

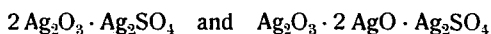
## ON THE HIGHER OXIDATION STATES OF SILVER

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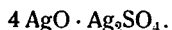
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Experimentally has been proved that the black product obtained from the oxidation of silver nitrate with peroxydisulfate contains silver(III) and silver(II) oxide, the composition of which greatly depends on the concentration-ratio of the reactants. On mixing silver nitrate and peroxydisulfate in a mole ratio of 2:1 and 4:1 resp. at pH 3



are formed and these after a longer standing decompose into



It has also been shown that due to the presence of silver(I) ions only the standard potential of silver(II) and silver(I) can be measured although these compounds contain trivalent silver.

In the early years of the last century it had been observed that when electrolyzing a solution of silver salt between Pt electrodes a black product forms on the anode. Soon after this a method had been developed to prepare this substance in greater amount so it became possible to determine its composition. This black product was firstly investigated by E. WALLQUIST [1] and according to him its composition was  $\text{Ag}_2\text{O}_3$ . But his analytical data proved to be inaccurate as later papers show. Detailed literature see in papers of O. SULC [2] and F. JIRSA [3].

In 1880 M. BERTHELOT [4] suggested a formula containing trivalent silver oxide. The existence of di- and trivalent silver ions seemed to be very likely on the basis of MENDELEIEFF's periodic system.

In the last decades of the century it had been observed, too, that it is possible to obtain a black coloured silver compound by oxidation with potassium peroxydisulfate, ozone or some other strongly oxidizing materials *e. g.* bismuth dioxide, fluorine and others.

The analyses of compounds so prepared even in the case of a substance obtained with the same procedure resulted in the most various formulas. The cause of this fact apparently is that there was not paid sufficient attention to the experimental conditions which may influence the composition of the compounds concerned. The disagreement in analytical data explains that most of the handbooks of inorganic chemistry give data on the higher oxidation states of silver with an attitude of reserve. In some books we can find not a single

reference about them and in others we can read only about the properties of silver(II) compound (*e. g.* RIESENFELD, NJEKRASOW, MACHU, SIDGWICK, *Mellors' Modern Inorganic Chemistry*).

In the present paper we are dealing with the properties and analysis of oxide compound from the reaction silver and peroxydisulfate ions. Besides we give a short communication on the higher silver oxide prepared by the reaction between silver(I), ozone and formic acid, respectively.

Data on the behaviour and composition of the black coloured compound obtained from the reaction between silver and peroxydisulfate ions are given up to 1925 in the papers of H. MARSCHALL and others (see references in F. JIRSA's report, *loc. cit.*).

Later M. YOST [5] has carried out investigations with similar purposes and found that independently from the concentration ratio of silver and peroxydisulfate,  $\text{Ag}_2\text{O}_3$  or basic sulfate of trivalent silver:  $\text{Ag}_2\text{O}_3 \cdot \text{Ag}_2(\text{SO}_4)_3$  are formed. Soon after this  $3\text{Ag}_2\text{O}_3 \cdot \text{AgNO}_3$  was formulated by BARBIER [6] and  $\text{Ag}_2\text{O}_2$  by PINKUS [7]. K. KIMURA and Y. MURAKAMI [8] reporting the analytical application of silver oxide prepared by peroxydisulfate assume that in the first stage of reaction silver peroxydisulfate is formed, the hydrolysis of which results in  $\text{Ag}_2\text{O}_2$ .

### *Results and discussion*

#### *The reaction between silver nitrate and peroxydisulfate*

At first it was investigated how the composition of the oxidation product is influenced by the way of preparation. We found that the oxidizing power of silver compound greatly depends on the ratio of the reactants. Further it was found that in a neutral medium the reaction takes place in few hours therefore a favourable concentration of hydrogen ions was chosen.

#### *The preparation of silver(x) oxide by mixing silver nitrate and peroxydisulfate at a mole ratio of 2:1*

On mixing the diluted solution ( $M/10$  and  $M/20$  resp.) of silver nitrate and peroxydisulfate at pH 3 the solution soon turned to brown colour and a greyish black product separated. The mixture was vigorously stirred for 20—25 minutes till the formation of the solid product visibly ceased. Then the solution containing the precipitate was centrifuged. After manifold washing with water the substance was dried in desiccator over calcium chloride and phosphorus pentoxide, resp. and was kept in darkness.

If the mixture of silver nitrate and peroxydisulfate solutions was allowed to stand on the precipitate more than half an hour, strong evolution of oxygen was observed. Similar gas evolution appeared when the washing was not carried out with sufficient quickness.

Testing the brown greyish solution it was found that it oxidizes momentarily the chloride, bromide and iodide ions into chlorine, bromine and iodine and it turns chromic ions into chromate and manganous ions into permanganate. Pouring this solution into ammonium hydroxide the ammonia smell disappears with vigorous gas evolution *i. e.* ammonia is oxidized into nitrogen.

Concerning the behaviour of the solid material mention may be done that its colour does not change during few weeks. Keeping it in desiccator the greyish tint fully disappears within a few months and we got a loose soot-like velvety black dust. The material dissolves in concentrated mineral acids with a violent gas evolution.

The test of the precipitate with titanous sulfate to hydrogen peroxide was negative. Similarly no formation of peroxochromic acid was observed. The solution of potassium permanganate is not decolorized by silver(x) oxide. The substance reacts with hydrogen peroxide with effervescence; it does not give peroxydisulfate reaction with Zwicker-reagent and oxidizes the oxalic acid to carbon dioxide immediately.

The reactions above prove that the solid substance obtained is neither peroxydisulfate nor peroxide so the high oxidizing power can be attributed to silver ions of higher valency. To prove this the total silver and oxygen content of the compound, the oxidizing power and the quantity of other ions present were analyzed, too. From this we hoped to make deductions on the ratio of silver ions in I, II and III valency states which may be present in the compound.

The total silver content was measured gravimetrically. About 0,1 g of the dry and carefully homogenized substance was dissolved in diluted nitric acid. After manifold treating with nitric acid the silver transferred to silver nitrate and from this silver chloride was precipitated with diluted hydrochloric acid. Results are summarized in Table I.

Table I  
Determination of total silver content

Taken g	Found Ag g	Ag content %
0,1106	0,0849	76,79
0,1010	0,0776	76,90
0,1056	0,0813	76,98
0,1003	0,0770	76,80
0,1009	0,0776	76,93

average value: 76,90 %

The filtrate obtained after the precipitation of the silver ions was evaporated. The dry residue was dissolved in water and detected whether it contains other anions besides chloride. The solution gave with barium nitrate a sulfate reaction. Then the quantitative determination of sulfate content was carried out gravimetrically. The determination resulted in 11,44% of  $\text{SO}_4$  content.

To clear up whether the compound contains other ions, perchloric acid was applied in the solvent. In the solution obtained after the precipitation of  $\text{Ag}^+$  with hydrochloric acid  $\text{NO}_3^-$  and  $\text{K}^+$  ions were detected as impurities (0,2—0,5 mg  $\text{NO}_3^-$  and  $\text{K}^+$  in 1 g solid material).

To determine the oxygen content the compound was reduced with hydrogen gas. About 20–25 mg solid material was measured into porcelain boat and heated in hydrogen current in a tube. The end-temperature was about 450°C. The water formed by the reduction was absorbed with phosphorus pentoxide. The amount of oxygen was estimated from the increase of weight. During the reduction the oxygen of the sulfate was reduced, too. After heating pure silver remained in the boat. The reduction of silver sulfate carried out under similar condition resulted in pure silver similarly. The result of the determination was in average 18,92% oxygen.

To determine the oxidizing capacity of the compound oxalic acid was found to be the most suitable. The mean value of the oxidizing capacity was equivalent to 9,70 ml 0,1 potassium permanganate (in 0,1 g silver(x) oxide).

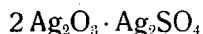
Some of our data are shown in Table II.

To evaluate our analytical data a comparative table was made in which the silver, oxygen and sulfate content and oxidation capacity of the different compounds were given.

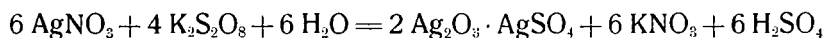
Table II

Taken g	Total Ag %	Oxidizing capacity ml	Sulphate content %	Total O %
0,1000	76,79	9,65	11,93	19,06
0,1000	76,90	9,81	11,80	—
0,1000	76,98	9,70	11,99	18,91
0,1000	76,80	9,66	11,90	—
0,1000	76,93	9,70	11,92	18,80
average value :	76,90	9,70	11,91	18,92

On comparing data of Table III with results of analyses given in Table II it seems to be very probable that the composition of the compound investigated is



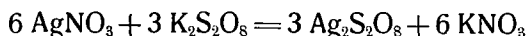
We can write the following overall equation for the formation of this compound :



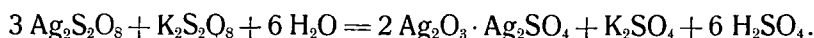
According to this equation 6 molecules of sulfuric acid are formed. Thus to settle the correctness of this equation we measured the change of the concentration of hydrogen ion during the reaction. To this end the neutral solutions of silver nitrate and peroxydisulfate were mixed and with a glass electrode the pH of the solution was measured. It was found that the pH of the solution decreased rapidly from the initial value of 6,8 and after 10 minutes 2,23 pH was measured. Then the silver oxide formed was collected on a filter and its oxidation capacity determined. From this data it was computed that according to the equation above what amount of sulfuric acid was to be formed. The calculation resulted in  $1,4 \cdot 10^{-2}$  M sulfuric acid concentration.

Considering the mean activity coefficient of sulfuric acid of 0,02 M ( $f=0,453$ ), 2,35 pH was computed. The value thus obtained is in a good agreement with the measured 2,23 pH.

Supposing that the reaction takes place through formation of silver peroxydisulfate



what on the effect of water and further peroxydisulfate turns



This way of reaction seemed to be proper because it gives explanation of our observation that in the presence of less quantity of peroxydisulfate a product of lower oxidizing capacity is formed.

Table III

Table for comparison of the composition of various higher silver oxide compounds

Supposed formule	Total Ag	Oxidizing* capacity ml	Sulphate content %/o	Total O %/o
2 Ag <sub>2</sub> O <sub>3</sub> Ag <sub>2</sub> SO <sub>4</sub>	72,12	9,55	11,44	19,06
Ag <sub>2</sub> O <sub>3</sub> · 2 AgO · Ag <sub>2</sub> SO <sub>4</sub>	78,62	7,29	11,67	17,49
4 AgO · Ag <sub>2</sub> SO <sub>4</sub>	80,18	4,95	11,90	15,85
(AgO) <sub>2</sub> SO <sub>4</sub> · 6 AgO	79,39	9,20	8,84	17,66
3 Ag <sub>2</sub> O <sub>2</sub> · AgNO <sub>3</sub>	82,69	6,57	—	—
Ag <sub>2</sub> O <sub>3</sub> · Ag <sub>2</sub> SO <sub>4</sub>	74,98	6,95	16,69	19,46
2 AgO · Ag <sub>2</sub> SO <sub>4</sub>	77,12	3,57	17,17	17,15
Ag <sub>2</sub> O <sub>3</sub> · 2 AgO · AgSO <sub>4</sub>	75,39	8,34	13,42	20,12
2 Ag <sub>2</sub> O <sub>3</sub> · AgSO <sub>4</sub>	73,74	12,30	13,14	21,87

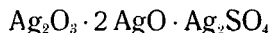
\* Related to 0,1 g of material

NB. In total O %/o the oxygen content of anions is taken into consideration, too.

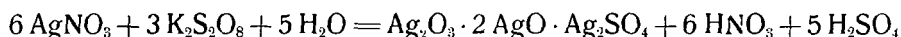
The possibility of the presence of trivalent silver in the compound is supported by the following experience, too. It had been supposed that silver(III) oxide compound obtained by peroxydisulfate is not stable and on having boiled with water decomposes to silver(II) oxide. As it had been expected, on heating the compound with water considerable decrease in the oxidizing capacity was found. The oxidizing capacity of 0,1 g substance boiled in 10—15 ml water for 4—5 minutes was equal to 4,64 ml. Supposing that all silver(III) was decomposed into silver(II) oxide the calculation resulted in 4,67 ml. During a longer standing the 2Ag<sub>2</sub>O<sub>3</sub> · Ag<sub>2</sub>SO<sub>4</sub> compound also decomposes. In the course of the decomposition a composition of



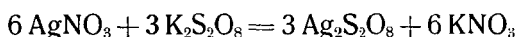
could be obtained. We succeeded in obtaining such a composition using less peroxydisulfate. When 0,1 *M* silver nitrate reacts with 0,025 *M* peroxydisulfate at pH 3 also a solid greyish black material is formed. The substance obtained was analyzed again and we received the results summarized in Table IV. On comparing these results with data in Table III the best agreement was found with the composition



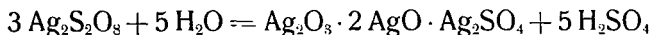
The formation of this compound may take place through the following reactions :



or supposing silver peroxydisulfate as intermediate:



which hydrolyzes :



The oxidizing capacity of this substance after boiling was found 5,06 ml of 0,1 *N* potassium permanganate. Comparing this datum with the calculated one, 4,86 ml, we can say that most of  $\text{Ag}_2\text{O}_3$  present was decomposed into AgO. The obtained silver(II) oxide had yet a very strong oxidizing power *e. g.* it oxidizes manganous ion to permanganate rapidly. The compound of  $\text{Ag}_2\text{O}_3 \cdot 2 \text{AgO} \cdot \text{Ag}_2\text{SO}_4$  composition was kept in desiccator and after 2—3 months its oxidizing capacity determined. The measured data were in good agreement with the composition of  $4 \text{AgO} \cdot \text{Ag}_2\text{SO}_4$ . Thus during this time the silver(III) oxide decomposed quantitatively into silver(II) oxide meanwhile the substance became loose and of velvety black colour.

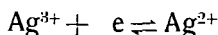
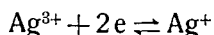
Table IV  
Summary of the average values of analytical data

Taken g	Total Ag %	Oxidizing capacity ml	Sulphate content %	Oxygen %
0,1000	78,45	7,40	11,91	17,40

To these previous results also a supplementary observation must be mentioned. During the preparation it had been experienced in every case that the amount of silver(x) oxide was nearly constant. On centrifuging the precipitate a water-pure solution had been obtained which after a short time became brownish and precipitate was formed again. Changing the mole ratios of reactants the quantity of the oxide obtained changed, too. The fact that the amount of oxide compound formed is always less than that of which may be formed from the reagents present can be attributed to the potential equilibrium of the solution.

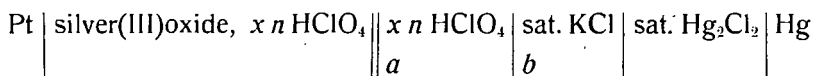
*Oxidation potentials of di- and trivalent silver compounds*

In order to give a sufficient explanation of the phenomena that in the course of the reaction between silver nitrate and peroxydisulfate always a definite quantity of silver(x) oxide is formed — namely less than may be expected on the basis of the amount of reactant present — we tried to estimate the oxidation potentials:



First the dependence of the potential of the system was measured on the hydrogen ion concentration of the solution. In connection with this it was found that the oxidation potential does not change practically in 0,6—3,0 M perchloric acid solution and independently from the amount of  $2 \text{Ag}_2\text{O}_3 \cdot \text{Ag}_2\text{SO}_4$ , in every case 1,561 V vs. S. C. E. was measured. The circumstance that the measured potential was independent from the taken amount of higher silver oxide (0,020—0,1000 g) shows that the solid material does not play any role in the potential controlling processes.

To estimate the standard oxidation potentials 50—100 mg silver(III) oxide was added to perchloric acid and the equilibrium potential of the following cells was recorded:



The setting in of the potential needs in most of the cases 10—15 minutes. The electrolyte contact between the half cells was made at place *a* with a sintered glass bridge of porosity G5, filled with *x N* HClO<sub>4</sub> and at place *b* with agar-agar gels in saturated Ba(ClO<sub>4</sub>)<sub>2</sub>.

After reading the equilibrium potential the solution was filtered on a sintered glass and the potential of the pure solution measured anew. No considerable difference between the potentials was found.

To estimate the oxidation potential one needs to determine the concentration of silver(I) and silver(III) ions. Since the determination of such a small silver(I) amount furnishes erroneous data, silver nitrate of great quantity was added to the solution.

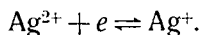
Being the amount of silver nitrate added more than hundredfolds of the concentration of silver(I) ions originally present the latter quantity may be left out of consideration. On the effect of addition of silver nitrate the potential decreased in a small extent and this decreased value was taken as a basis for the calculations.

In order to determine the amount of silver(III) oxide, oxalic acid was pipetted into the solution the excess of which was back-titrated with potassium permanganate.

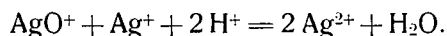
Substituting the data obtained into the well known Peters' equation

$$E = E_0 + \frac{0,0591}{n} \log \frac{[\text{Ag (higher)}]}{[\text{Ag}^+]}$$

we received 1,92 V value for the standard oxidation potential vs.  $N H_2$  electrode. This value is in a good agreement with 1,914 V, determined by NOYES and KOSSIAKOFF [9] for the system



Therefore we must suppose that under experimental condition applied the trivalent silver ions are reduced by silver(I):



From this follows that the original purpose *i. e.* to determine the standard potential of  $Ag(III)/Ag(II)$  and  $Ag(III)/Ag(I)$ , resp. in the presence of silver(I) ions is not possible.

#### *Preparation of higher silver oxide with ozone*

The higher valency state of silver may be obtained easily with ozone. Bubbling ozone into acidified solution of silver nitrate greyish black dust-like substance forms which is very similar to that of obtained with peroxydisulfate. The progress and velocity of the oxidation depend on the concentration of ozone, silver and hydrogen ions.

It had been also observed that there did not form more than a definite quantity of higher silver oxide in spite of bubbling forth ozone through the silver nitrate solution. Removing the precipitate the reaction between silver nitrate and ozone starts anew. This shows that the product formed gets into equilibrium with the oxidizing agent.

Since the properties of the substance formed by ozone were similar to higher silver oxide prepared by peroxydisulfate we disregard to give back these reactions in detail.

The product obtained with ozone was analysed and the total silver content was 79,90%. The oxidizing capacity was equal to 8,57 ml 0,1 potassium permanganate. These data prove a composition



(The calculated total silver content is 80,37%, the oxidizing capacity 8,69 ml.)

To decide the correctness of the ratio of silver(II) oxide thermal decomposition was applied. After boiling the oxidizing capacity was determined. It was found to be 6,62 ml while the calculated datum 6,45 ml.

#### *Preparation of higher silver oxide with formic acid*

On treating a freshly prepared silver(I) oxide with diluted formic acid visible change takes place: the brownish compound turns into black dust-like substance. The colour of the compound depends on the amount of the oxide added and on the time of shaking. After a longer shaking whitish grey metal silver was formed.



To prepare a higher silver oxide, 10 g silver(I) oxide was shaken with 60–70 ml formic acid of 2% for a few minutes and the product obtained centrifuged and dried in desiccator.

The substance thus obtained oxidizes mangan(II) and cerium(III) ions in acidic medium into permanganate and cerium(IV) ions. Ammonia is transformed into nitrogen. Iodides and bromides are oxidized into iodine and bromine but the oxidation of chloride cannot be observed. With titanium(IV) sulphate it does not give peroxide reaction. With hydrogen peroxide it reacts with vigorous gas evolving.

It had been also investigated whether the oxygen had any role besides formic acid in the formation of this compound. To this end silver(I) oxide was made react with formic acid in oxygen, nitrogen and carbon dioxide atmosphere. In all the three vessels a greyish-black substance was formed. The most black coloured substance was obtained in oxygen atmosphere but in presence of nitrogen and carbon dioxide the product also had the mentioned oxidizing properties. Thus for the formation of the oxidizing power of the compound formic acid is of first importance.

The analytical data of the compound prepared with formic acid do not permit to decide whether Ag(II) or Ag(III) are there present.

\* \* \*

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