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HIGHER OXIDATION STATES OF SILVER—I

REACTION OF OZONE WITH SIMPLE SILVER SALTS*

J. SELBIN and M. USATEGUI
Coates Chemical Laboratories, Louisiana State University, Baton Rouge

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Abstract—Aqueous solutions of the silver salts $AgNO_3$, Ag_2SO_4, $AgClO_4$, AgF and $AgC_2H_3O_2$ have been ozonized, the black crystalline products isolated and partially characterized by their composition, oxidizing power, magnetic properties and X-ray powder diffraction patterns. Oxidized products of the above compounds were found to have the empirical formulas $Ag_7O_8NO_3$, $Ag_7O_8SO_4$, Ag_4O_5, AgO and AgO, respectively. The nitrate and the new sulphate were found to be relatively stable in air, but they both decomposed to AgO upon being suspended in boiling water. Their X-ray patterns were indexed as face-centred cubic, with the sulphate having the slightly larger cell constant. The Ag_4O_5 compound was quite unstable, decomposing on standing within minutes. It was indexed with a simple cubic lattice and lines were also present due to AgO, which is monoclinic. All samples were paramagnetic except the AgO compounds obtained from AgF and $AgC_2H_3O_2$, which were diamagnetic. Partial replacement of silver was effected only with Cd^{2+} although Ba^{2+}, Mg^{2+} and Zn^{2+} were also tried. Suggestions are made concerning the formulation and structure of some of the higher oxides.

THERE are no reliable reports of simple compounds containing trivalent silver. Other than a few poorly characterized "higher oxides" of silver supposed to contain some Ag_2O_3, there are at least four well-substantiated complex ions which contain silver in this unusual oxidation state.⁽¹⁾ These include $[Ag(IO_6)_2]^{7-}$ and $[Ag(TeO_6)_2]^{9-}$ as potassium and sodium mixed and acid salts, $[AgF_4]^{1-}$ as potassium or cesium salt, and $[Ag\ edbg]^{3+}$ (where edbg = ethylenedibiguanide) as sulphate, nitrate, perchlorate and hydroxide. Compounds of divalent silver are more numerous, but aside from AgF_2 and AgO the only well-characterized compounds are complexes, all of which, curiously, contain a ligand with a pyridine or pyridine-like nitrogen as at least one of the donor atoms. We shall not be concerned in this paper with complexes but will consider only those compounds obtainable by oxidation of simple silver salts. Future papers will deal with complexes of silver in higher oxidation states.

Recently there has been some renewed interest in AgO and higher oxides of silver,⁽²,³⁾ undoubtedly stimulated partially by the rather confused state of the literature in this field, which was last reviewed by BAILAR⁽⁴⁾ in 1944. Since that time at least fifteen papers⁽⁵⁾ have appeared, each of which has contributed toward clarifying the earlier literature concerning AgO, Ag_2O_3 and compounds of intermediate formulas.

At least part of the confusion in the literature is due to the various methods

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(1) J. KLEINBERG, W. J. ARGERSINGER, JR. and E. GRISWOLD, *Inorganic Chemistry*, pp. 594–95, 600–1. D. C. HEATH, Boston (1960).

(2) T. P. DIRKSE and B. WIERS, *J. Electrochem. Soc.* **106**, 284 (1959).

(3) W. C. GRAFF and H. H. STADELMAIAR, *J. Electrochem. Soc.* **105**, 446 (1958).

(4) J. C. BAILAR, JR., *J. Chem. Educ.* **21**, 523 (1944).

(5) References to eight of these may be found in Ref. 3,– 4 more in Ref. 2. Also: R. L. DUTTA, *J. Indian Chem. Soc.* **32**, 95 (1955); V. SCATTURIN, P. L. BELLON and R. ZANNETTI, *J. Inorg. Nucl. Chem.* **8**, 462 (1958).

employed in obtaining higher oxidation state compounds. The nature of the oxidized product appears to be somewhat dependent upon (1) oxidizing agent used, (2) which silver (I) salt is employed, and (3) the pH, salt content and temperature of the solution being oxidized. In general higher oxides may be obtained by (a) anodic oxidation or (b) chemical oxidation. The latter has been effected by $K_2S_2O_8$, O_3, $KMnO_4$, ClO^-, PbO_2 and F_2, with the first reagent being the most commonly employed chemical oxidizing agent.(2,3,4)

In addition to the higher oxides of silver which apparently contain only silver and oxygen, there is some literature agreement that the black compound obtained by anodic(6) or peroxydisulphate(7) oxidation of $AgNO_3$ in nitric acid solution has the empirical formula $Ag_7O_8NO_3$. This curious formula suggests the presence of both divalent and trivalent silver (since no peroxide linkage is present) in the compound and of course the univalent state may also be present. Ozone has also been used to oxidize silver nitrate solutions containing nitric acid and while no solid products were isolated, NOYES and his students* made many valuable measurements on the oxidized solutions. Among other things they measured the rate of reaction between ozone and silver nitrate in nitric acid and found that it was proportional to the concentration of each of the reactants, suggesting as the slow step:

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

but since they found only divalent silver in the solution they assumed a rapid reaction leading to its formation as follows:

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

They believed the Ag(II) to be present in some sort of nitrato complex. WEBER,(8) who had oxidized silver nitrate anodically, postulated in 1917 the presence of $Ag^{II}(Ag^{III}O_2)_2$ in the oxidized solutions on the basis of electrolysis experiments which showed $\frac{1}{3}$ of the silver to be cathodic and $\frac{2}{3}$ anodic.

We have now ozonized aqueous solutions of the following silver salts, $AgNO_3$, Ag_2SO_4, $AgClO_4$, AgF and $AgC_2H_3O_2$, isolated the black crystalline products and attempted to characterize them by their composition, oxidizing power, magnetic properties and X-ray powder diffraction patterns. These results are reported here along with some additional observations concerning the reactions and the products.

EXPERIMENTAL

1. *Reagents*

All chemicals were of reagent grade quality and were used without further purification. Demineralized water was used to prepare all solutions. The aqueous solution of silver (I) fluoride was prepared from Ag_2O and hydrofluoric acid and contained an excess of HF. Ozone was obtained from a Welsbach Model T-23 Laboratory Ozonizer using tank oxygen which was predried. The flow rate was 0·3 l./min of gas containing 2–3 mole per cent O_3 in O_2.

2. *Procedure*

The general procedure employed in the study of each silver salt was as follows. The silver salt was dissolved in water, the pH measured, the solution placed in the reaction vessel (a gas adsorption

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* For references to a series of five excellent papers entitled *Argentic Salts in Acid Solution*, see Ref. 4.

(6) G. A. BARBIERI, *Atti Accad. Lincei* (5) **15**, i, 500 (1906); F. JIRSA, *Chem. Listy* **19**, 3 (1925); *Z. Anorg. Chem.* **148**, 130 (1925); A. A. NOYES *et al.*, *J. Amer. Chem. Soc.* **59**, 1326 (1937).

(7) G. A. BARBIERI, Atti accad. Lincei **13**, 882 (1931).

(8) WEBER, *Trans. Amer. Electrochem. Soc.* **32**, 391 (1917).

bottle fitted with a course sintered glass filter) and ozone bubbled through for 1–2 hr. The black solid product was collected on a sintered glass filter and either (1) analysed immediately (within 5 min) for the ratio of oxidizing power to total silver content; (2) washed with water until the washings gave a negative test for Ag^+ and then similarly analysed (to see if water free of ozone would reduce the product); (3) washed free of Ag^+ with water, then washed with acetone and air dried for 10 min and analysed separately for oxidizing power, silver content and for any other constituent besides oxygen which might be present. (All of these analyses were completed within 25 min); or (4) washed and dried as in (3) and allowed to stand for 24 hr before complete analysis. It is important to mention that no purification of a product is possible other than that afforded by simple washings.

Ozonizations of the silver salts were also carried out in the presence of one to tenfold excesses of the corresponding salts of Ba^{2+}, Mg^{2+}, Zn^{2+} and Cd^{2+}. Cadmium was the only other cation to be found in the oxidized product of $AgNO_3$, Ag_2SO_4 and $AgClO_4$.

All experiments reported here were run at room temperature (25–27°C).

3. *Analytical analysis*

In order to determine the ratio of oxidizing power to total silver content as rapidly as possible the following procedure was used. The freshly filtered precipitate was placed in a 250 ml Erlenmeyer flask and treated with 25·00 ml of 0·100 N oxalic acid solution, 35 ml of water and heated to boiling. Then 15 ml of an 0·8 M solution of H_2SO_4 was added and the excess oxalic acid back-titrated with 0·100 N $KMnO_4$ solution. This same solution was then titrated with 0·100 N KNCS solution using $FeNH_4(SO_4)_2$ as the indicator. The ratio of the results from the first titration to those in the second yields the oxidizing power (in electrons) per silver content (in atoms). This is the same procedure which was used to analyze 0·100 g samples of washed and dried products for oxidizing power and silver content. The time required for this analysis was just under 25 min from the time the product was filtered from the ozone-saturated reaction solution.

Analysis for sulphate was carried out as follows. The product was reduced with concentrated ammonia, the solution diluted with water and neutralized with concentrated HCl. The AgCl formed was removed by filtration and a 5% $BaCl_2$ solution was added to the filtrate. The sulphate was then determined by the standard gravimetric procedure. Nitrogen analysis was obtained by a commercial laboratory. Perchlorate and acetate were tested for in the products obtained from ozonization of $AgClO_4$ and $AgC_2H_3O_2$ respectively, by examination of the infra-red spectra of the products. Nitron also was used to test for perchlorate. Neither ion was found in any of the products. Fluoride could not be detected in the product from the ozonization of AgF by use of Li^+, Ca^{2+} or $PbCl_2$. The latter reagent yields very insoluble PbClF with F^-.

Cadmium ion was analysed by two independent procedures. In both methods the weighed black precipitate was first reduced with concentrated ammonia, the solution diluted, neutralized and the silver removed as insoluble AgNCS. In the first method the Cd^{2+} was precipitated and weighed as $Cd\,py_2(NCS)_2$. In the second method the Cd^{2+} was precipitated and weighed as cadmium bis-(8-hydroxyquinolinate).

The analytical data reported on stoicheiometry and oxidizing power represent the result of averaging at least two separate runs, but in most cases four to six runs were made in each study. Duplicate analyses on the same sample agreed within ±1 per cent and on different samples to within ±4 per cent. All samples responded negative to tests for the peroxide linkage.

4. *Physical measurements*

a. *X-ray.* X-ray powder diffraction measurements were obtained with a Norelco X-ray Diffractometer using Ni-filtered Cu K_α doublet radiation. Peaks were detected with a Geiger tube counter and recorded electrically.

b. *Infra-red.* Infra-red spectra were obtained using a Perkin-Elmer Model 21 Recording Spectrophotometer. Both the KBr pellet and Nujol mull techniques were used.

c. *Magnetic.* Magnetic susceptibilities were measured to a precision of ±6 per cent on a magnetic balance designed and built by DAY. It is described elsewhere.(9) Ferrous ammonium sulphate was used for calibration and copper sulphate pentahydrate was used to check the accuracy and precision.

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(9) M. C. DAY, L. D. HULETT and D. WILLIS, *Rev. Sci. Instrum.* **31**, 1142 (1960).

TABLE 1.—SUMMARY OF DATA ON HIGHER OXIDES OF SILVER

1. Compound oxidized	$AgNO_3$	Ag_2SO_4	$AgClO_4$	AgF	$AgC_2H_3O_2$
2. Proposed formula for black product	$2Ag_2O_3 \cdot 2AgO \cdot AgNO_3$ $(Ag_7O_8NO_3)$	$2Ag_2O_3 \cdot 2AgO \cdot AgSO_4$ $(Ag_7O_8SO_4)$	$Ag_2O_3 \cdot 2AgO$ (Ag_4O_5)	AgO	AgO
3. Concn. (M) of starting material	0·10	0·016	0·50	0·50	0·060
4. pH of solution					
a. at start	4·4	4·4	3·0	5·9	7·0
b. at end	2·0	2·3	1·8	5·8	5·7
5. Ratio of oxidizing power to Ag content $\left(\frac{e^-}{Ag}\right)$					
a. Theoretical	1·43	1·58	1·50	1·00	1·00
b. Found					
(1) unwashed (<5 min)	1·38	1·52	1·50	1·01	1·00
(2) washed and dried (<25 min)	1·39	1·53	1·41	1·00	0·94
(3) washed and dried—after 24 hr	1·37	1·25–1·46	0·99	0·87	0·90
(4) sample ozonated twice as long	1·39	1·54	1·49	—	—
(5) after boiling 1 hr	0·95	0·93	0·98	—	—
6. Analyses					
a. % purity based on oxidizing power (<25 min)	98	99	95	100	94
b. % purity based on Ag content (<25 min)	101 100*	102 99*	100	100	99
c. % purity based on other (indicated) analyses	99 (N)	101 (SO_4^{2-})	(no ClO_4^-)	(no F^-)	(no $C_2H_3O_2^-$)
7. Magnetic properties	$6,379 \times 10^{-6}$	$14,549 \times 10^{-6}$	800×10^{-6}†	Diamag.	Diamag.
χ_m, range	$3,515 \times 10^{-6}$	$2,350 \times 10^{-6}$	$1,645 \times 10^{-6}$		

* After boiling 1 hr, based on AgO

† After 24 hr.

RESULTS AND DISCUSSION

Table 1 summarizes some of the pertinent data collected for the several silver salts which were oxidized by ozone.

Silver fluoride and silver acetate. The silver fluoride reaction solution contained hydrofluoric acid which served to buffer the solution at a pH of 5·9 and this dropped only to 5·8 after 1 hr of ozonization. The silver acetate reaction solution was at a pH of 7·0 before ozonization and this value dropped to 5·7 at the end of an hour of ozonization. The possible significance of these pH values in determining the product produced will be discussed further on. The black product obtained from each of these solutions proved to be silver (II) oxide. This was verified by oxidizing power and silver content determinations (Table 1), with the product from the acetate salt showing less stability of oxidizing power than the product from the fluoride salt. We have no explanation for this stability difference but it should be mentioned that our survey of the literature on AgO has revealed that its stability seems very definitely to depend upon its mode of preparation. Both products were diamagnetic, which is in agreement with SUGDEN's(10) findings for an AgO sample obtained by oxidation of $AgNO_3$ using $K_2S_2O_8$. KLEMM(11) found an AgO sample to be very weakly paramagnetic, but does not say how he obtained the sample. Both of our samples gave essentially identical (within experimental error) X-ray powder diffraction patterns, which agreed satisfactorily with the patterns reported in the literature (Table 2). The pattern has recently been indexed as monoclinic,(3,12) analogous to CuO. The absence of any but possibly trace amounts of fluoride or acetate in these oxides has been established chemically and spectrally.

TABLE 2.—X-RAY DATA ON AgO

Source	Four strongest lines with relative intensities			
O_3 + AgF	2·774 100	2·418 86	2·623 39	2·288 33
O_3 + $AgC_2H_3O_2$	2·777 100	2·420 83	2·630 38	2·284 32
$K_2S_2O_8$ + $AgNO_3$ (in strong base)*	2·762 100	2·410 80	2·618 34	2·278 29
Anodic oxn. of $AgClO_4$*	2·760 100	2·410 77	2·608 41	2·275 22
Boiled sample from anodic oxn. of $AgNO_3$*	2·771 100	2·414 65	2·618 31	2·284 29
Merck and Co. "Divasil"*	2·768 100	2·410 88	2·615 35	2·281 35

* From reference 4.

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(10) S. SUGDEN, *J. Chem. Soc.* 161 (1932).

(11) W. KLEMM, *Z. Anorg. Chem.* **201,** 32 (1931).

(12) J. A. MCMILLAN, *Acta Cryst.* (Abstr.) 7, 640 (1954); V. SCATTURIN, P. L. BELLON and R. ZANNETTI, *J. Inorg. Nucl. Chem.* **8,** 462 (1958).

Silver perchlorate. The 0·5 M solution of silver perchlorate had a pH of 3·0 which dropped to 1·8 at the end of 1 hr of ozonization. Immediate analysis (<5 min) of the black product showed it to have a ratio of oxidizing power to total silver content (which we shall call R from now on) of 1·50, which is just the theoretical value for a higher oxide of composition Ag_4O_5 (assuming only Ag(II) and Ag(III) to be present). Analysis for total silver content supports this formulation, but because one oxygen more or less affects the silver content within our experimental error, we cannot say that it proves it. The following values illustrate this point.

Formula	Ag%	R
Ag_3O_4	83·49	1·67
Ag_4O_5	84·36	1·50
Our compound	84·7	1·50
Ag_5O_6	84·89	1·42
Ag_6O_7	85·25	1·25

The high value for our compound (compared with the theoretical value for Ag_4O_5) can be accounted for at least in part by the known rapid deterioration of the product which, if it occurs by release of oxygen, would raise the percentage of silver. As can be seen from the values in Table 1, the oxidizing power drops rapidly, by about 5–6 per cent within 20 min, and all the way to that equivalent to AgO in 24 hours. There is some justification for writing the formula for this compound as either $Ag_2O_3 \cdot 2AgO$ or $Ag_3O_4 \cdot AgO$. The X-ray powder diffraction pattern was indexed to show a simple cubic lattice, with lattice constant $a_0 = 8{\cdot}509 \pm 0{\cdot}029$, in addition to the lines for the monoclinic lattice of AgO (Table 3). Presumably the simple lattice is for Ag_2O_3 or Ag_3O_4, with the latter being more likely since the simple cubic lattice lines are much stronger than the AgO lines. The wide range of uncertainty in the lattice constant is probably caused by structural changes which are occurring even in the time it takes to run an X-ray pattern. Thus samples run 12–24 hr after preparation give primarily the AgO pattern. CARMAN(13) found that the R value for a higher oxide of silver remained 1·50 for many hours as long as it was in the presence of the oxidizing agent, $K_2S_2O_8$. He claimed that the product initially formed was pure Ag_2O_3, on the basis that he got $R = 2{\cdot}0$ when he analysed the product immediately after its formation. He reported that after two hours reaction the R value fell to 1·50 and remained at that value. From this it would appear that we are dealing with the same compound that he was, but he made no additional study of it. If an unstable Ag_2O_3 is formed in our reaction using ozone as oxidant, it was not detectable by our methods of analysis. Ozonization had to be continued for at least 30 min in order to obtain enough product for our analysis and this may in part account for our failure to detect the pure Ag_2O_3.

All products obtained from the ozonization of $AgClO_4$ solutions were found to be paramagnetic, but a range of values for the magnitude of the paramagnetism was observed which appeared to be independent of the variables which were being controlled in our experiments. We are tempted to suggest that what we are observing is not normal paramagnetism (AgO is diamagnetic despite the odd number of electrons in silver (II)) but rather ferrimagnetism or possibly antiferromagnetism. However,

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(13) P. C. CARMAN, *Trans. Faraday Soc.* **30**, 574 (1934).

this question must remain an open one until detailed X-ray examination and detailed magnetic studies involving temperature and field strength changes can be made.

Silver nitrate. There is still controversy in the literature concerning the exact composition and nature of the compound obtained by oxidation of silver nitrate solutions,(3,4,6,7,14) despite the outstanding work of Noyes and his students in this area.

Table 3.—X-ray data on Ag_2O_3·2AgO*

Obsd. *d*	I/I_0	Calcd. a_0	*hkl*
2·875	7		
(2·780)^1	24		
2·723	24		
2·687	100	8·496	310
(2·626)^3	9		
2·509	20		
(2·420)^2	18		
2·305	7		
(2·293)^4	15		
2·268	20		
2·202	6		
2·125	6	8·500	420
1·912	6	8·550	
(1·748)	15	8·563	422
(1·702)	15	8·510	500, 430
(1·626)	11	8·449	511, 333
1·575	7	8·481	520, 432
1·567	7	8·582	521
1·537	16		
1·533	10		
1·502	5	8·497	440
(1·483)	6	8·520	522, 441
1·461	7	8·519	530, 423
(1·454)	4		
(1·395)	6	8·486	610
1·360	4		
1·152	5	8·465	721, 633, 552

Ave. lattice spacing = 8·509 ± 0·029, simple cubic

* The *d* spacing values in parentheses belong to the AgO pattern and the superscript numbered ones are the four strongest AgO lines in order $1 > 2 > 3 > 4$.

Our work strongly supports the unusual formulation $Ag_7O_8NO_3$ for the product (see Table 1), in which the nitrate, presumably as $AgNO_3$, is an integral part of the structure. No $AgNO_3$ lines are present in the X-ray powder pattern of this compound and this leads us to postulate that the $AgNO_3$ is either physically trapped by the lattice of the higher oxides of silver or actually incorporated into the lattice. The nitrate cannot be washed from the product and the stability and analysis of the aged product seem to establish its importance in the structure. Upon being suspended in boiling water for an hour or more the product decomposes to slightly impure (and insoluble) AgO, the silver nitrate being released to the solution.

(14) H. Braekken, *Kgl. Norske Videnskab. Selskabs Forh.* 7, 143 (1935).

The X-ray powder diffraction pattern was readily indexed as face-centred cubic (Table 4) with lattice constant, $a_0 = 9{\cdot}895 \pm 0{\cdot}004$. SWANSON, *et al.*(15) obtained the same value and also reported four formula groups per unit cell. It is very interesting that the spinel structure oxides, having formulas AB_2O_4 (or $AO{\cdot}B_2O_3$) (where A may be identical with B) also have face-centred cubic lattices with eight formula units per unit cell. Our compound, which may be formulated as $2(AgO{\cdot}Ag_2O_3){\cdot}AgNO_3$ might possibly have a spinel structure which is stabilized by the presence of the $AgNO_3$. Such incorporation of other species in spinel lattices is not unknown.(16) Magnetic susceptibility measurements showed a range of paramagnetic values (Tables 1), again suggesting that the lattice is responsible for the magnetism rather than the divalent silver ion. There was a very slight difference in the lattice constant, a_0, for samples showing large and small paramagnetic behaviour, but no composition differences could be established by our methods of analysis.

TABLE 4.—SUMMARY OF X-RAY DATA ON HIGHER OXIDES OF SILVER

Compound	Type of lattice	Lattice constants
$Ag_7O_8NO_3$	Face-centred cubic	$a_0 = 9{\cdot}895 \pm 0{\cdot}004$ $9{\cdot}893 \pm 0{\cdot}003$ (17) $9{\cdot}890 \pm 0{\cdot}006$ (4)
$Ag_7O_8SO_4$	Face-centred cubic	$a_0 = 9{\cdot}924 \pm 0{\cdot}004$
$Ag_3O_4{\cdot}AgO$	Simple cubic (+monoclinic)	$a_0 = 8{\cdot}50 \pm 0{\cdot}01$
AgO (from AgF)	Monoclinic	
AgO (from $AgC_2H_3O_2$)	Monoclinic	

Silver sulphate. Analysis of the product obtained by ozonization of silver sulphate solutions (see Table 1) has led us to formulate it like the nitrate compound, i.e. $Ag_7O_8SO_4$ or $2(AgO{\cdot}Ag_2O_3){\cdot}AgSO_4$. The difference arises in the oxidizing power which for the sulphate indicates the presence of only divalent and trivalent silver and no monovalent silver. As can be seen from the data in Table 1, the sulphate compound is not as stable on standing or toward boiling water as is the nitrate compound. Our sulphate analysis (on a water-washed sample) definitely supports the presence of a stoicheiometric amount of sulphate and the X-ray powder diffraction pattern shows the compound to be completely analogous to the nitrate compound (Table 4). The slightly larger lattice constant might be expected in light of the larger radius of the sulphate ion (NO_3^-, 1·89 Å; SO_4^{2-}, 2·30 Å). It might be of interest to point out that the still larger size of the perchlorate ion (2·36 Å) may explain the failure of $AgClO_4$ to be incorporated into the higher oxide structure. Bromate (1·91 Å) and iodate (1·82 Å) have not yet been investigated, but might help clarify this point.

Magnetic susceptibility measurements of the sulphate products (Table 1) showed the greatest range of values of any of the compounds. No explanation can be offered at the present time.

Replacement of silver (II). Attempts were made to replace the Ag(II) in the higher oxides by carrying out the ozonizations of the silver salts in the presence of one- or tenfold excesses of the following ions: Ba^{2+}, Mg^{2+}, Zn^{2+} and Cd^{2+}. No replacement

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(15) H. E. SWANSON, *et al.*, *Nat. Bur. Standards Circ.* 539, Vol. IV (1955).

(16) A. F. WELLS, *Structural Inorganic Chemistry*, (2nd Ed.), pp. 379–385. Oxford (1950).

at all was observed with the first three ions, but Cd^{2+} was found to replace from 10 to 15 per cent of the Ag(II) in the products obtained from $AgNO_3$, Ag_2SO_4 and $AgClO_4$ salts. Cd^{2+} is closer in size to the Ag^{2+} than are the other cations (1·03 Å vs. 0·93 Å est., respectively). The lattices were somewhat expanded by the substitution of Cd^{2+} for Ag^{2+} but the compounds were not as stable toward decomposition.

pH changes. In all of the silver salt solutions ozonated a drop in pH was noted indicating that the overall oxidation process must be producing hydrogen ions. Without kinetic data we cannot say anything concerning possible mechanisms which would account for this pH drop. However, it is possible now, in light of our work and the available literature, to postulate that above a certain pH we should not expect any silver (III) to be permanently formed but that AgO will be the expected product. Thus when alkaline solutions of silver (I) salts are oxidized anodically, with $K_2S_2O_3$(2,3) or with O_3, the product is invariably AgO. That we obtained AgO and no higher oxides from AgF and $AgC_2H_3O_2$ may be traced to the relatively high initial and final pH of the solutions. When the pH of the nitrate, sulphate and perchlorate solutions was raised to the point where silver (I) oxide would just begin forming, ozonization produced only AgO. Therefore it would appear that above a pH of 5, AgO can be expected, but below a pH of 4·5, higher oxides may form.

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