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The Chemistry of Argentic Oxide. The Formation of a Silver(III) Complex with Periodate in Basic Solution[1]

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$Na_5H_2Ag^{III}(IO_6)_2\cdot 16H_2O$ has been prepared by reaction of AgO with KIO_3 in basic solution and subsequent treatment with NaOH. The periodate present in the complex is formed by oxidation of the iodate by AgO. This compound has also been prepared by oxidation of Ag(I) with $K_2S_2O_8$ in the presence of KIO_4. Spectroscopic analysis, X-ray diffraction studies, and magnetic susceptibility measurements as well as classical analytical procedures show that the two preparations yield the same compound.

Introduction

For many years it was thought that argentic oxide (AgO) was a true oxide of Ag(II). Recent physical measurements, however, have shown that in the solid state AgO contains equimolar amounts of Ag(I) and Ag(III).[4] Although chemical studies have shown that, when dissolved in acid, AgO does indeed yield Ag(II),[5] the seeming contradiction could be accounted for by the equilibrium[6]

$$Ag^{III}O^{+} + Ag(I)^{+} + 2H^{+} \rightleftharpoons 2Ag(II)^{2+} + H_2O$$

McMillan[7] has suggested that Ag(III) hydroxy complexes are present in 1 *N* KOH solutions saturated with AgO. Other workers have claimed either that there is no higher-valent species present in KOH in contact with AgO,[8] or that there is a silver(II) species present in such solutions.[9] No one has, however, previously presented definite evidence for the presence of any Ag(III) species in solution arising from AgO.

It has been known for some time that Ag(III) complex compounds are formed when Ag(I) is oxidized in the presence of a stabilizing ligand. In this manner compounds of Ag(III) with periodate,[10,11] tellurate,[12] and ethylenebis(biguanide)[13] have been prepared. This investigation was undertaken in order to explore the formation of complex Ag(III) compounds starting with AgO in basic medium.

The formation of sodium diperiodatoargentate(III) is described in this paper, with a view toward showing that a Ag(III) species results in solutions in which AgO is the only source of silver and is the strongest oxidant present.

Experimental

Materials.—AgO used for this work was supplied by Handy and Harman. The method of analysis described by Jirsa[14] showed this to be 95% AgO. The potassium iodate, potassium periodate, potassium hydroxide, potassium persulfate, and silver nitrate were all either Fisher Certified or Baker Analyzed reagents. All water used was doubly distilled from alkaline permanganate solution in order to remove any oxidizable impurities.

Preparation of Diperiodatoargentate(III) Salts from AgO.—To a solution of 25 g. of KOH and 20 g. of KIO_3 in 200 ml. of water heated to 50° was added 20 g. of AgO. The solution was brought to a boil and immediately removed from the heat. After the solid, a mixture of Ag_2O and unreacted AgO, had settled, the solution was dark red. This solution was recovered by filtering through a medium porosity fritted glass filter. To this solution was added 40 g. of NaOH, whereupon a voluminous orange precipitate appeared. This precipitate was recovered by filtration through a medium porosity fritted glass filter crucible, washed three times with cold water, added to about 50 ml. of H_2O, and the mixture heated, with stirring, to 80°. Some of the solid dissolved to form a dark red solution. The mixture was then filtered hot, and the dark red filtrate set to cool, whereupon orange crystals separated out. The residue proved to be a mixture of $AgIO_3$ and $NaIO_3$. The orange crystals were recrystallized once from water (product 1). *Anal.* Calcd. for $Na_5H_2Ag(IO_6)_2\cdot 16H_2O$: H, 0.21; Na, 11.99; Ag, 11.25; IO_6, 46.49; H_2O, 30.06; equivalents of I liberated per mole of Ag, 18. Found: H, 0.21; Na, 12.01; Ag, 11.27; IO_6, 46.56; H_2O, 29.97; equivalents of I, 18.1.

A second crystalline material (product 2) was separated from another red solution prepared as described above. This material contained some potassium, and the empirical formula was found to be $Na_{4.6}K_{0.4}H_2Ag(IO_6)_2\cdot 13.6H_2O$. The crystals of this latter material were larger and somewhat redder than those of the former compound. There is at present no explanation available as to why the two different types of materials were formed in solutions which were treated identically. *Anal.* Calcd. for $Na_{4.6}K_{0.4}H_2Ag(IO_6)_2\cdot 13.6H_2O$: Ag, 11.70; IO_6, 48.35. Found: Ag, 11.65; IO_6, 48.37.

A third compound, containing only potassium, was prepared in the following manner. To a solution of 1.5 g. of KOH and 20 g. of KIO_4 in 200 ml. of H_2O was added 10 g. of AgO. This solution was heated to 65° and kept stirring at this temperature for 5 hr., after which time it was filtered at the elevated temperature through a fine porosity fritted glass filter, and the filtrate set to cool. The residue was a mixture of Ag_2O and unreacted AgO. Upon cooling, orange crystals (product 3) separated from the filtrate which remained dark red. This product was recrystallized once from water. *Anal.* Calcd. for $K_3H_4Ag(IO_6)_2\cdot 3H_2O$: H, 0.55; K, 16.09; Ag, 14.80; IO_6, 61.15; H_2O, 7.41. Found: H, 0.55; K, 15.97; Ag, 14.74; IO_6, 60.85; H_2O, 7.89.

Preparation of Sodium Diperiodatoargentate(III) by *in Situ*

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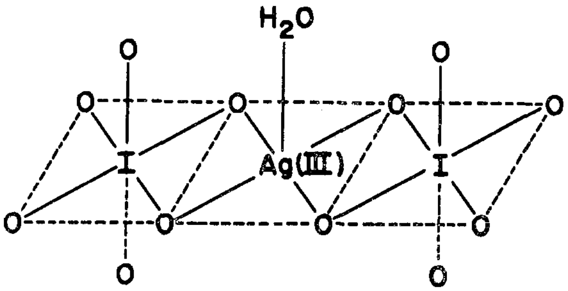

Figure 1.

Oxidation of Ag(I).[10]—*To a solution of 28 g. of* KOH *and 23 g. of* KIO_3 in 100 ml. of H_2O was added 8.5 g. of $AgNO_3$. This mixture was heated just to boiling, 20 g. of $K_2S_2O_8$ added slowly, and the mixture allowed to cool. After cooling, a dark red solution was again observed. This solution was treated as described above, and an orange crystalline material (product 4) was isolated. *Anal.* Found for $Na_5H_2Ag(IO_6)_2 \cdot 16H_2O$: H, 0.21; Na, 12.07; Ag, 11.65; IO_6, 46.95; H_2O, 29.12; equivalents of I, 18.1.

Chemical Analysis.—The compounds prepared as described above were analyzed for silver and periodate by acidifying a solution of the material with HCl, recovering and weighing the AgCl, and titrating the iodine liberated when excess KI was added to the filtrate. Analysis for total oxidizing power was performed by addition of a large enough excess of KI to a solution of the complex to dissolve all of the AgI that formed, acidification of the solution, and titration of the liberated iodine with $Na_2S_2O_3$. The water content was determined by drying under vacuum over P_2O_5 at 80° for 5 days, and alkali metals were determined by flame photometry. Hydrogen was determined by difference.

Instrumental Analysis.—Ultraviolet–visible spectra were measured on a Beckman Model DU spectrophotometer. X-Ray powder and single crystal diffraction patterns were determined by means of a Norelco X-ray photometer. Magnetic susceptibilities were determined by a modified Curie method with an Ainsworth automatic balance as the indicating instrument.

Results

X-Ray powder analysis showed no difference in products 1 and 4, but product 2 was shown to be different. Products 1 and 4 were triclinic crystals with one molecule per unit cell. Product 2, the one containing potassium as well as sodium, was found to be a pure compound, crystallizing in the monoclinic system. The cell dimensions agree very closely with those recently reported for a diperiodatocuprate(III) compound, for which the formula reported was $Na_3KH_3Cu(IO_6)_2 \cdot 14H_2O$.[15] Table I shows a comparison of the cell dimensions.

In aqueous solution, three absorption maxima with large extinction coefficients, indicative of charge-transfer bands, were found for all of the compounds prepared. These occur at 216, 255, and 362 mμ. For a concentration of 5.36×10^{-5} *M* complex the extinction coefficients were found to be 1.54×10^4, 1.45×10^4, and 1.40×10^4 l. mole^{-1} cm.$^{-1}$, respectively. The intensity of absorption is independent of the nature of the cation in the compound.

Magnetic susceptibility studies show the compounds to be diamagnetic, with a small magnetic moment. This is in agreement with Malatesta.[10]

Table I

Composition	$Na_{4.6}K_{0.4}H_2Ag(IO_6)_2 \cdot 13.6H_2O$	$Na_3KH_3Cu(IO_6)_2 \cdot 14H_2O$
Crystal system	Monoclinic	Monoclinic
Cell dimensions		
a, Å.	14.71	14.84
b, Å.	25.53	25.18
c, Å.	6.11	6.12
β	97°	97°30′
Cell volume, Å.^{3}	2276	2267
Molecules/unit cell	4	4
Space group	$P2_1/a$	$P2_1/a$

Discussion

When the complex was allowed to react with KI for determination of total oxidizing power, the Ag(III) was reduced to Ag(I) with the liberation of 2 equivalents of I^0 per mole of Ag prior to acidification. Also, the periodate was partially reduced at this stage. Upon acidification, a total of 8 equivalents of I^0 was liberated for each mole of periodate. Thus, in the compound under discussion there should be a total of 18 equivalents of I^0 liberated for each mole of silver if 1 mole of Ag(III) is present along with 2 moles of periodate. This was found to be the case.

From the nature of the product formed when AgO is allowed to react with KIO_3 in basic solution, the over-all reaction can be written as

$$12AgO + 10OH^- + 4IO_3^- \longrightarrow 5Ag_2O + 2Ag(IO_6)_2^{-7} + 5H_2O$$

While no mechanism study has been performed on this reaction, it is suggested that the first step involves oxidation of iodate to periodate by the Ag(III); additional Ag(III) then combines with the newly formed periodate. It is, however, impossible to say at this stage whether there is a species of Ag(III) present in solutions in contact with AgO when no stabilizing ligand is present.

All of the instrumental methods employed showed that the compounds prepared were the same whether AgO was used as a starting material or Ag(I) was oxidized *in situ*.

The chemical analyses described above confirm the presence of Ag(III) in the complex and show that the mole ratio of Ag to periodate is 1:2. Kinetic studies of silver ion catalyzed oxidation reactions are consistent with the formation of Ag(III) when $S_2O_8^{2-}$ reacts with Ag(I),[16-19] although the alternate formulation

$$Ag^+ + S_2O_8^{2-} \longrightarrow Ag(II)^{2+} + SO_4^{2-} + SO_4^-$$

is also a possibility.[20] Analysis of complex compounds formed[10-13] showed that Ag(III) results when Ag(I) is oxidized by $S_2O_8^{2-}$.

The fact that the compound was found to be diamagnetic is consistent with the electronic structure of Ag(III), which has eight d electrons in its outer shell. The Cu(III) compound previously mentioned was found

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to have a square-planar configuration, with the plane formed by one edge from each of the two periodate octahedra, and with one water molecule at a distance of about 2.7 Å. from the copper atom.[15] By analogy, the silver(III) compound can be pictured as shown in Fig. 1. It is thought that the periodate acts as a bidentate ligand and contributes to the stabilization of the Ag(III).

Conclusion

In the reaction between AgO and KIO_3, the iodate is oxidized to periodate, which then forms a complex compound with Ag(III). This compound is identical with one formed by oxidation of Ag(I) with $K_2S_2O_8$ in the presence of iodate. Previously, definite proof has been presented for the existence of a soluble species of silver with a valence greater than one arising from AgO in acid solution only. In these cases, only silver(II) species have been found.[5] In this work we have shown that in basic solution, when nothing is present that could oxidize the AgO, a silver(III) species results. This is consistent with physical evidence for the presence of Ag(III) in AgO.

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Ion Exchange in Mixed Solvents. II. Monovalent Cations on a Weak Acid Exchanger[1]

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Ion-exchange behavior of Li^+, Na^+, and K^+ against NH_4^+ on a carboxylic acid type of exchanger has been studied in mixed solvents. From the various reversals of affinities observed, it has been postulated that, in weak-acid exchanger in aqueous medium, ion-pair formation of the solvent-shared type predominates and that the contact type of ion pairs increases with increase of organic solvent in the solution phase.

Introduction

In a previous communication,[2] it was postulated that addition of water-miscible organic solvents to the solution phase enhances the contact type of ion-pair formation in the resin phase of a strong-acid exchanger in the inverse order of hydrated ionic radii of Li^+, Na^+, and K^+. Even though various thermodynamic properties of methacrylic acid exchanger have been studied,[3] little work has been reported on the exchange behavior of alkali ions except by Bregman[4] and Gregor, *et al.*,[5] in aqueous medium. This paper deals with the exchange equilibria of Li^+, Na^+, and K^+ against NH_4^+[6] on a carboxylic acid exchanger in aqueous and mixed-solvent media.

Experimental

Materials.—The weak acid exchanger Merck IV, supplied by E. Merck AG., Darmstadt, Germany, is a polyacrylic acid derivative capable of swelling. About 200 g. of this exchanger of 100 to 200 mesh size was taken in a column of conventional design and then converted several times into NH_4^+ and H^+ forms alternatively with ∽2 *N* ammonium hydroxide and hydrochloric acid. Finally the exchanger in NH_4^+ form was prepared by passing a sufficient amount of a mixture of ammonium chloride and hydroxide and then washing with de-ionized water until free of chloride.[8] The exchanger was then dried over a hot water bath and stored in a stoppered Pyrex bottle.

The moisture content of the exchanger, estimated by heating a known quantity at 110 ± 2° for 4 hr.,[9] was 17.2%. The exchange capacity of this wet resin was found to be 5.15 mequiv./g. by treating a known quantity of it in a column with excess standard acid and titrating the excess acid.[10]

Alkali chlorides, 1-propanol, 2-propanol, and acetone were of B.D.H. AnalaR grade, while methanol and ethanol were distilled in the laboratory.

Procedure.—Various volumes of water, organic solvent, and 1.0 mequiv. of alkali chloride were added into Pyrex quick-fit flasks, each containing 1.0 g. of the exchanger, to maintain a total volume of 50 ml. at 25 ± 2°. After equilibrating for 24 hr.,[11] an aliquot of the solution phase was analyzed for the alkali content flame photometrically using a Beckman Model DU spectrophotometer with flame attachment and oxy-hydrogen flame.

The equilibrium exchange coefficient $K^{C^+}{}_{NH^+_4}$ (= $[NH_4^+][RC]/[C^+][RNH_4]$) of the exchange reaction $C^+ + RNH_4 \rightleftharpoons RC + NH_4^+$ (C^+ represents Li^+, Na^+, or K^+) was calculated using mole

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(11) Kunin and Barry[7] have observed that equilibrium is attained rapidly with carboxylic acid exchanger in the salt form, although not in H^+ form. During the present studies, it has been observed that equilibrium is attained within about 3 hr. in the presence of mixed solvents.