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Argentic Salts in Acid Solution. I. The Oxidation and Reduction Reactions

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Outline of this Investigation

The purpose of this research was a quantitative investigation of the reaction that takes place between ozone and argentous salts in acid solutions, and a study of the properties of the resulting solution containing salts of silver in a higher state of oxidation, hereafter called argentic salts. This method of preparing argentic solutions has, over that employing peroxysulfate, the great advantage that the excess of the oxidizing agent, here ozone, can finally be rapidly and completely removed by a current of air.

The over-all reaction which occurs in nitric acid solution is presumably expressed (disregarding hydrolysis of the argentic salts) by one or the other of the two following equations, depending on whether the argentic silver proves to be bipositive or tripositive

$$2Ag^{+}NO_3^{-} + 2H^{+}NO_3^{-} + O_3(g) = 2Ag^{++}(NO_3^{-})_2 + H_2O(l) + O_2(g) \qquad (1)$$

$$Ag^{+}NO_3^{-} + 2H^{+}NO_3^{-} + O_3(g) = Ag^{+++}(NO_3^{-})_3 + H_2O(l) + O_2(g) \qquad (2)$$

It was found that this reaction takes place only until there has been oxidized a moderate proportion of the silver, depending upon its concentration and that of the acid and ozone and upon the temperature. A steady state then results, but this does not represent the equilibrium of the reaction, since it was proved, as described below, that a slow current of oxygen passed through the solution contains, after the dissolved ozone is once driven out, no detectable trace of ozone. The steady state results, on the contrary, from the reduction of the argentic silver by the water according to one of the over-all reactions

$$4Ag^{++}(NO_3^{-})_2 + 2H_2O = 4Ag^{+}NO_3^{-} + 4H^{+}NO_3^{-} + O_2 \qquad (3)$$

$$2Ag^{+++}(NO_3^{-})_3 + 2H_2O = 2Ag^{+}NO_3^{-} + 4H^{+}NO_3^{-} + O_2 \qquad (4)$$

It will be shown in the second article of this series that, contrary to the prevailing opinion, the argentic silver exists wholly or almost wholly in the *bipositive state*, at any rate when the nitric acid is concentrated, and, anticipating this result, the conclusion that the oxidized silver is almost wholly bipositive will be employed throughout these articles. For brevity, the reaction by which argentic silver is produced will be called the *oxidation reaction*, and that by which it is destroyed, the *reduction reaction*.

This first article will be devoted to a description of these reactions in their general aspects and to semiquantitative measurements of their rates, as determined by our thus far completed investigations. The second and third articles of the series will present the results of researches upon the state of oxidation of argentic silver, and upon its oxidation potential. A later article will describe more exact measurements now in progress upon the rates of the oxidation and reduction reactions and of the steady states reached by them, as well as a fuller discussion of the molecular mechanisms involved.

Throughout all these investigations we have had the constant advice of Prof. Ernest H. Swift, whose invaluable suggestions have contributed greatly to the success of the work. We are also greatly indebted to Mr. C. D. Coryell for assistance in preparing these papers for publication. To the detailed researches, which have extended through four years, many other persons have contributed, as will be acknowledged as the presentation proceeds. The kindness of Professor T. H. Morgan has, by making available a large laboratory for the purpose, made it possible to continue these researches in the summers in the Kerckhoff Marine Biological Laboratory of the California Institute at Newport Beach, California.

Previous Work on the Higher States of Oxidation of Silver

Solid Argentic Compounds.—The main purpose of this research was, as stated above, an investigation of the reaction between ozone and argentous salts in acid solutions and of the properties of the resulting mixtures containing salts of silver in a higher oxidation state. It is desirable, nevertheless, to review briefly some of the existing knowledge regarding the solid compounds of silver in higher oxidation states because of its bearing on the nature of the oxidized salts existing in acid solution, with which we are here primarily concerned.

Compounds of silver more highly oxidized than argentous salts were early obtained as black deposits at the anode in the electrolysis of a neutral solution of silver nitrate by many investigators.[1] Similar compounds were shown to be produced by treating argentous salts with potassium peroxysulfate or with ozone.

The oxidation products were later shown (Barbieri, 1906)[2] to have, when dissolved in nitric acid, reactions which clearly indicated that they contained not a true peroxide (one of the hydrogen peroxide type), as had previously been supposed, but a compound or mixture of compounds corresponding to a higher oxidation state of silver. Thus it was shown that the oxidized substance is not destroyed by permanganate, manganese dioxide, or lead dioxide, as are peroxy compounds; also that, when dissolved in acids, it does not yield hydrogen peroxide, as proved by the titanium test.[3]

The anodic oxidation product has been shown to have, in relation to the silver present, greater oxidizing power than that corresponding to the oxide AgO, indicating that it contains some Ag_2O_3 or corresponding salt. Indeed, there has been isolated a fairly stable oxysalt salt of the composition $Ag_7O_8NO_3$, to which the formula $2Ag_2O_3 \cdot 2AgO \cdot AgNO_3$ is often assigned.[4] By heating this compound with water and drying the residue Jirsa[5] isolated the oxide AgO in the pure state. The solid oxide Ag_2O_3, however, could not be obtained, because of its instability.

The early electromotive force investigation of Luther and Pokorny[6] confirmed the existence of two solid black compounds containing silver in the bipositive and in the tripositive state, respectively; and the potential measurements of these investigators yielded apparently reliable values of the oxidation potentials for these two solid oxidation products. For, although the tripositive compound is not pure Ag_2O_3 and may be variable in composition, yet it gave, even after different treatments, the same reproducible electromotive force values—a fact which may be due to its always containing some free Ag_2O_3. Indeed, the electromotive forces of cells involving both these compounds have been measured with concordant results by Luther and Pokorny, by Jirsa, by Barbieri,[7] and by Carman.[8]

Acid Argentic Solutions.—The early investigators obtained by dissolving the anodic silver deposits in fairly concentrated nitric acid or in sulfuric acid black argentic solutions possessing strong oxidizing power. Argentic solutions were also early prepared by Marshall and by Marshall and Inglis (Ref. 11) by adding potassium peroxysulfate to nitric or sulfuric acid solutions of argentous salts. More recently a nitrate solution free from other anions was obtained by Jirsa[5] by dissolving his pure solid oxide AgO in nitric acid.

The chemical behavior of these argentic solutions in nitric acid has been qualitatively studied by many investigators. The most striking general result of their researches is that the argentic compound present is not only (thermodynamically) an unusually powerful oxidizing agent, but also (kinetically) a highly reactive one. Thus acid argentic solutions have been shown to oxidize in the cold almost instantaneously hydrogen peroxide to oxygen, manganous salts to permanganate, chromic salts to chromate,[3] cerous to ceric salts,[2] thallous to thallic salts (see below), vanadyl salts to vanadate,[9] iodate to periodate,[10] and ammonia to nitrogen and its oxides.[8,11,12,13] On the other hand, the argentic solutions have been produced from argentous nitrate only by the most powerful oxidizing agents, thus by ozone, peroxysulfuric acid,[8,11] lead dioxide,[14] bismuth dioxide,[14] and fluorine,[15] and by anodic oxidation. Quantitative studies of the rate of reduction of peroxysulfuric acid by ammonia and other substances in the presence of argentous salt have been made by Yost and by Carman.

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(1) References to the very early work are given by Barbieri (Ref. 2), and to the work in the intervening years up to 1925 by Jirsa (Ref. 5). References bearing on the topics to which later articles of this series are devoted are cited in those articles.

(2) Barbieri. *Atti accad. Lincei.* [5] **15**, 508–515 (1906): *Ber.*, **40**, 3371 (1907).

(3) Yost. THIS JOURNAL. **48**, 152–164 (1926).

(4) It seems unlikely that this compound contains silver in three different oxidation states: it is more probable that it is represented by the formula $AgONO_3 \cdot Ag_2O_3 \cdot 4AgO$. which could readily yield, upon moderate heating or boiling with water. as found by Jirsa, $AgNO_3 + 6AgO + O_2$ (Ref. 5). It is interesting to note that the solid prepared by Yost from the oxidation product of silver sulfate with peroxysulfate, by dissolving this in strong nitric acid and reprecipitating by dilution, has an empirical composition expressible by the formula $(AgO)_2SO_4 \cdot 6AgO$.

(5) Jirsa. (a) *Z. anorg. Chem.*, **148**, 130–140 (1925): (b) **158**, 33–60 (1926): (c) Jirsa and Jelinek. **158**, 61–66 (1926).

(6) Luther and Pokorny. *ibid.*, **57**, 290–310 (1908).

(7) Barbieri. *Atti accad. Lincei.* [6] **13**. 882–887 (1931).

(8) Carman. *Trans. Faraday Soc.*, **30**, 566–577 (1934).

(9) Yost and Claussen. THIS JOURNAL, **53**, 3349–3354 (1931).

(10) Barbieri. *Ber.*, **60**. 2427–2428 (1927).

(11) Marshall. *Proc. Royal Soc. Edinburgh.* **23**, 163–168 (1900); Marshall and Inglis. *ibid.*, **24**, 88–93 (1901).

(12) Yost. THIS JOURNAL. **48**, 374–383 (1926).

(13) King. *ibid.*, **49**, 2689 (1927); **50**, 2080. 2089 (1928): **52**, 1493 (1930).

(14) Barbieri. *Atti accad. Lincei.* [5] **16**, 77–79 (1907).

(15) Fichter and Goldach. *Helv. Chim. Acta.* **13**. 99–102 (1930).

The marked catalytic effects which argentous salts exert on oxidations have been shown to arise from the intermediate formation of the more reactive argentic salt. Thus this is true of the oxidation of manganous salts and chromic salts by lead dioxide and bismuth dioxide,[2] on the oxidation of manganous salts[1] and of ammonia[11,12,13,14] by peroxysulfate, and on the oxidation of chromic salts[3] and vanadyl salts[9] by peroxysulfate. Another significant fact of different character is that, in spite of the opaqueness of the acid solutions, optical tests indicate that they contain no colloidal particles.[5]

With respect to the nature of the argentic compound existing in the acid solutions, certain salient facts will be here mentioned, without attempting any molecular interpretation till the results of this investigation have been presented. One of these is that the black argentic compound shows the same strong oxidizing power, for example, the property of instantly converting in the cold manganous salt to permanganate, however the solution may have been prepared, indicating that the oxidized silver is always predominatingly in the *same* oxidation state, thus not sometimes bipositive and sometimes tripositive (in considerable proportion). Other general facts are that the argentic compound is much more stable, both with respect to its reduction to argentous salt and to its precipitation upon dilution, in the presence of nitric acid than in the presence of sulfuric acid or perchloric acid; and that its stability increases with the concentration of nitric acid (at least up to 10–15 normal), but decreases with the concentration of the other acids after a moderate concentration is attained.

Apparatus and Experimental Methods

Preparation and Analysis of the Ozone.—The ozone used in most of the experiments described in this article was prepared as follows. Commercial oxygen from a tank was passed successively through a soda-lime tube, concentrated sulfuric acid, a capillary flowmeter containing concentrated sulfuric acid, and phosphorus pentoxide. The dry gas was then submitted to a silent discharge between the walls of two coaxial Pyrex glass cylinders. The average diameter of the inside tube was 35 mm., the distance between the walls was about 3 mm., and the length was 45 cm. The outer tube was sheathed in copper, and was grounded. the inner tube was filled with 6 *N* sulfuric acid, and the whole was surrounded with a brass tube through which tap water at 18° was circulated. A 15,000-volt transformer of 0.45 k. v. a. capacity. operated from a 110-volt, 50-cycle a. c. circuit was connected with the acid in the inner tube by a stiff copper wire extending down the axis of the tube. The primary current was varied from 0.3 to 2.0 amperes by means of a rheostat in this circuit.

The ozone content of the gas was determined by absorbing a known volume (measured in a graduated flask) in potassium iodide solution in the presence of solid boric acid (to prevent the solution from becoming alkaline), adding a little sulfuric acid to liberate the iodine from the iodate that is always formed, and titrating with 0.1 *N* sodium thiosulfate. In other cases the iodide solution was buffered with Na_2HPO_4 and NaH_2PO_4. Approximately neutral conditions must be maintained, for only then does one O_3 liberate just one I_2.

The ozone content of the gas was found not to be reproducible on different days, but under continuous operation for several hours with a steady rate of flow of gas and constant electric current, it became fairly constant (say within 2%), for example, at about 5 mole per cent. of ozone with a rate of flow of 2 to 3 liters of gas per hour. When two ozonizers like that described were connected in series a 7% ozone was obtained with a flow of 5 liters per hour, or a 5% ozone with a flow of 15 liters per hour.

Apparatus for Determining the Reaction Rates and Steady State.—A 90-liter water-filled heat-insulated metal tank was used as a thermostat. In most of the experiments, which were at about 0°, the liquid was stirred by a turbine and cooled by placing in part of the upper section of the tank the cooling unit of an electric refrigerator, which was so regulated that its coils remained thickly covered with ice, producing a temperature of +0.3 to 0.8°.

For holding the reaction mixtures and nitric acid blanks 500-ml. Jena glass gas bottles with vaselined ground-glass stoppers were used. These bottles were provided with a horizontal sintered glass plate 1 cm. above the bottom (for distributing the gas bubbles) and with a vertical side-arm along the outside for admitting the gas below the sintered plate. The side-arm and the exit-tube in the glass stopper were fitted with interchangeable glass joints so that all glass connections could be made between the various bottles and with the ozonizer. At the end of the train a tube filled with granular manganese dioxide, or better with sodium hydroxide, was attached to destroy the escaping ozone.

Procedure for the Reaction Rate Experiments.—Two gas bottles of the kind above described were charged with a known volume (about 400 ml.) of nitric acid of the desired concentration, placed in the 0° bath, and connected in series with the ozonizer. Ozonized oxygen was passed through the bottles for about half an hour; then a measured quantity (5 to 10 ml.) of cold standard concentrated silver nitrate solution was added from a pipet to the second bottle, and an equal quantity of cold water to the first bottle, and the time noted. After measured intervals of time samples (25 or 50 ml.) were withdrawn with a pipet from the second bottle, and delivered immediately into a known volume of 0.02 *N* ferrous sulfate solution; and the unoxidized excess of ferrous salt was titrated with 0.03 to 0.05 *N* potassium permanganate. The ferrous salt reduced immediately both the argentic silver and the ozone present. To determine the ozone content, another sample was taken from the first gas bottle (containing no silver) and added to a known quantity of standard ferrous sulfate, and the excess of the latter titrated. By subtracting this from the previous result the number of oxidation equivalents of argentic salt was ascertained. This involved the assumption that the ozone concentration in the two solutions was the same—an assumption which was later found to introduce some error. From time to time, the partial pressure of the ozone issuing at the end of the train was determined by passing through buffered potassium iodide solution 500 ml. of the gas and titrating the liberated iodine with thiosulfate, incidentally the absolute rate of flow being also determined.

Samples were taken out and analyzed from time to time until the steady state was shown to be established. Then the bottles were disconnected from the ozonizer, the ozone was blown out by a rapid current of air for two minutes (though its odor was gone in half a minute), and a sample of the silver solution was taken out immediately and analyzed with ferrous sulfate. Other samples were similarly analyzed at intervals, so as to determine the rate of the decomposition by the water.

Special experiments proved that excess of ferrous salts reacts instantly with ozone as shown by the disappearance of its odor, and with argentic salt as shown by disappearance of the black color; also that the silver is not reduced to metallic form, and that the nitric acid present in a solution diluted so that the acid is less than 2 *N* does not at room temperature oxidize ferrous sulfate appreciably.

Proof that the Oxidation Reaction is Unidirectional

Before proceeding with the detailed study of the reactions it seemed important to determine whether or not the oxidation reaction takes place appreciably in the reverse direction. For this purpose the following experiment was made for us by Mr. Alexander Kossiakoff.

Through 400 ml. of a 0.03 *N* silver nitrate solution in 2 *N* nitric acid in a gas bottle 8% ozone was passed at 0° for about twelve hours. Then the ozone was completely expelled by passing a current of oxygen through the solution at 0° for an hour, after which the argentic concentration (Ag^{II}) was about 5 milliformal. Finally oxygen was bubbled through the solution at 0° for ten hours at the rate of 2 liters per hour, and the gas was passed at 0° into a gas bottle containing 250 ml. of 0.05 *N* potassium iodide buffered by 75 ml. of 0.3 *f* Na_2HPO_4 and 2 ml. of 6 *N* sulfuric acid, giving a H^+ concentration slightly less than 10^{-7} (so as to neutralize any small amount of nitric acid spray carried into the iodide solution). To the iodide solution were then added starch solution and 10 ml. of 6 *N* sulfuric acid. No color was produced, even though during the experiment about 1 milliequivalent of argentic silver had been reduced and 0.05% of this amount of iodine would have shown itself.

This conclusion that ozone is not formed under these conditions by the reaction of oxygen with argentic silver is confirmed by the value of its oxidation potential, derived in a subsequent article; for this potential is too small, in relation to that of ozone, to make this possible.

The Initial Rate of the Oxidation Reaction

In this investigation there were studied the rate of the oxidation reaction in its earlier stages, the steady-state, and the rate of reduction of the argentic silver by water after the removal of the ozone. In spite of the effective bubbling, considerable error was later found in the assumption employed that the ozone gas is dissolved by the nitric acid solution almost as rapidly as it is consumed by its reaction with the argentous silver. This affected the calculations not only of the ozone concentration, but also of the argentic concentration in the oxidation reaction and in the steady state (but not the results of the reduction reaction).

Nevertheless, even though these measurements of the oxidation reaction do not furnish exact reaction rate constants, they are sufficiently accurate to lead to interesting general conclusions, and to establish the mechanism of that reaction. In view of their approximate character, these earlier results are presented in the form only of diagrams. In experiments now in progress, these difficulties have been largely overcome, and fairly accurate reaction rate constants have been obtained, which will be published in a subsequent paper.

The results of representative experiments (made mostly by K. S. Pitzer) at 0.5 ± 0.2° on the rate of the oxidation reaction in its early stages are shown on a large-scale diagram (Fig. 1). In this are plotted as abscissas the elapsed time expressed in minutes, and as ordinates the argentic concentrations $10^3(Ag^{II})$ in milliformula weights per liter, calculated under the assumption that substantially all the argentic silver is bipositive. Along each graph as a legend are shown the volume formality (HA) of the nitric acid, the volume milliformality $10^3(\Sigma\ Ag)$ of total silver and the millimolal solubility $10^3(O_3)$ of ozone at the prevailing partial pressure of the gas (these last two concentrations being denoted simply by Ag and O_3 in the figure).[16] These concentrations

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(16) In Expt. III a third measurement, not included in the diagram, showed that 12.26 mfwt./l. of argentic silver was produced in forty-eight minutes, a result which would be represented by a point lying exactly on an extension of graph III.

remain nearly or quite constant throughout any one experiment, but they were varied in the different experiments. The measured values are shown by dots and circles, used alternately on adjoining graphs. Through them the best representative straight lines are drawn. In Experiments IV and VI an amount of sodium nitrate equivalent to the nitric acid was also present.

The fact that straight lines represent the data satisfactorily in the case of all the graphs shows that in any one experiment the concentration (Ag^{II}) of argentic silver produced during the first fifty minutes is proportional to the elapsed time, that is, that $d(Ag^{II})/dt$ is during this interval constant, in correspondence with the nearly constant argentous and ozone concentrations.[17] The average rate during this interval is therefore substantially identical with the initial rate for any specified mixture; and the slope expressing it may be compared with the initial concentrations in the case of different mixtures.

By comparing the slopes of graphs II and III or of graphs IV and V, representing experiments with equal acid concentration and nearly equal ozone concentration, it is found that doubling the initial argentous concentration increases the initial rate 1.8 fold or 2.2 fold, respectively, showing that the rate is directly proportional to the argentous concentration. Furthermore, at the sensibly equal concentrations of the acid and silver that prevailed in Experiments I and II, increasing the ozone concentration 2.7 fold caused the rate to increase approximately 2.6 fold, that is, proportionally. Many other experiments made later also show that the rate of oxidation is within the experimental error proportional to the product of the argentous and ozone concentrations.

A comparison of graphs VI and IV shows that increasing the acid concentration from 0.89 to 1.78 *N* made no change in the rate when account is taken of the change in the silver–ozone product. Stronger acid seems, to be sure, to cause increase of rate; thus in Experiment III, with 3.51 *N* nitric acid the silver–ozone product is 2.64 times that in Experiment V with 1.78 *N* nitric acid, whereas the slope is 3.3 times greater. However, this result may be disregarded, for such an effect is not shown by the later, more accurate experiments. Even if there be some effect of acid at higher concentrations, it seems probable that the acid is not involved directly in the rate mechanism, but that it affects the rate by its influence on the molecular state (ionization, hydrolysis or complex formation) or on the activity of the salts.

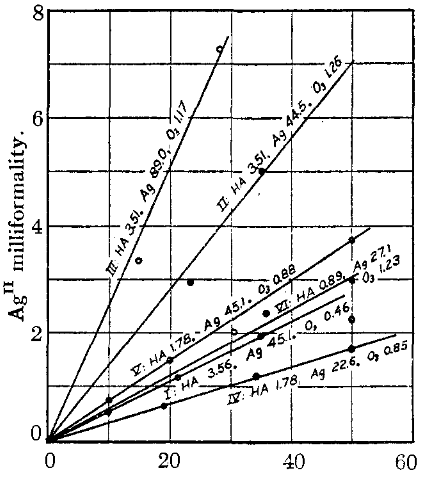

Fig. 1.—Initial oxidation rates at 0.5°.

The rate of the oxidation reaction, at least in its early stages and up to moderate acid concentration, is therefore given by the expressions

$$d(Ag^{II})/dT = k_O(Ag^{I})(O_3) \qquad (5)$$

$$d(Ag^{II})/dT \not\approx f(H^+) \qquad (6)$$

The oxidation of argentous silver by peroxysulfuric acid has been found by Yost[12] and Carman[8] to be subject to corresponding laws, namely, to be proportional to the concentration of argentous silver and to that of the oxidizing agent, and to be not much influenced by the strength of the acid.

The above given rate equation shows, since one O_3 reacts with only one Ag^+, that the mechanism of the reaction involves primarily the production of tripositive silver. Taking into account the conclusion that H^+ has little or no influence and the fact (shown in the following article) that the silver finally exists mainly in the bipositive state, the mechanism is most simply expressed by the chemical equations

$$Ag^+ + O_3(g) = AgO^+ + O_2(g) \text{ (slow rate)} \qquad (7)$$

$$AgO^+ + Ag^+ + 2H^+ \rightleftharpoons 2Ag^{++} + H_2O \text{ (rapid equilibrium)} \qquad (8)$$

The oxygenated ion of tripositive silver (AgO^+) is assumed to be formed to accord with the familiar kinetic principle that there first is produced that derivative of a given oxidation state

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[17] This result may seem remarkable in view of the occurrence of the reduction reaction in the opposite direction, but the rate of this reaction will be seen later to be proportional to the second (or still higher) power of the bipositive silver, and it can be shown to have only very little effect in slowing up the oxidation at the concentrations of argentic silver here prevailing.

which involves the simplest rate mechanism, that is, the smallest number of molecules of the reacting substances.

The assumption of an oxygenated ion is reasonable, moreover, since it is probable that tripositive silver, in so far as it exists in aqueous solution, is largely hydrolyzed, for the dilution of strong acid solutions is attended by the precipitation of solid phases containing oxygenated salts of trivalent silver. In regard to this and the equilibrium expressed by equation 8, see the following article.

The conclusion that tripositive silver or its oxygen compound AgO^+ is the immediate product of oxidation implies that silver is capable of existing in this oxidation state or as this oxygenated ion, but, contrary to the conclusion drawn by Carman,[8] it does not prove that trivalent silver (or one of its ions) is present in the solution in any considerable proportion.

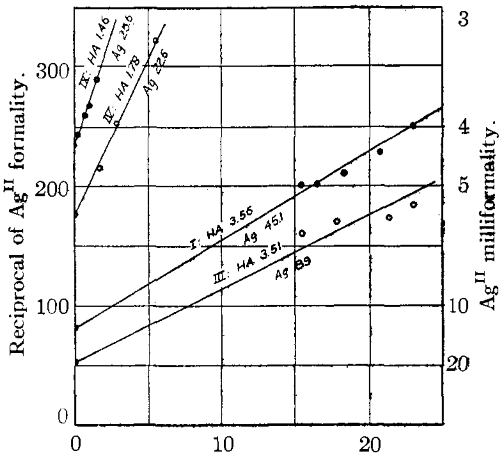

Fig. 2.—Reduction rates at 0.5°.

Finally, it may be mentioned that a comparison of Experiments IV and V, in the former of which an amount of sodium nitrate equivalent to the nitric acid was added, seems to show (since the slope varies only proportionally with the silver concentration) that increase in ionic strength has little effect on the rate of oxidation. This conclusion is confirmed by other experiments. It is in accord with Brönsted's theory,[18] which predicts this result in the case of any mechanism like this one where only one of two reacting substances is in the form of an ion.

The Rate of the Reduction Reaction

The measurements at 0.5° on the rates of the reduction of argentic salts by water, taking place in accordance with equation 3, were made by K. S. Pitzer with some of the steady-state mixtures obtained by oxidizing the nitric acid solutions of argentous nitrate of Fig. 1 with ozone. Those at 24 ± 1° were made earlier by J. L. Hoard, with other mixtures so obtained. From these mixtures the ozone was removed quickly by a rapid current of oxygen, and at a noted moment (taken as time zero) a sample was removed, added to standard ferrous sulfate solution, and titrated with permanganate to determine the oxidizing power. After measured intervals other samples were withdrawn and analyzed. The results of these measurements are shown in Figs. 2 and 3.

In these figures are plotted as ordinates the reciprocals of the argentic concentration expressed in formula weights per liter, that is, the values of $1/(Ag^{II})$, as shown along the left-hand edge of the table; and there are plotted as abscissas the elapsed times, expressed in hours, as shown along the foot of the table. Along the right-hand edge of the plot are shown the values of $10^3(Ag^{II})$ which correspond to the reciprocals shown on the left-hand edge. The graphs of Fig. 2 are numbered as in Fig. 1, in so far as the solutions used were the same as in the oxidation experiments. As legends in that figure are given after HA the initial volume formalities of the nitric acid, and after Ag the volume milliformalities of the total silver. The legends in Fig. 3 are similar except that the symbol of the acid, HNO_3 or H_2SO_4, is used in place of HA. In all the experiments of Fig. 3 the total silver concentration was 0.033 formula weights per liter of solution. The

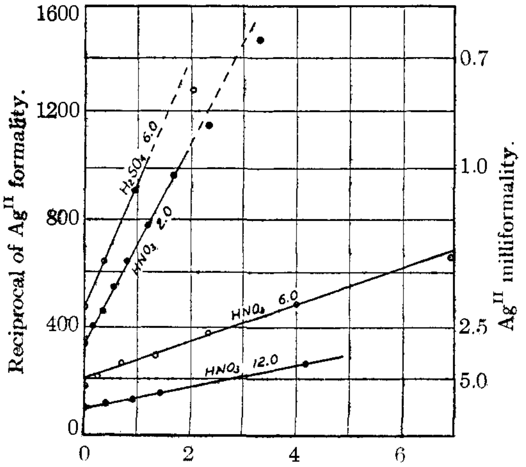

Fig. 3.—Reduction rates at 24°.

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[18] See La Mer, *Chem. Reviews*, 10, 180–186 (1932).

measured values are shown by dots and circles, alternated on adjoining graphs, as in Fig. 1.

It will be seen from Figs. 2 and 3 that throughout any one experiment, at least until after a considerable part of the argentic salt has been reduced, the increase in the reciprocal of its concentration is closely proportional to the time. This is true, not only in the nitric acid solutions, but also in 6 N sulfuric acid. This shows that the rate itself is directly proportional to the square of the argentic concentration. That is

$$\mathrm{d}\,\frac{1}{(\mathrm{Ag^{II}})} = k_\mathrm{R}\,\mathrm{d}t; \text{ or}$$

$$-\frac{\mathrm{d}(\mathrm{Ag^{II}})}{\mathrm{d}t} = k_\mathrm{R}\,(\mathrm{Ag^{II}})^2 \qquad (9)$$

This result does not show whether the argentous concentration ($\mathrm{Ag^I}$) has an influence, for this varies comparatively little throughout any one experiment. But, by comparing different experiments in which ($\mathrm{Ag^I}$) has different initial values and nitric acid the same value, the effect of ($\mathrm{Ag^I}$) can be determined. That this has a retarding effect on the rate was shown by comparing the slopes of these earlier experiments (thus in graphs I and III); and the more extensive and accurate experiments of Messrs. Stitt, Kossiakoff and Coryell to be described in a later article prove that, other conditions being the same, the rate $-\mathrm{d}(\mathrm{Ag^{II}})/\mathrm{d}t$ is inversely proportional to ($\mathrm{Ag^I}$), so that equation 9 should be modified to read

$$-\frac{\mathrm{d}(\mathrm{Ag^{II}})}{\mathrm{d}t} = k_\mathrm{R}\,\frac{(\mathrm{Ag^{II}})^2}{(\mathrm{Ag^{I}})} \qquad (10)$$

Moreover, these later measurements, analyzed mathematically by Mr. C. D. Coryell, indicate that there is superposed on the reduction reaction corresponding to this rate equation another reduction reaction whose rate is proportional directly to $(\mathrm{Ag^{II}})^4$ and inversely to ($\mathrm{Ag^I}$), and that this latter reaction may even predominate under certain conditions, especially in more concentrated argentic solutions. Discussion of this superposed reaction and of its mechanism will be postponed until the later work is published.

The graphs of Figs. 2 and 3 obviously show that the reduction is greatly retarded by increasing the nitric acid concentration. Thus from Fig. 3 it is found that at 24° (with the total silver 0.038 formal) the slopes of the graphs have relative values as follows: 100 with 2 N nitric acid, 18 with 6 N nitric acid, and 10.5 with 12 N nitric acid. Hence between the first two nitric acid concentrations, which increase three-fold, the rate decreases 5.6-fold, which is equal to about $3^{1.6}$-fold. Similarly, graph IX of Fig. 2 (with only slightly greater argentous concentration) shows a greater slope than graph IV, corresponding to the lesser acid concentration in the former case. These experiments are, however, not accurate nor numerous enough to determine satisfactorily the form of the function of the acid concentration. This is even more true of the function of the hydrogen-ion concentration because of the added theoretical difficulties of evaluating its activity at the high acid concentrations involved. Full discussion of this matter will therefore be postponed till the later more exact experiments now in progress are completed and published.

A probable mechanism corresponding to rate equation (10) will, however, be mentioned here, because of its bearing on matters to be considered in the next two articles. The occurrence of the function $(\mathrm{Ag^{II}})^2/(\mathrm{Ag^I})$ in the rate equation suggests, as called to our attention by Mr. C. D. Coryell, that, in correspondence with the equilibrium $2\mathrm{Ag^{++}} \rightleftharpoons \mathrm{Ag^+} + \mathrm{Ag^{+++}}$, it is tripositive silver in some form which is primarily reduced by the water. The large retarding effect of acid suggests further that it is a hydrolyzed form of the $\mathrm{Ag^{+++}}$ ion, such as $[\mathrm{Ag^{III}O}]^+$ or $[\mathrm{Ag^{III}OH}]^{++}$, that is directly involved in the mechanism. Tripositive silver and such oxygenated ions are in fact probably present in argentic solutions in small quantity (as shown in the following article by Noyes, Pitzer and Dunn). The former ion might result from the following equilibrium

$$2\mathrm{Ag^{++}} + \mathrm{H_2O} \rightleftharpoons \mathrm{AgO^+} + \mathrm{Ag^+} + 2\mathrm{H^+} \qquad (11)$$

The mass action expression for this equilibrium is, however

$$(\mathrm{AgO^+}) = K\,\frac{(\mathrm{Ag^{++}})^2(\mathrm{H_2O})}{(\mathrm{Ag^+})(\mathrm{H^+})^2} \qquad (12)$$

The whole mechanism might then be expressed by the following chemical equations

$$\mathrm{AgO^+} + \mathrm{H_2O} = \mathrm{Ag^+} + \mathrm{H_2O_2} \text{ (slow rate)} \qquad (13)$$

$$2\mathrm{Ag^{++}} + \mathrm{H_2O} \rightleftharpoons \mathrm{AgO^+} + \mathrm{Ag^+} + 2\mathrm{H^+} \text{ (rapid equilibrium)} \qquad (14)$$

$$\mathrm{H_2O_2} + 2\mathrm{Ag^{++}} = \mathrm{O_2} + 2\mathrm{H^+} + 2\mathrm{Ag^+} \text{ (rapid rate)} \qquad (15)$$

Assuming in accord herewith that the rate is simply proportional to ($\mathrm{AgO^+}$) and substituting for it the above given equilibrium expression (equation 12), one obtains for the mechanism as a whole, the reaction-rate expression

$$-\frac{\mathrm{d}(\mathrm{Ag^{++}})}{\mathrm{d}t} = k_\mathrm{R}(\mathrm{AgO^+}) = k_\mathrm{R}K\,\frac{(\mathrm{Ag^{++}})^2(\mathrm{H_2O})}{(\mathrm{Ag^+})(\mathrm{H^+})^2} \qquad (16)$$

Assuming that the tripositive silver forms a very small part of the total argentic silver, this evidently corresponds to empirical equation 10, so far as the silver concentrations are concerned.

The assumption that hydrogen peroxide is the intermediate compound in the production of oxygen gas will be discussed in the subsequent article by Noyes and Kossiakoff on the argentous–argentic oxidation potential.

Two other qualitative conclusions drawn from Figs. 2 and 3 may, however, be mentioned. The first relates to the effect of temperature on the reduction reaction. A rough estimate of this may be made by comparing the slope of the graph for 2 *N* nitric acid at 24° in Fig. 3 with the slope obtained for 2 *N* nitric acid at 0.5° by extrapolating from graphs IX and IV in Fig. 2. The ratio of these slopes, and therefore of the corresponding reaction rates $d(1/Ag^{II})/dt$, is thus found to be 21. From later experiments with 6.1 and 3.3 *N* nitric acid the ratios 53 and 38 were obtained by Mr. C. D. Coryell. These effects are very much greater than the influence of temperature on most reactions, which seldom exceeds 9-fold for 23.5°. This is further indication that the complete mechanism involves an equilibrium reaction whose equilibrium constant, like that of a hydrolysis, varies much with the temperature, so that it contributes largely to the change in the observed rate-constant with the temperature.

The second conclusion relates to the relative effects of sulfuric and nitric acids. The slopes of the two upper graphs in Fig. 3 show that at 24° the rate of reduction in 3 formal (6 *N*) sulfuric acid is not greatly different from that in 2 formal nitric acid. With increase in acid concentration, however, a very marked difference between the two acids develops. Namely, whereas, as above shown, increase in the nitric acid concentration, up to about 12 *N*, greatly retards the reduction of the argentic salt, yet increase in the sulfuric acid concentration hastens its decomposition. Thus an experiment (not reproduced in Fig. 3) made by J. L. Hoard at 24° with 9 formal (18 *N*) sulfuric acid gave a slope approximately three times as great as that given by the experiment with 3 formal (6 *N*) sulfuric acid. The fact that an enormous increase in the rate of decomposition takes place also with nitric acid between 12 and 21 *N*, as shown below, indicates that the decrease may be due to a dehydration effect in both cases, but occurring at much lower concentrations with sulfuric acid.

Steady State between the Oxidation and Reduction Reactions

Measurements were also made of the steady state finally reached by many of the mixtures subjected to the oxidation reaction, but, unfortunately, because of the above mentioned uncertainty as to the ozone concentration, the results are not accurate enough to test satisfactorily the kinetic relation existing between the steady state and the rates of the opposing reactions. Such measurements are, therefore, being repeated in this Laboratory, using an improved procedure, and the results will be duly communicated. The measurements already made, however, indicate some general features of the reaction under consideration, and a few of the results will therefore be presented briefly here.

In Table I in the column headed 100 $(Ag^{II})/(\Sigma Ag)$ are given the percentages of the total silver which were found to be converted into argentic silver in several of the oxidation experiments represented in Fig. 1 after a steady state had been reached. The table also contains the results of orientating experiments made at various times with much higher concentrations of nitric acid. These latter results are only rough approximations, inasmuch as it is not certain that the steady state was fully attained and inasmuch as the acid concentration was not always precisely determined. The values given in the table are those in steady-state mixtures when the partial pressure of the ozone was 0.05–0.06 atm. and when the temperature was 0.5° (except as otherwise noted).

TABLE I

PERCENTAGE OF SILVER OXIDIZED IN STEADY-STATE MIXTURES IN NITRIC ACID SOLUTION

(HNO_3)	(ΣAg)	$100(Ag^{II})/(\Sigma Ag)$
1.78	0.045	18
1.78	.023	27
3.51	.089	25
3.53	.045	32
10.0	.585	38
12.0	.033	90
15.2	.366	59
15.2	.319	77
15.2	.061	84 (at −5.8°)
21.2	.036	0.3 (at −2.2°)

It is evident from Table I that the percentage of silver oxidized increases greatly with increasing nitric acid concentration up to about 10 to 15 *N*. The last experiment, made for us by Mr. Charles D. Coryell, with still more concentrated acid

(21.2 N, 90% nitric acid, density 1.49) gave, however, the striking result that, as the acid becomes nearly anhydrous, scarcely any argentic silver is produced—after seventy-five hours not even enough to give more than a slight brown color to the solution. The table further shows that the percentage of argentic silver produced at any given acid concentration decreases, though its absolute concentration increases, when the total silver concentration increases. It is seen that a reagent 0.2 formal in $Ag(NO_3)_2$ can be prepared in 10 or 15 N nitric acid.

Summary

It has been shown that at 0 and 24° ozone slowly oxidizes argentous nitrate in nitric acid solution to a black soluble argentic nitrate; but that the reaction ceases before it has become complete, with the establishment of a steady state. This steady state is shown to arise, not at all from the occurrence of the reverse reaction, but from the reduction of the argentic salt by the water with evolution of oxygen. (For the overall reactions see the equations at the beginning of this paper.) The argentic salt is assumed to consist mainly of bipositive silver on the basis of the results of the next following paper.

The initial rate of the silver oxidation at 0° was found to be proportional to the argentous and ozone concentrations. This is accounted for by the following mechanism which involves the direct production of tripositive silver in the form of an oxygenated ion

$$Ag^+ + O_3 = AgO^+ + O_2 \text{ (slow), and}$$
$$AgO^+ + Ag^+ + 2H^+ = 2Ag^{++} + H_2O \text{ (fast)}$$

The initial rate is found to be only slightly affected by the acid concentration or by the ionic strength.

The rate of the argentic decomposition by water (at 0 and 24°) was found as a first approximation to be proportional to the square of the argentic concentration (except when the latter is high), and inversely proportional to the argentous concentration, and to be greatly diminished by increasing the acid concentration. The mechanism is discussed (see equations 13, 14, and 15); but complications in the reaction make the conclusions somewhat uncertain. The effect of temperature on the reaction rate was found to be very much larger than for most reactions.

The steady state at 0° was roughly determined at various acid concentrations. The percentage of the silver converted into the argentic form varied from 18% in 1.8 N nitric acid to about 90% in 12 N nitric acid when the total silver was about 0.04 formal, but in 21 N (90%) nitric acid scarcely any formation of argentic salt resulted.

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Argentic Salts in Acid Solution. II. The Oxidation State of Argentic Salts

BY ARTHUR A. NOYES, KENNETH S. PITZER AND CLARENCE L. DUNN

Purpose of this Investigation

In the preceding article Noyes, Hoard and Pitzer[1] described the general nature and the rates of the reactions by which argentic salt is produced by the ozone oxidation of acid argentous nitrate, and by which it is reduced by water. Before proceeding further with the description of these researches, however, it seemed essential to establish the state of oxidation, whether bipositive or tripositive, in which argentic silver exists in nitric acid solution. To a description of experiments made with this purpose this article is devoted.

It is remarkable that this question has remained unanswered so long in the case of a readily obtainable oxidation state of a common element—an oxidation state, moreover, that explains the striking catalytic effects of silver salts. Furthermore, the question is of much theoretical interest in relation to the valence states compatible with the periodic system, inasmuch as copper exists mainly unipositive and bipositive, and gold unipositive and tripositive.

Previous Investigations

The most definite indications previously existing as to the oxidation state of argentic silver in its solutions were furnished by the composition of the solid phases that separate in preparing or

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(1) Noyes, Hoard and Pitzer, THIS JOURNAL, **57**, 1221 (1935).