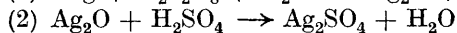
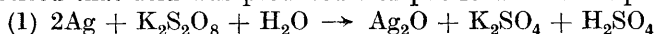


CCXXXVI.—*The Reaction between Persulphates and Silver.*

By GEOFFREY ISHERWOOD HIGSON.

THE action of solutions of persulphates on metallic silver was first noticed by Marshall (*J. Soc. Chem. Ind.*, 1897, **16**, 396), who found that the silver gradually went into solution and that at the same time a black deposit was formed, which he considered was a peroxide, AgO. The reaction was further investigated by Levi, Migliorini, and Ercolini (*Gazzetta*, 1908, **38**, i, 583), who noticed that acid was produced and put forward the equations :



as representing the course of the reaction. The solution might thus remain neutral or become acid, according to the relative velocities of the reactions (1) and (2). By the action of persulphates upon silver nitrate solution, Marshall (*Proc. Roy. Soc. Edin.*, 1900, **23**, 168) obtained a similar black precipitate, which he considered was the same peroxide, but Austin (T., 1911, **99**, 262) concluded, on account of its high sulphate content, that it was a mixture of silver peroxide and silver persulphate, whilst Tarugi (*Gazzetta*,

1902, **32**, ii, 383) considered it to be the silver salt of Caro's acid, namely, Ag_2SO_5 .

There is some doubt as to the composition of silver peroxides, which are usually obtained, mixed or combined with salts, as anodic deposits in the electrolysis of solutions of silver salts in a divided cell. For example, by the use of silver nitrate solution a black, crystalline powder of metallic appearance is obtained (Ritter, *Gehlen's neues J.*, 1804, **3**, 561), which, on washing, immediately commences losing oxygen, silver nitrate being set free and passing into solution. The undecomposed crystals have the empirical formula $\text{Ag}_7\text{O}_{11}\text{N}$ (Sulc, *Zeitsch. anorg. Chem.*, 1896, **12**, 89; Tanatar, *ibid.*, 1901, **28**, 331) and later work has shown that they are very probably a double compound corresponding with the formula $\text{AgNO}_3 \cdot 2\text{Ag}_3\text{O}_4$ (Babarovský and Kužma, *Zeitsch. physikal. Chem.*, 1909, **67**, 48; Brown, *J. Physical Chem.*, 1916, **20**, 680). Since oxygen is lost during the washing, the original peroxide may, however, contain a higher proportion of oxygen; on the other hand, from the anodic decomposition curves of both nitrate and sulphate solutions, Bose (*Zeitsch. anorg. Chem.*, 1905, **44**, 237) concluded that the oxide was Ag_2O_2 .

In opposition to the view that these substances are double compounds of a peroxide of silver and ordinary silver salt—the peroxides are never obtained pure by this method—Watson (T., 1906, **89**, 578) concluded that the black silver deposit $\text{Ag}_7\text{O}_{11}\text{N}$ was a "peroxynitrate," that is, a definite compound, since he obtained it under varying conditions. He found that, on boiling, the dioxide, Ag_2O_2 , was formed, and he described the properties of this and verified its composition.

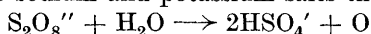
In the course of some experiments on the action of persulphates on the photographic negative, it was necessary to investigate the action of persulphate on silver, both in the metallic and the ionic form, and it has been found that sodium or potassium persulphate solution converts metallic silver into a peroxide containing a greater proportion of oxygen than corresponds with the formula Ag_2O_2 , whilst the acidity of the solution at the same time increases. When a strong (20 per cent.) solution of the sodium salt is used, the peroxide can rapidly be obtained in quantity, but owing to the much smaller solubility of the potassium salt the reaction with this is much slower (for example, eighteen hours) and the yield much lower, for the peroxide is unstable and decomposes continuously from the time of its formation. With the ammonium salt, no peroxide is formed, but the ammonium radicle is oxidised to nitric acid (compare Marshall and Ingliss, *Proc. Roy. Soc. Edin.*, 1902, **24**, 88). When the reaction is continued for more than about

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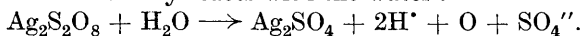
one hour, the product is contaminated with sulphate, which is always present to a slight extent.

It has been found that the same peroxide is produced when persulphates react with silver nitrate, again with increase in acidity, but in this case the contamination with silver sulphate is greater.

An explanation of this contamination has been found in the catalytic decomposition of persulphates by silver ions, previously noticed by Marshall in the case of the ammonium salt, whereby in the case of the sodium and potassium salts the reaction



is immensely accelerated. The HSO_4' ions thus formed react continuously with silver ions, and as these are present in much greater quantity when silver nitrate is used, the amount of silver sulphate formed is consequently greater in this case. Moreover, the catalytic effect increases with increase of concentration of the silver ions, and this again tends to produce more contamination when silver nitrate is used in the preparation. A possible explanation of this catalytic effect is the intermediate formation of silver persulphate, which then immediately reacts with the water :



As might be expected, it has been found that the presence of an oxidisable substance, such as gelatin, prevents the formation of peroxide, whilst it is itself oxidised; but it does not prevent the catalytic decomposition of the persulphate, with formation of acid sulphate. The application of this result to the action of persulphate as a photographic reducer is obvious, and will be discussed in another place.

EXPERIMENTAL.

Preparation of the Peroxide from Sodium Persulphate.

Metallic silver was obtained in the finely divided, crystalline form by precipitation from silver nitrate with metallic magnesium (compare Dodgson, *Phot. Jour.*, 1911, **51**, 265). The excess of magnesium was removed with dilute sulphuric acid, and the silver, which was of a grey colour, and in the form of crystals about 0.001 mm. in length, thoroughly washed by decantation. About 3 grams of this were introduced, wet, into a solution in 100 c.c. of water of 20 grams of sodium persulphate. This was the purest commercial product, but was considerably contaminated with acid sulphate, due to decomposition. It was not purified—a difficult matter—since acid sulphate is rapidly formed again during the reaction. The mixture was then stirred mechanically. It almost immediately darkened and after half an hour the grey silver

appeared to have been converted into a black powder, whilst at the same time the acidity of the mixture increased. It was found that the solid consisted of a peroxide, with a considerable amount of unconverted silver, which usually persisted after the reaction had continued for an hour or more. Since the sulphate content rises with increase of time of reaction, the product, when free from silver, was contaminated with silver sulphate. It was washed with dilute sulphuric acid and water, and obtained as a black, metallic-looking powder, which, after drying on a porous tile over calcium chloride, lost its metallic appearance and finally resembled manganese dioxide. It decomposed continuously from the time of its formation, whether wet or dry, losing oxygen and becoming alkaline owing to the formation of silver oxide.

The substance thus obtained exhibits all the properties of the dioxide described by Watson; for example, it gives deeply coloured solutions with concentrated nitric acid or concentrated sulphuric acid, which decompose with loss of colour, gradually at the ordinary temperature, and rapidly on heating. It is, as might be expected, a strong oxidising agent; for example, it liberates iodine from acidified potassium iodide and converts quinol in acid solution into *p*-benzoquinone.

The same procedure was carried out in 5 per cent. gelatin solution. No peroxide was formed, although the silver gradually dissolved and the solution became strongly acid.

Analysis of the Product.

From numerous analyses it became evident that the more rapidly the product was removed from the filter and analysed, the higher was the percentage of the available oxygen. Since a period of a few minutes is sufficient substantially to alter the amount of oxygen, it seems that the analyses by Austin and by Watson (*loc. cit.*) of the dried products are of doubtful value.

To ascertain, if possible, towards what limit this available oxygen tended, experiments were made in which the washing of the product was carried out with ice-cold acid and water, in order to retard the decomposition. No evolution of gas was apparent under these conditions, but the procedure does not avoid decomposition during the formation of the peroxide, which cannot conveniently be carried out at 0° owing to the slowness of reaction at this temperature.

The analyses were made according to the method of Babarovský and Kužma (*loc. cit.*), the product being thrown wet into a known quantity of *N*/10-oxalic acid and an excess of 2*N*-sulphuric acid, and rapidly stirred to promote reaction with the oxalic acid, which

was oxidised to carbon dioxide. Solution was completed by heating to boiling and the excess of oxalic acid estimated by titration with permanganate. The slight excess of this was then removed by oxalic acid, and after cooling, the silver estimated by Volhard's thiocyanate method.

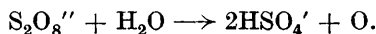
Results of Analyses.—The ratio is that of atoms of total oxygen to atoms of silver, that is, it would be 1 for Ag_2O_2 , and 1.33 for Ag_3O_4 .

Preparation.	Time of keeping. (days).	Conditions.	Ratio.
No. 62	6	Exposed to air.	0.777
	"	Kept over CaCl_2 .	0.735
	11	" " "	0.718
No. 63	0	Taken wet from the filter.	1.047
	"	" " "	1.044
	"	" " "	1.033
	1	Kept over CaCl_2 .	0.965
No. 66	0	Washed at 0° and taken wet from the filter.	1.245
			1.251
			1.185
No. 70	"	" " "	1.29
			1.29

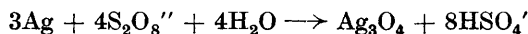
These results show that the undecomposed peroxide contains more oxygen than corresponds with the formula Ag_2O_2 , but on no occasion was quite sufficient oxygen obtained to justify the formula Ag_3O_4 .

Mechanism of the Reaction.

The explanation of Levi, Migliorini, and Ercolini, that the increase of acidity is due to the formation of sulphuric acid and undissolved silver oxide simultaneously, is obviously unsatisfactory; the acidity must arise from the decomposition of water during the reaction, the oxygen going to form the silver peroxide, while the hydrogen gives acid sulphate :



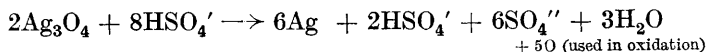
It should therefore be possible to trace the course of the reaction by determining the ratio between the increase of acidity and the quantity of silver converted into peroxide. Unfortunately, oxygen is invariably evolved during the reaction, either from actual decomposition of peroxide already formed, or directly from the reaction between the persulphate and water, this reaction being, as will be shown below, catalysed by silver ions, and this method is useless. If the peroxide has the formula Ag_3O_4 , the reaction must be of the form



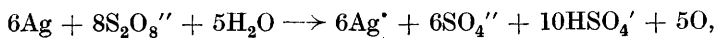
and the increase of acidity is considerable in comparison with the silver dissolved.

When an oxidisable substance is present, the peroxide apparently reacts with this at once, for the silver goes into solution without any production of black peroxide, as may easily be demonstrated by mixing the persulphate solution with a gelatin solution containing colloidal silver.

This requires a reaction of the form



and therefore the complete reaction for the solution of silver in persulphate when an oxidisable substance is present must be of the form



a reaction considerably more complex than any that has been previously proposed, and further complicated by the fact that the persulphate ion alone may react directly with the water.

Preparation of the Peroxide from Silver Nitrate.

Sodium persulphate, although invariably contaminated with acid sulphate, gave much better results than the slightly soluble potassium salt used by Austin, since the more dilute solutions favoured decomposition.

Ten grams of silver nitrate dissolved in 10 c.c. of water, and 8 grams of sodium persulphate in 60 c.c. of water, were cooled to 0° , and the solutions rapidly mixed, the mixture being kept cold in ice. There was an immediate, grey precipitate formed, which was collected at once in a Gooch crucible, and on analysis was found to consist of almost pure silver sulphate containing only a slight trace of available oxygen. The filtrate, on keeping at 0° , commenced to throw down a black precipitate in less than five minutes; after fifteen minutes the precipitation appeared to be complete, and the product was collected, washed with ice-cold water, and analysed immediately. It was found to contain a large percentage of sulphate, but otherwise exhibited all the reactions of the peroxide, and appeared to be a mixture of silver peroxide and silver sulphate.

Analysis of the Product.

The analysis was carried out on two separate portions. In one portion the ratio of available oxygen to silver was obtained as described above, and in the other portion the ratio of sulphate to

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silver was determined by decomposing the product with hydrochloric acid, removing the silver as chloride, and estimating the sulphate in the filtrate as barium sulphate. From these two ratios it is possible to calculate the value of x when the formula is expressed as $\text{Ag}_2\text{SO}_4(\text{AgO}_x)_n$, that is, the formula of the admixed peroxide.

Preparation No. 79.—The peroxide-sulphate mixture was prepared at 0° as described above, and washed four times with water at 0° . Two determinations were made of the ratio of available oxygen to silver, the mean being taken, and one of sulphate to silver. Formula calculated: $\text{Ag}_2\text{SO}_4(\text{AgO}_{1.295})_{1.654}$, that is, the product is a mixture of 1 part of silver sulphate with 1.654 parts of a peroxide containing slightly less oxygen than corresponds with the formula Ag_3O_4 .

A similar determination of another preparation gave the result $\text{Ag}_2\text{SO}_4(\text{AgO}_{1.287})_{1.59}$, and there seems to be little doubt that the precipitate is a mixture of peroxide and sulphate.

Catalysis by Silver Ions of the Decomposition of Persulphates.

From experiments with mixtures of solutions of silver nitrate and of neutral sodium or potassium persulphate it was found that the acidity increased continuously from the time of mixing. It was therefore obvious that the decomposition of persulphates in solution, namely, $\text{S}_2\text{O}_8'' + \text{H}_2\text{O} \rightarrow 2\text{HSO}_4' + \text{O}$, is catalysed by the silver ions, since this decomposition takes place only very slowly at the ordinary temperature with neutral solutions (Green and Masson, T., 1910, **97**, 2083). The extent of this catalysis was determined for potassium persulphate, which is the most convenient salt to obtain pure.

A $N/20$ -solution of potassium persulphate, with additions of silver nitrate, was maintained at 18° and estimations made of the acidity of portions removed at known intervals after the addition of the silver. To render the acidimetry possible without formation of silver oxide, the solution to be tested was run into an amount of sodium chloride solution rather greater than that necessary to convert all the silver into silver chloride.

Since the reaction can be only approximately monomolecular owing to the side reaction with the silver, the values of $\frac{1}{t} \log_e \frac{a}{a-x} = k$, the velocity constant, were found to be somewhat irregular, but when the formula $k = \frac{1}{t-t_1} \log_e \frac{a-x_1}{a-x}$ was employed, where t_1 was about five minutes, the constancy was reason-

ably good, errors due to the side reaction being eliminated, as the following results for $N/250$ -concentration of silver nitrate indicate. Temperature 18° ; a , the original concentration of persulphate expressed as c.c. of standard alkali, is 24.25.

t in mins.	x =c.c. of alkali required for neutralisation.	$k = \frac{1}{t-6} \log \frac{a-0.2}{a-x}$.
2	0.05	—
6	0.2	—
11	0.3	0.0008
30	0.8	0.0010
60	1.3	0.00086
90	1.7	0.00077
150	2.4	0.00066
195	3.05	0.00067
		Mean 0.00079

The results of this and similar experiments are as follows :
Temperature 18° . Concentration of potassium persulphate = $N/20$.
 c = concentration of silver nitrate.

c .	k .	k/c .
$N/250$	0.00079	0.20
$N/100$	0.0021	0.21
$N/50$	0.00375	0.19

These results show that the catalysed decomposition of the persulphate is an approximately monomolecular reaction, and that the velocity of decomposition is approximately proportional to the concentration of the silver ion.

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