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Argentic Salts in Acid Solution. III. Oxidation Potential of Argentous–Argentic Salts in Nitric Acid Solution

By Arthur A. Noyes and Alexander Kossiakoff

Plan of the Investigation

The electromotive forces of cells having at the electrodes one or both of the two solid higher oxides of silver (AgO and Ag_2O_3) have been studied with concordant results in four independent researches, namely, by Luther and Pokorny,[1] Jirsa,[2] Barbieri,[3] and Carman.[4] The electrode potential of dissolved argentous and argentic salts with respect to each other in acid solution has however, not been measured. Yet this quantity is of great interest in relation to the oxidizing power of solutions of argentic salts, which are among the most powerful oxidizing agents known and which are involved in many striking catalytic actions. We have, therefore, undertaken the determination of its value.

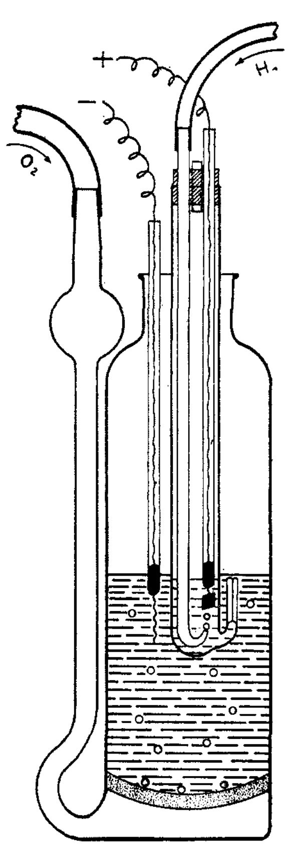

Fig. 1.

The plan of the investigation was as follows. Nitric acid solutions (1 to 4 *N*) containing argentous and argentic salts in approximately the steady-state proportions were prepared in a gas bottle by the action of ozone on argentous nitrate solutions at 0° by the process described by Noyes, Hoard and Pitzer.[5] Then in a thermostat at 0° a cell containing a so-prepared solution was set up of the following type

$$\mathrm{Pt} + \mathrm{H_2}\,(1\text{ atm.}),\ \mathrm{HClO_4}(c'),\ \left\{\mathrm{HNO_3}(c) + \begin{matrix}\mathrm{Ag^{II}}\,(c_{\mathrm{II}})\\ \mathrm{Ag^{I}}\,\ (c_{\mathrm{I}})\end{matrix}\right\},\ \mathrm{Pt}.$$

Samples were withdrawn for analysis from time to time as the argentic salt decomposed, potential measurements being made at the same time.

The Electrolytic Cell.—The gas bottle used for preparing the argentic solutions served as the electrolytic cell. The cell was arranged as shown in Fig. 1. The bottle was nearly filled with a freshly prepared steady-state mixture, from which the ozone was expelled by passing for twenty minutes through the side-arm a rapid current of oxygen, after which a slower current was passed to stir the solution and thus avoid local concentration changes. Into this solution was introduced through the neck of the bottle a bright platinum wire partly enclosed in a glass tube. There was also introduced a vessel containing about 10 ml. of solution, which constituted the hydrogen half-cell. It contained the perchloric acid, a platinized platinum foil electrode, and a tube through which hydrogen was bubbled in. The hydrogen was prepared by electrolyzing a sodium hydroxide solution between a nickel cathode and platinum anode, and was purified by passing it through a tube containing a platinum wire kept red-hot by an electric current. The gas emerged at the top of the hydrogen half-cell through a small "bubbler" (not shown in the figure). The hydrogen half-cell was provided with a short vertical capillary side arm (also filled with perchloric acid) which opened into the argentic solution just below its surface.

Method of Potential Measurements.—A definite weight of dry silver nitrate was dissolved in a definite weight of nitric acid in a gas bottle, giving a solution of known weight concentration. Ozone was passed through the solution kept at 0° for about four hours, which sufficed nearly to establish the steady state. The ozone was then blown out with a stream of oxygen for twenty minutes. after which it was found that the issuing gas neither smelled of ozone nor colored acidified iodide solution.

During the expulsion of the ozone, the hydrogen half-cell was checked against a 1 *N* HCl calomel electrode at 0°. Then the half-cell was inserted in the gas bottle, in the position shown in the figure, with the end of the capillary just below the surface of the liquid, so as to make contact and yet prevent convection. The other electrode was set in, and both were connected to the potentiometer. Readings were taken until a nearly constant potential was obtained. The flow of oxygen was adjusted until the potential showed no change upon increasing the stirring.

After taking a series of readings. the flow of oxygen was momentarily shut off, and a sample was removed for analysis with a previously cooled pipet. The oxygen was again turned on, and after two minutes another series of potential readings was made, and the mean of the two series was taken. These differed, however, only by 0.2 to 0.8 millivolt, showing that a significant decomposition of the argentic silver had not taken place. The half-cell was then taken out and checked against the calomel electrode.

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(1) Luther and Pokorny, *Z. anorg. Chem.*, **57**, 290–310 (1908).

(2) Jirsa and Jelinek, *Z. anorg. allgem. Chem.*, **158**, 61 (1926).

(3) Barbieri, *Att accad. Lincei*, [6] **13**, 882–887 (1931).

(4) Carman, *Trans. Faraday Soc.*, **30**, 575–577 (1934).

(5) Noyes, Hoard and Pitzer, This Journal, **57**, 1221 (1935).

TABLE I

OBSERVED AND CALCULATED ELECTROMOTIVE FORCES AT 0°

HNO_3 c	$HClO_4$ c'	ΣAg $c_I + c_{II}$	Ox. Eq. $\times 10^3$	Ag^I/Ag^{II} c_I/c_{II}	$E_{obs.}$	E_C	E_L	E_H	E°	E°_{III}
1.000	1.000	0.0250	2.24	10.2	1.866	0.055	−0.002	−0.005	1.914	1.896
(α, 0.706)	(α′, 0.803)	.0300	2.91	9.3	1.865	.053	.002	.005	1.911	1.894
			1.83	15.4	1.859	.065	.002	.005	1.917	1.893
			1.66	17.0	1.855	.068	.002	.005	1.916	1.891
								Mean	1.9145	
2.000	2.000	0.0250	4.00	5.3	1.862	0.039	−0.008	+0.023	1.916	1.906
(α, 0.789)	(α′, 1.295)		3.79	5.6	1.861	.041	.008	.023	1.917	1.906
			2.06	11.1	1.845	.057	.008	.023	1.917	1.897
			1.85	12.5	1.841	.060	.008	.023	1.916	1.895
			1.41	16.7	1.829	.067	.008	.023	1.911[a]	1.886[a]
								Mean	1.9165	
4.000	1.000	0.0500	4.70	9.6	1.837	0.054	+0.027	−0.005	1.913	1.895
(α, 0.959)	(α′, 0.803)		3.49	13.3	1.829	.061	.027	.005	1.912	1.891
			2.62	18.1	1.823	.068	.027	.005	1.913	1.888
			2.27	21.0	1.818	.072	.027	.005	1.912	1.885
								Mean	1.9125	
1.370	1.158	0.0300	3.74	7.0	1.866	0.047	±0.000	±0.000	1.913	1.899
(α, 0.730)	(α′, 0.864)		3.55	7.5	1.864	.048	.000	.000	1.912	1.897
								Mean	1.9125	
								General Mean	1.914	

[a] These last values, obtained with the smallest argentic concentration, are disregarded in taking the mean and in the subsequent discussion.

Method of Analysis.—The determination of the argentic silver in the samples was made by pipetting the sample into a measured excess of standard thallous nitrate, which immediately reduces it to unipositive silver. The flask was weighed before and after the sample was added, to determine the weight of the sample withdrawn; then this was divided by weight into two parts, to make possible check analyses. Each part was diluted to 400 ml., made about 1 *N* in hydrochloric acid by adding the proper amount of sodium chloride and strong hydrochloric acid, heated to 50–60°, and titrated for the excess of thallous thallium with standard potassium bromate, using methyl orange as indicator.[6] The oxidizing power was considered to correspond to bipositive silver, and from the known total silver concentration the unipositive silver was calculated by subtraction.

The Observed and Calculated Electromotive Forces

The volume formalities (that is, the concentrations in formula weights per liter) of the substances in the cells and the observed electromotive forces $E_{obs.}$ are given in the first six columns of Table I. Below their concentrations the activity coefficients α of the two acids are given, these being interpolated from the results of Abel, Redlich and v. Lengyel[7] for nitric acid, and from those of Pearce and Nelson[8] for perchloric acid at 25°. The values of the electromotive force corrections, computed as described below, are given in the three following columns of the table. In the next to last column are given the final corrected values of the formal electrode potential E°, calculated by the logarithmic formula for equal formalities of bipositive and unipositive silver, and referred to the standard molal hydrogen electrode H_2 (1 atm.), H^+ (activity 1 *m*). The last column contains the formal electrode potential E°_{III} computed, in the way described below, under the assumption that all the oxidized silver is in the tripositive state. The significance of these results will be later considered.

Owing to the high acid concentrations and the unknown ratio of the ion activity coefficients of the two silver salts, the electrode potential could be calculated from the observed electromotive forces only approximately. Fortunately, however, the ion activity coefficients α and α′ for nitric acid and for perchloric acid are known, and these were taken into account.

From the measured electromotive force $E_{obs.}$ which is that of the cell formulated at the begin-

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(6) See Noyes, Pitzer and Dunn, THIS JOURNAL, **57**, 1229 (1935).

(7) Abel, Redlich and v. Lengyel, *Z. physik. Chem.*, **132**, 204 (1928).

(8) Pearce and Nelson, THIS JOURNAL, **55**, 3080 (1933).

ning of this article, there has been derived approximately the formal electrode potential E° for $Ag^{II} + E^{-I} = Ag^{I}$, which is considered to be equal to that of the cell

$$H_2\,(1\text{ atm.}),\ H^+\,(1\ m)\ \|\left\{ HNO_3\,(c.f.) + \begin{matrix} Ag_{II}\,(1\ f.) \\ Ag_{I}\ \ (1\ f.) \end{matrix}\right\}, Pt$$

This derivation has been carried out by adding to $\mathrm{E}_{\text{obs.}}$ the following three quantities (in which RT/F at 0° has the value 0.0542).

(1) $\mathrm{E_C} = (RT/F)\ \ln\ (c_{\mathrm{I}}/c_{\mathrm{II}})$; so as to provide for equiformal concentrations of unipositive and bipositive silver, their total concentrations c_{I} and c_{II} being substituted for the ion activities of Ag^{I} and Ag^{II} in the Nernst equation.

(2) $\mathrm{E_L} = (\mathrm{T_H} - \mathrm{T_A})(RT/F)\ \ln\ (\alpha c/\alpha' c')$, so as to eliminate to a large extent the small liquid potential, namely, to the extent that this arises from the different ion activities αc and $\alpha' c'$ of the nitric and perchloric acids (but not from their different ion mobilities, here considered to be equal). The estimated values 0.87 and 0.13 have been taken for $\mathrm{T_H}$ and for $\mathrm{T_A}$ as the mean transference numbers of the ions of the two acids at 0°.

(3) $\mathrm{E_A} = (RT/F)\ \ln\ \alpha' c'$, so as to refer the value to the molal hydrogen electrode at 0°.

To test the reliability of corrections $\mathrm{E_L}$ and $\mathrm{E_A}$ an experiment was made in which the concentrations of the two acids were such that the activity of the hydrogen ion in each solution was exactly 1 molal, thus eliminating these two corrections (but not $\mathrm{E_C}$). The results are recorded in the last two rows of the table. It will be seen that these check within 2 millivolts with the mean of those with the 1.0 N acids.

It will be seen from Table I that the formal oxidation potential values E° remain remarkably constant when the ratio $(Ag_{\mathrm{I}})/(Ag_{\mathrm{II}})$ is varied two-fold or more, while keeping the nitric acid constant. The table also shows that there is no pronounced variation even when the acid concentration is increased from 1 to 4 N nitric acid. The mean value **1.914** ± 0.002 volts may therefore be taken as the argentic–argentous oxidation potential at 0° under all these concentration conditions.

The fact that this oxidation potential remains nearly constant through the range of acid concentration 1 to 4 N nitric acid shows that within this region there is very little change in the ratio $(Ag^{++})/(Ag^{+})$, and therefore that such reactions as $Ag^{++} + H_2O = AgOH^+ + H^+$ and $2Ag^{++} + H_2O = Ag^+ + AgO^+ + 2H^+$ do not occur to a large extent within these limits of acid concentration, proving that tripositive silver is still not being produced in considerable proportion.

Although the work of Noyes, Pitzer and Dunn seems to have fully proved that the oxidized silver is almost wholly bipositive, at any rate in 10 to 15 N nitric acid solution, yet it is perhaps worth while to show that the electromotive force results afford in still another way confirmation of the conclusion that the argentic silver not only does not exist solely in the tripositive form, as some investigators have assumed, but does not exist even largely in that form, even in acid as dilute as 1 to 4 N. To show this we have calculated the concentration ratio $c_{\mathrm{I}}/c_{\mathrm{III}}$ for unipositive and tripositive silver and the corresponding value of the concentration correction $(RT/2F)\ \log\ c_{\mathrm{I}}/c_{\mathrm{III}}$ (where the coefficient of the logarithm has the value 0.0271, instead of 0.0542 as in case of the bipositive assumption). Without recording these quantities here, we have given in the last column of Table I the final values of the formal oxidation potential $\mathrm{E}^\circ_{\mathrm{III}}$ for the reaction $Ag^{III} + 2E^{-I} = Ag^{I}$ computed under the assumption that all the oxidized silver is in the tripositive form. It will be seen that these separate potential values vary by 11 and 10 millivolts within the series with 2 and 4 N nitric acid, whereas those assuming bipositive silver are constant in these series. The difference is less conclusive in the series with 1 N nitric acid, but this is probably less accurate.

Argentic Salts in Relation to other Strong Oxidizing Agents

Few values are known for the molal oxidation potentials of very strong oxidation agents in aqueous solution, but some of these which have interest in relation to the argentic–argentous potential are given in Table II. When the values are based on the total concentration of the ion constituents, instead of the ion itself, symbols like Ag^{I} and Ag^{II} are used.

For assistance in preparing the data for this table we are much indebted to Professor D. M. Yost of this Laboratory.

The value 1.914 found for the argentic–argentous oxidation potential explains some of the striking oxidizing properties of argentic salts. Thus this value is sufficiently below the potential (2.07) for ozone to account for the oxidation of argentous salt by ozone and for the fact that this

TABLE II

OXIDATION POTENTIALS OF STRONG OXIDIZING AGENTS

Oxidized state	Reduced state	Volts	Authority
$F_2(g) + 2E^-$	$2F^-$	2.88	Yost, Hatcher[9]
$O(g) + 2H^+ + 2E^-$	$H_2O(l)$	2.419	Johnston, Walker[10]
$O_3(g) + 2H^+ + 2E^-$	$O_2(g) + H_2O(l)$	2.07	Kassel[11]
$Ag^{II} + E^{-I}$	Ag^{I}	1.914[a]	Noyes, Kossiakoff
$H_2O_2 + 2H^+ + 2E^-$	$2H_2O(l)$	1.77	Lewis, Randall[12]
$MnO_4^- + 4H^+ + 3E^-$	$MnO_2(s) + 2H_2O(l)$	1.586	Brown, Tefft[13]
$MnO_4^- + 8H^+ + 5E^-$	$Mn^{++} + 4H_2O(l)$	1.447	Brown, Liebhafsky[14]
$PbO_2(s) + 4H^+ + 2E^-$	$Pb^{++} + 2H_2O(l)$	1.444	Randall[15]
$Ce^{IV} + E^{-I}$	Ce^{III}	1.44[b]	Kunz[16]
$^1/_2O_2(g) + 2H^+$	$H_2O(l)$	1.225	Lewis, Randall[12]

[a] In nitrate solution. [b] In sulfate solution.

reaction does not take place at all in the opposing direction. Furthermore, this value is still so far above that for most other strong oxidizing substances, such as that for the permanganate–manganous couple, as to account for the complete oxidation of these substances by argentic salts.

The marked catalytic power of argentous salts in many oxidations by ozone and peroxysulfuric acid must of course arise from a combination of the high oxidation potential of argentic salts with a kinetic activity much greater than that of ozone or peroxysulfuric acid.

It has been suggested by Noyes, Hoard and Pitzer[5] that the production of hydrogen peroxide may be the first (slow) reaction in the mechanism which causes argentic salts to be reduced by water with production of oxygen gas, this reaction being followed by the (instantaneous) reaction $H_2O_2 + 2Ag^{++} = O_2 + 2Ag^+ + 2H^+$. The fact that the argentic–argentous potential 1.914 is considerably larger than the potential 1.77 for the decomposition of hydrogen peroxide shows that the former reaction is thermodynamically possible. This is of much interest, for, if further substantiated, this hypothesis will afford a criterion for predicting the reducibility by water of the higher oxidation states of metal-forming elements in general, namely, the criterion that these states must possess an oxidation potential not much less than 1.77, the value corresponding to the reaction $H_2O_2(1\ m) + 2H^+ (1\ m) + 2E^- = 2H_2O(l)$.

On the other hand, the high potential 2.419 volts for monatomic oxygen gas shows that the alternative assumption that this is an intermediary in the production of diatomic oxygen gas from argentic salts and water is thermodynamically not admissible.

The fixing of the value of the oxidation potential for the very reactive argentic salt makes it possible to locate the unknown potential of other oxidizing agents with reference to this value, either above or below it in the oxidation series. This may be done by testing qualitatively whether, upon bringing together the appropriate substances, the black argentic compound is produced or is destroyed, care being taken not to be misled by an exceptionally slow reaction. Thus peroxysulfuric acid, bismuth dioxide in strong nitric acid, and lead dioxide in strong nitric acid, all of which oxidize argentous nitrate, must have oxidation potentials larger than 1.91 or at least of magnitudes comparable with it.[17]

Summary

This article describes measurements of the electromotive force between platinum electrodes of the combination comprising as one half-cell a solution of argentous and argentic nitrates in 1.0 to 4.0 *N* nitric acid and as the other half-cell 1.0 to 2.0 *N* perchloric acid kept saturated with hydrogen gas. From these measurements the formal oxidation potential E° of the reaction $Ag^{II} + E^{-I} = Ag^{I}$ has been computed to have the value of 1.914 ± 0.002 volts, and to remain constant at this value when the ratio of $(Ag^{II})/(Ag^{I})$ is varied two-fold and when the nitric acid concentration is changed from 1 to 4 *N*. The constancy of this potential through this range of nitric acid concentration shows that the bipositive

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[9] Yost and Hatcher, *J. Chem. Educ.*, **10**, 330 (1933).

[10] Johnston and Walker, THIS JOURNAL, **55**, 187 (1933).

[11] Kassel, *J. Chem. Phys.*, **1**, 414–417 (1933).

[12] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 607–8.

[13] Brown and Tefft, THIS JOURNAL, **48**, 1128 (1926).

[14] Brown and Liebhafsky, *ibid.*, **52**, 2595 (1930).

[15] Randall, "International Critical Tables," 1929, Vol. VII, pp. 232, 248.

[16] Kunz, THIS JOURNAL, **53**, 98 (1931).

[17] This oxidizing action of lead dioxide may seem inconsistent with its oxidation potential given in Table II, but that potential (at 1 *m*) at 25° theoretically increases 0.24 volt for a 10-fold increase in $[H^+]$ and 0.12 volt for a 10-fold decrease in $[H_2O]$; so that in 15 *N* nitric acid it may well become of sufficient magnitude to oxidize silver nitrate.

silver ion is not changing much in concentration, for example, through dismutation into unipositive and tripositive silver ions.

Furthermore, the rate of change of the potential with the silver concentrations is shown to be inconsistent with the assumption that the argentic silver is wholly or mainly tripositive. This confirms by a fourth method the conclusion that it is mainly bipositive, already drawn from three types of experiments in the preceding article, and shows that this is true even in nitric acid as dilute as 1 to 4 *N*.

The significance of this value in determining the behavior of argentic salts toward other strong oxidizing agents is considered in many of its different aspects. Of special interest seems the hypothesis that argentic silver and the higher oxidation states of other elements are decomposed by water with evolution of oxygen because of the tendency to form hydrogen peroxide, and hence only when their oxidation potential approaches or exceeds the potential (1.77 volts) of the reaction $H_2O_2 + 2H^+ + 2E^- = 2H_2O(l)$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Electron Affinity of Free Radicals. VI. The Strength of the Carbon–Carbon Bond in Certain Substituted Dixanthyls

BY HENRY E. BENT AND EARLE S. EBERS

The strength of a carbon–carbon bond has frequently been inferred from the ease with which a reaction takes place to give a sodium addition compound. Thus Conant has distinguished between various classes of compounds by determining the activity of sodium which is required to produce a reaction. For this purpose the three materials which have been used are dilute sodium amalgam, 40% sodium amalgam, which is liquid at room temperature, and sodium–potassium alloy.[1] Whether sodium or potassium has been the reactive material in the alloy has usually not been determined. The investigation of concentrated sodium amalgams by Gilfillan[2] indicates that the activity of sodium in 40% amalgam is the same as that of the pure metal in the solid state at the same temperature. Since sodium dissolves readily in sodium–potassium alloy the activity of the sodium in the alloy must be less than that of the solid metal and therefore less than that of sodium in 40% amalgam. The fact that some compounds react with sodium–potassium alloy which do not react with 40% amalgam must therefore be attributed either to the velocity of the reaction or more probably to the fact that the potassium is the reactive metal in the alloy.

The previous papers of this series have shown that the free energy change associated with the addition of sodium to an organic free radical is very little affected by the nature of the various groups attached to the central carbon atom. The maximum range in the values for the free energy change is 6 kcal. If we consider, however, the effect of changing only one substituent at a time on the central carbon we find that this produces a change of not more than 1 kcal. This fact makes it possible to calculate the strength of the carbon–carbon bond in compounds which are not appreciably dissociated into free radicals providing an equilibrium can be established with a dilute sodium amalgam in which the activity of sodium is known. The increase in the activity of the sodium necessary to cause addition to the carbon–carbon bond will then be a measure of the strength of that bond.

For the purposes of this investigation the xanthyl series was chosen. Compounds of this series have been studied by Conant and co-workers.[3] Many of them are not appreciably dissociated at room temperatures but give evidence of dissociation as the temperature is raised. The substituents which have been considered by Conant and co-workers were aliphatic groups and it became imperative to study at least one free radical containing an aliphatic group in order to determine the effect on the electron affinity of this group. Fortunately Conant, Small and Sloan[4] found that diisopropyldixanthyl is almost completely disso-

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[1] Conant and Garvey, THIS JOURNAL, **49**, 2599 (1927).

[2] Gilfillan and Bent, *ibid.*, **56**, 1505 (1934).

[3] Conant and co-workers, *ibid.*, **47**, 572, 3068 (1925); **48**, 1743 (1926); **49**, 2080 (1927); **51**, 1925 (1929).

[4] Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926).