The Oxidation States of Silver

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THE common valence of silver is +1. A few textbooks of general chemistry mention other valences but the great majority either make no mention of them, or state that silver shows only the one oxidation state. In view of the fact that the other members of Periodic Group IB, copper and gold, show higher valence states, this is quite surprising, and often elicits questions from students. As a matter of fact, there is good evidence to support the assumption that all three of these metals show valences of +1, +2, and +3. In the case of silver, with which this paper is concerned, the two higher oxidation states are well established, and have been the subject of many researches. Compounds of divalent silver have been known for 140 years. They are easily prepared and, at ordinary temperatures, are stable almost indefinitely. Most of the compounds of trivalent silver decompose in a few hours, but there is ample evidence for their existence, and a few are entirely stable at ordinary temperatures.

TRIPOSITIVE SILVER

Many investigators have studied the black crystalline precipitate which is formed on the anode when a solution of a silver salt is electrolyzed (*1, 2, 3, 18*). There has been some disagreement as to its nature, but agreement is fairly general that its composition (when obtained from silver nitrate) approaches the formula $Ag_7O_8NO_3$. Treatment of AgO with nitric acid gives a material approaching this same composition. Similar products can be obtained by the action of chemical oxidizing agents such as fluorine (*13*) and peroxysulfates (*3, 4, 5, 6*) on argentous salts. The products are unstable, and analyses must be performed quickly if the presence of tripositive silver is to be demonstrated. From the action of potassium peroxysulfate on silver nitrate, Carman (*4*) obtained precipitates, which, if analyzed within 15 minutes, were shown to contain almost exactly two equivalents of "available" oxygen for each atom of silver. This corresponds to the formula Ag_2O_3:

$$Ag_2O_3 \rightarrow Ag_2O + 2[O]$$

Delayed analyses, however, showed lower and lower ratios of available oxygen to silver, the final value being reached in about three hours. In all of Carman's experiments, this final value approximated 1.5, which corresponds to the formula $Ag_2O_3 \cdot 2AgO$, which represents a stable compound.

As might be expected, these compounds of trivalent silver are powerful oxidizing agents. They convert chromic ion to chromate, ammonia to nitrogen, and manganous ion to manganese dioxide or permanganate.

It has been shown that silver salts owe their catalytic power in certain oxidations to the formation of the unstable Ag^{+++} ion (*8, 9, 10, 14*). For example, the rate of oxidation of VO^{++} ion to VO_3^- by peroxysulfate ion (*9*) is proportional to the concentration of $S_2O_8^{--}$ ion and to that of added Ag^+ ion, but not to that of the vanadyl ion. This indicates a slow reaction involving one Ag^+ ion for each $S_2O_8^{--}$ ion:

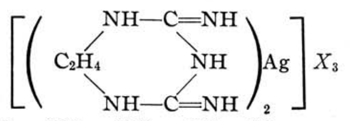
$$Ag^+ + S_2O_8^{--} \rightarrow Ag^{+++} + 2SO_4^{--}$$

followed by a very rapid reaction, too fast to affect the rate measurements:

$$Ag^{+++} + 2VO^{++} + 4H_2O \rightarrow Ag^+ + 2VO_3^- + 8H^+$$

An ion which is a strong oxidizing or reducing agent is so because it does not have the correct number of electrons to make the most stable structure. If the number of electrons be altered by coordinating the ion with other ions or molecules, it may often be made much more stable toward reduction or oxidation. This is a very general phenomenon (*7*), and is illustrated in the formation of stable salts of both divalent and trivalent silver.

Ray (*35*), for example, has prepared 4-coordinated salts of trivalent silver with ethylenebiguanide:



$X = NO_3^-, ClO_4^-, OH^-, SO_4^{--}$

These salts are a deep, permanganate red, and are quite stable at ordinary temperatures. The nitrate can be recrystallized from warm, dilute nitric acid. These salts liberate two equivalents of iodine from potassium iodide per mole of salt. Their conductivity at infinite dilution corresponds to that of other salts of the type MX_3. The Ag^{+++} in these compounds has the same electronic configuration as Ni^{++}; in conformity with this structure, the salts are diamagnetic. The divalent silver ion and its derivatives, on the other hand, are paramagnetic because of the unpaired electron.

DIPOSITIVE SILVER

Compounds of argentic silver can be readily obtained in a variety of ways. The material $Ag_7O_8NO_3$, on boiling with water, is quickly converted to AgO, which undergoes no further change, even though the boiling be continued for many hours (*18*). The same oxide is obtained by treating silver nitrate with a mixture of sodium carbonate and potassium peroxysulfate (*21*). It is a black powder, which will dissolve in sulfuric, nitric, and perchloric acids, to give solutions of strong oxidizing power. In dilute nitric acid, the material slowly decomposes with the liberation of oxygen, but in concentrated nitric acid, it may be preserved for some time. These solutions give no test for the presence of peroxide.

Silver difluoride has been prepared by the action of fluorine on silver and silver salts (*11, 12*). It is a dark brown powder, stable at moderate temperature, but decomposed on strong heating to argentous fluoride and fluorine. It has evidently not been obtained in pure form, for analysis of even the best samples indicated the presence of about 25 per cent AgF. The divalency of the silver is clearly indicated, however, by measurements of magnetic susceptibility, which show it to be strongly paramagnetic. It is decomposed in moist air, liberating oxygen or ozone. It oxidizes alcohol to acetaldehyde, manganese dioxide to permanganate, and chromic ion to chromate. It converts SO_2 to SO_2F_2, CO to COF_2 and reacts violently with many metals as well as with sulfur, phosphorus, carbon, and hydrogen. It is a powerful fluorinating agent, effecting the conversion of carbon tetrachloride to carbon tetrafluoride.

The fact that argentous salts in nitric acid solution are readily oxidized to the argentic state has been known for a long time. For example, Barbieri (*20*) observed that the action of lead dioxide on a solution of silver nitrate in nitric acid converted at least 90 per cent of the silver to the divalent salt. More recently, A. A. Noyes and his students have published a series of papers under the title "Argentic salts in acid solution" (*14, 15, 16, 17, 18*). Everyone interested in the application of physical chemistry to inorganic problems should read these papers. They not only report researches which were brilliantly conceived and executed, but they are examples of splendid scientific writing.

Only a brief résumé of them can be given here. Noyes and his students measured the rate of reaction between ozone and argentous nitrate in nitric acid, and found it to be proportional to the concentration of each of the reactants. This would indicate the formation of tripositive silver by some such reaction as:

$$Ag^+ + O_3 \rightarrow AgO^+ + O_2$$

but only dipositive silver was found in the solution. They therefore concluded that the initial reaction, which proceeds at a measurable rate, is followed by a fast reaction leading to the formation of divalent silver:

$$AgO^+ + Ag^+ + 2H^+ \rightarrow 2Ag^{++} + H_2O$$

While the divalent silver ion was not isolated from the solution, its character was carefully studied. That it is dipositive was shown by measurement of its magnetic susceptibility, and by analysis of the solution for silver and for oxidizing power. The decomposition of the divalent silver to the argentous state is slow enough that very satisfactory analyses could be obtained.

The exact nature of the silver-containing compound in these solutions is not known, but it is evident that the silver is in some sort of a nitrato complex. This was shown by studies of the color and the oxidizing potential of the solution, and by the increase in solubility of the compound with increasing concentration of nitrate ion (*18*). Weber (*19*) had previously come to the same conclusion through transference experiments.

A. A. Noyes and Kossiakoff (*16*) measured the oxidation-reduction potential of the argentic-argentous couple in nitric acid solution, and found the argentic ion to be nearly as strong an oxidizing agent as ozone. Their results are shown in Table 1.

TABLE 1

OXIDATION POTENTIALS OF STRONG OXIDIZING AGENTS

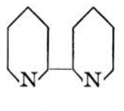
Oxidized State	*Reduced State*	*Volts*
F_2 (g) + $2E^-$	$2F^-$	2.88
O (g) + $2H^+$ + $2E^-$	H_2O (*l*)	2.419
O_3 (g) + $2H^+$ + $2E^-$	O_2 (g) + H_2O (*l*)	2.07
Ag^{II} + E^{-I}	Ag^I	1.914*
H_2O_2 + $2H^+$ + $2E^-$	$2H_2O$ (*l*)	1.77
MnO_4^- + $4H^+$ + $3E^-$	MnO_2 (s) + $2H_2O$ (*l*)	1.586
MnO_4^- + $8H^+$ + $5E^-$	Mn^{++} + $4H_2O$ (*l*)	1.447
PbO_2 (s) + $4H^+$ + $2E^-$	Pb^{++} + $2H_2O$ (*l*)	1.444
Ce^{IV} + E^{-I}	Ce^{III}	1.44 †
$^1/_2$ O_2 (g) + $2H^+$	H_2O (*l*)	1.225

* In nitrite solution.
† In sulfate solution.

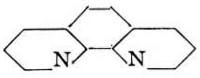
These solutions of argentic ion in nitric acid oxidize ammonia to nitrogen and oxides of nitrogen, vanadyl ion to vanadate, iodate to periodate, and chromic ion to chromate almost instantly.

The salts of many coordinated argentic ions are highly crystalline compounds which are readily obtained and easily kept. The leadership in the preparation of such compounds has been taken by the Italian chemist Barbieri, who has been active in the field for nearly 40 years. He first prepared $[Ag(pyridine)_4]S_2O_8$ by the action of potassium peroxysulfate on a solution of silver nitrate in pyridine (*22*) and established the divalency of the silver by showing that the compound is isomorphous with the corresponding cupric salt. He later showed (*16*) that it is also isomorphous with the corresponding cadmium salt. While the compound is stable toward light, it is instantly reduced by ammonia. Sodium hydroxide displaces the pyridine, precipitating AgO. Barbieri (*23*) prepared the nitrate of this tetrapyridyl argentic ion by the electrolytic oxidation of silver nitrate in 40 per cent pyridine. It formed orange-red prisms which he found to be isomorphous with those of the corresponding cupric salt. These salts, and several others of similar nature, have been shown to be paramagnetic, as would be expected of divalent coordinated silver ions (*24, 25, 28*).

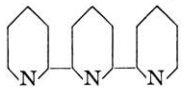
Dipyridyl



coordinates more firmly than pyridine itself, and complex dipyridyl argentic ions have been studied extensively (*24, 26, 27, 28*). They are of two types—$[Ag(dipy)_2]^{++}$ and $[Ag(dipy)_3^{++}$. The closely related orthophenanthroline



gives a similar ion, $[Ag(o\text{-phen})_2]^{++}$ (*25, 30*). The salts of these ions are reddish brown. They oxidize ammonia to nitrogen, halides to the free elements, and hydrogen peroxide to oxygen. A series of compounds of the formula [Ag tripy *X*] *X* has been prepared from tripyridyl,

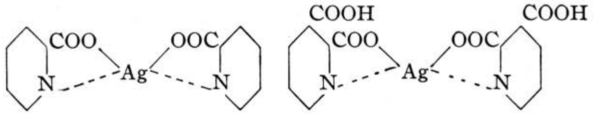


(*29*), a tridentate amine.

The heterocyclic acids picolinic

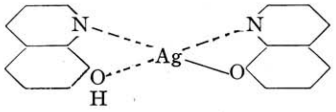
(*31, 32*) and quinolinic

(*33*) likewise form red crystalline compounds with the argentic ion. In these, the acid ion serves both to neutralize the charge on the silver ion, and to fill the coordination sphere:

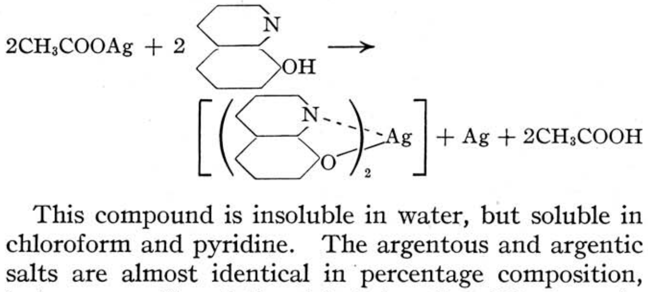


The former has been shown by x-ray analysis to be planar, rather than tetrahedral, and to be isomorphous with the analogous cupric salt.

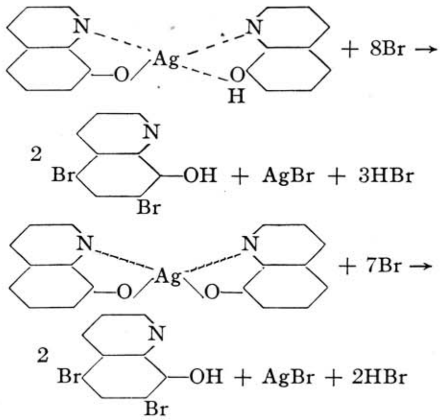
If solutions of silver acetate and 8-hydroxyquinoline are mixed at room temperature, the yellow argentous compound



is precipitated. If the solutions are hot, however, the deep green argentic salt is formed (*34*):



This compound is insoluble in water, but soluble in chloroform and pyridine. The argentous and argentic salts are almost identical in percentage composition, but are readily distinguished by the differences in color and other properties. Both compounds are destroyed by bromine water, but the molecule of the argentous salt, because it contains one hydrogen atom more than the argentic compound, requires an additional bromine atom:



CONCLUSIONS

While the common silver salts of commerce contain argentous silver, it is evident that higher oxidation states are easily attained. Their omission from textbooks of general chemistry is to be deplored, as it leads students to the conclusion that the periodic relationships of the coinage metals are very imperfect.

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