	
			179	7.06					
									1.94
2a	1.90	0.0284	0	0					
					1.06	59	..	2.02	
			28	1.66					
					1.05	40	1	1.50	
			61	2.99					
					0.95	38	5	1.88	
			130	5.65					
					0.87	17	33	2.60	
			207	6.95					
									2.00
3a	2.69	0.0282	0	0					
					0.99	72	..	2.69	
			35	2.51					
					0.96	40	2	1.74	
			64	3.66					
					1.01	42	5	1.95	
			101	5.21					
					1.10	38	14	2.16	
			158	7.39					
					1.13	13	34	2.06	
			244	8.52					
									2.12
4a	2.69	0.0564	0	0					
					0.95	109	..	2.06	
			14	1.53					
					0.85	95	..	2.09	
			43	4.28					
					0.80	89	3	2.25	
			65	6.23					
					0.81	98	13	2.78	
			92	8.87					
					0.90	44	36	1.92	
			151	11.44					
					1.00	19	60	1.78	
			203	12.43					
									2.15
5a[a]	3.38	0.0272	0	0					
					1.00	70	..	2.62	
			15.5	1.08					
					0.84	57	..	2.66	
			36	2.24					
					0.79	51	1	2.74	
			75	4.22					
					0.87	37	4	2.10	
			107	5.40					
					0.96	36	10	2.29	
			155	7.15					
					1.00	20	13	1.69	
			204	8.13					
					1.04	6	29	1.79	
			265	8.48					
									2.27
								Mean	2.10

[a] "Reduction rate" calculated using equation 2 and mean values of k_2 and k_4 from Table V.

initial stages of the oxidation it is necessary to take into account the reduction rate as well. Accordingly, if no new factors complicate the oxidation rate, the equation

$$d(Ag^{II})/dt = k_0(Ag^+)(O_3) - \text{reduction rate} \quad (8)$$

should represent the rate over the whole course of the reaction.

In Table VII are shown values of k_0 calculated from equation (8). The values of $d(Ag^{II})/dt$ in equation (8) used in calculating k_0 are the observed $\Delta(Ag^{II})/\Delta t$ values for successive intervals between experimental points. From the large scale (Ag^{II}) *vs.* time plots for the reduction runs the value of $-d(Ag^{II})/dt$ at the average (Ag^{II}) for the interval was taken for the reduction rate term of equation (8). The values of k_0 thus calculated for any one run are very sensitive to experimental error and so vary considerably. Experimental error is rather large due to the limited number of samples available for one run, the appreciable variation of ozone concentration in solution during a run, and the necessity of determining the ozone concentration in a separate sample from that used for determining the sum of the argentic and ozone concentrations. However, the mean value of k_0 for a given run is much less dependent on experimental error, and it is seen in Table VII that this mean value is essentially the same for all runs at various argentous and acid concentrations.

The steady state reached on prolonged passage of ozone through nitric acid solutions of silver nitrate presumably corresponds to conditions at which the oxidation and reduction rates are equal. If equation (2) is used for the reduction rate term of equation (8), for the steady state ($d(\mathrm{Ag^{II}})/dt = 0$) one finds

$$k_0\,(\mathrm{Ag^+})(\mathrm{O_3}) = k_2\,\frac{(\mathrm{Ag^{II}})^2}{(\mathrm{Ag^+})} + k_4\,\frac{(\mathrm{Ag^{II}})^4}{(\mathrm{Ag^+})} \qquad (9)$$

TABLE VIII

COMPARISON OF THE CALCULATED OXIDATION AND REDUCTION RATES AT THE STEADY STATE

$(\mathrm{HNO_3})$, m./l.	$(\mathrm{Ag^{II}})$, millim./l.	$(\mathrm{Ag^+})$, millim./l.	$(\mathrm{O_3})$, millim./l.	Oxidation rate, 10^{-6}(m./l.) min.$^{-1}$	Reduction rate, 10^{-6}(m./l.) min.$^{-1}$
1.89	8.09	20.3	1.14	49	65
	7.52	20.9	1.10	48	49
	7.61	20.8	0.99	43	51
	7.73	20.7	1.02	44	54
2.68	9.02	19.2	1.09	43	55
	9.06	19.1	1.06	42	56
	9.60	18.6	1.25	48	70
	13.49	42.9	1.05	95	104
	13.42	43.0	1.08	98	102
	12.14	44.3	0.91	85	68
	12.50	43.9	.88	81	77
	12.76	43.6	.88	81	83
3.37	8.09	11.5	0.98	24	41
	8.01	11.5	1.04	25	39
	8.14	11.4	1.06	25	42
	8.05	11.5	1.08	26	40
	13.60	40.8	0.70	60	71
	13.67	40.7	.69	59	72
	17.88	72.7	.47	72	111
	18.00	72.6	.52	79	114

In Table VIII there are tabulated the values of the left- and right-hand members of equation (9) for all observed steady state conditions. The mean values of k_0, k_2, and k_4 given in Tables V and VII were used in the calculations. Due to fluctuations in the ozone concentration experimental error is increased by the uncertainty of the attainment of equilibrium. However, it seems probable from the approximate equality of the calculated oxidation and reduction rates that no new factors complicate the steady state phenomenon.

As suggested in the earlier paper,[2] the simplest reaction accounting for the observed oxidation rate is

$$\mathrm{Ag^+ + O_3 = AgO^+ + O_2} \qquad (10)$$

The $\mathrm{AgO^+}$, then, either directly or indirectly, is probably almost completely reduced by $\mathrm{Ag^+}$ to bivalent silver in accordance with the equilibrium (3).

Summary

The rate of reduction by water of nitric acid solutions of argentic nitrate has been studied at various acid strengths at 0 and at 25°. The data are found to be represented adequately by the rate equation

$$\frac{-d(\mathrm{Ag^{II}})}{dt} = k_2\,\frac{(\mathrm{Ag^{II}})^2}{(\mathrm{Ag^+})} + k_4\,\frac{(\mathrm{Ag^{II}})^4}{(\mathrm{Ag^+})}$$

where both k_2 and k_4 decrease greatly as the nitric acid concentration is increased. This equation is accounted for by assuming the occurrence of two independent reduction reactions both of which involve trivalent silver in equilibrium with uni- and bivalent silver.

The rate of oxidation by ozone of nitric acid solutions of silver nitrate has been studied over the whole course of the reaction including the steady state. When the expression for the initial oxidation rate derived in the first paper[2] of this series is corrected for the reduction rate it is found to represent the rate of the reaction over its entire course.

The action of a number of reducing agents on nitric acid solutions of argentic silver and of ozone has been observed. Direct titration of argentic nitrate solutions using the disappearance of the brown-black color as end-point was found possible with a number of reducing agents.

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