XXXI.—*The Interaction of Silver Nitrate and Potassium Persulphate and its Catalytic Effect in the Oxidation of Organic Substances.*

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When aqueous solutions of silver nitrate and potassium persulphate are mixed, a black precipitate is formed, of which no analysis has hitherto been published. This subject has already received attention by Marshall (*Proc. Roy. Soc. Edin.*, 1900, **23**, 163), and by Marshall and Inglis (*ibid.*, 1902, **24**, 88). The assumption was made that silver persulphate is first formed, and that this rapidly decomposes with water according to the equation:

$$Ag_2S_2O_8 + 2H_2O = Ag_2O_2 + 2H_2SO_4.$$

At the suggestion of Professor Inglis, I have investigated this product, and have also studied the catalytic effect produced by adding a trace of silver nitrate to aqueous solutions of potassium persulphate in the presence of organic substances. A study of the results obtained by careful analysis indicates the correctness of the above assumption, the black precipitate consisting of a mixture of silver peroxide, silver persulphate, and water, in proportions which varied somewhat, according to the conditions under which it was prepared. The appended results were all obtained from the same specimen.

In the preparation of the precipitate for analysis, various proportions were tried, the best results being obtained by using about two molecules of potassium persulphate to one of silver nitrate. Owing to the sparing solubility of potassium persulphate in water, the solutions employed were necessarily very dilute. The dilution used was also sufficient to prevent the separation of silver sulphate, the presence of which was at one time suspected.

Ten grams of silver nitrate dissolved in 100 c.c. of distilled water were added to a solution of 30 grams of potassium persulphate in a litre of water, at the ordinary temperature, in a large separating funnel, the mixture being thoroughly shaken. The formation of the black precipitate, although not immediate, quickly followed. Owing to the difficulty of filtering such a solution, since the persulphate attacks filter-paper, it was kept for about an hour, by which time the bulk of the precipitate had settled and could be drawn off. It was immediately shaken with distilled water, washed three or four times by decantation, and finally filtered and washed again. It was then spread out on a watch-glass and dried in a vacuum desiccator over sulphuric acid. The drying was found to require several days. The substance was indeed allowed to remain thus for some weeks, when it was transferred to a stoppered weighing bottle, and kept in a desiccator. Owing to its hygroscopic nature, it could not be weighed on an open watch-glass. The substance was then analysed.

Heating it in a crucible gave unsatisfactory results, since it decomposes explosively at about 110°, and although several trials were made by heating it in covered crucibles in the air-oven, there was always a loss by spirting. A qualitative examination of the residue, which was soluble in nitric acid, showed the presence of a sulphate. This might have been originally present as such or as persulphate. The residue was also tested for nitrate by dissolving in sulphuric acid and applying the ferrous sulphate test. No trace of nitrate could be found. Eventually determinations were made of silver by conversion into silver chloride; of sulphur as sulphate; of the total oxygen obtained by ignition, and of water.

To estimate the silver and sulphur, a weighed quantity was boiled with dilute hydrochloric acid until no more chlorine was evolved, and the whole of the black substance disappeared. The solution was then found to contain sulphuric acid, which was precipitated and weighed as barium sulphate after the silver chloride had been transferred to a Gooch crucible. That all the silver was thus converted to chloride was certain, since the same result was obtained by dissolving the original substance in dilute nitric acid, and then adding hydrochloric acid. The latter method was, however, unsuitable for the precipitation of barium sulphate, which then followed. Water was determined by weighing the original substance in a porcelain boat and heating it in a current of dry air in a combustion tube, which was packed at each end with ignited asbestos to prevent scattering. The water was collected and weighed in a U-tube containing sulphuric acid.

The estimation of the total oxygen expelled on heating was carried out in the following way. A weighed quantity of the substance was mixed with dry sand, and heated in a Jena-glass test-tube attached to a Toepler pump. As it decomposes explosively on heating, the test-tube was well packed with asbestos to prevent spirting. Before heating, the air was exhausted, and after heating, the total oxygen was drawn off and measured. Attempts were also made to estimate the amount of "available" oxygen by treating known quantities with potassium iodide solution and dilute sulphuric acid, and titrating the liberated iodine with sodium thiosulphate. The results obtained were, however, very variable, and therefore untrustworthy, since the available oxygen did not react quantitatively under these conditions:

0·7477 gave 0·7804 AgCl and 0·1801 $BaSO_4$. Ag = 78·57; SO_4 = 9·90.
0·4970 „ 0·5179 AgCl „ 0·1203 $BaSO_4$. Ag = 78·44; SO_4 = 9·95.
0·4452 „ 0·4682 AgCl „ 0·1067 $BaSO_4$. Ag = 79·14; SO_4 = 9·86.
0·2646 „ 0·2772 AgCl. Ag = 78·85.
0·2682 „ 0·0068 H_2O. H_2O = 2·53.
0·2080 „ 15·65 c.c. O_2 (dry) at 15·1° and 764 mm. O = 10·25.
0·2561 „ 19·27 c.c. O_2 (dry) „ 14·7° „ 770 mm. O = 10·34.

Mean: Ag = 78·75; SO_4 = 9·90; H_2O = 2·53; total oxygen expelled by heat = 10·29 per cent.

Interpretation of the Results.

It may now be considered what light these results throw upon the constitution of the substance. That it is an oxidising agent is shown by its action on dilute hydrochloric acid, from which chlorine is liberated. Hence possible constituents are an oxide of silver, together with silver persulphate or silver sulphate. Now one would expect silver sulphate to remain unchanged on heating; hence the total oxygen expelled by heat would be derived from the oxide of silver. Theoretically, 9·90 grams of SO_4 require 22·23 grams of silver for the formation of silver sulphate. Therefore we should have 56·52 grams of silver combined with 10·29 grams of oxygen; expressed in percentages, this gives Ag = 84·58; O = 15·40. Hence the atomic ratio obtained, namely, 1 : 1·228, is not a simple one.

On the other hand, if silver persulphate be present, it would lose oxygen on heating, giving silver pyrosulphate,

$$2Ag_2S_2O_8 = 2Ag_2S_2O_7 + O_2.$$

Now, 9·90 grams of SO_4 require 11·115 grams of silver to give 21·015 grams of silver persulphate, which, on heating, would lose 0·82 gram of oxygen. Hence, 78·75 − 11·12 = 67·63 parts of silver combine with 10·29 − 0·82 = 9·47 parts of oxygen; this gives Ag = 87·7 and O = 12·28 per cent., values which stand in the atomic ratio of 1·06 : 1, thus corresponding fairly well with the formula Ag_2O_2.

Evidently the latter view is the more reasonable, and accords well with the assumption made by Marshall (*loc. cit.*).

Under these conditions the results may be tabulated thus:

Ag	= 78·75	
S_2O_7	= 9·08	[$Ag_2S_2O_7$ being the final product on heating $Ag_2S_2O_8$]
H_2O	= 2·53	
Total oxygen	= 10·29	
	100·65	

We may therefore conclude that the specimen analysed contained approximately: $Ag_2S_2O_8$ = 21; Ag_2O_2 = 77; H_2O = 2·5 per cent.

Use of Silver Nitrate as a Catalytic Agent in Oxidations with Potassium Persulphate.

I. *Oxidation of Toluene.*—The catalytic effect of silver nitrate is very pronounced in this case. Two parallel experiments were made under similar conditions for the sake of comparison, using a trace of silver nitrate in one case only. In each experiment, 10 grams of potassium persulphate (3 mols.) were dissolved in 120 c.c. of slightly warm distilled water. One gram of toluene (1 mol.) was added, and in one case 5 c.c. of *N*/10-silver nitrate solution. (This quantity of water proved to be insufficient to retain all the potassium persulphate in solution on cooling.) The flasks were corked, well shaken, and allowed to remain. In the one containing silver nitrate, the liquid quickly became turbid, then yellow; soon a yellow oil separated. On the following day this was extracted with ether. On evaporation of the ether, a yellow oil was obtained, which reduced silver nitrate, giving a mirror, and had the odour of benzaldehyde. Benzoic acid was also formed and was extracted by shaking some of the ethereal solution with dilute sodium hydroxide, and acidifying. Crystals were obtained, which on recrystallisation from hot water melted at 119—120°.

In the other experiment, neither turbidity nor colour was observed, and on extracting with ether at the same time that the first was extracted, only unchanged toluene was found.

II. *Oxidation of Thymol.*

While the above experiments were in progress, a paper by Henderson and Boyd (Trans., 1910, **97**, 1659) appeared, in which it was stated that the oxidation of thymol in alkaline solution by potassium persulphate led only to tarry products, the bulk of the substance remaining unchanged, whereas hydrogen peroxide gave tetrahydroxycymene. This experiment was repeated with the persulphate, omitting the alkali and adding a trace of silver nitrate. Forty grams of potassium persulphate were dissolved in two litres of slightly warm water, and introduced into a flask with 20 grams of finely powdered thymol and 5 c.c. of *N*/10-silver nitrate. The mixture was allowed to remain for several days with frequent shakings. After a few hours, the solid turned brown. (In a parallel experiment without silver nitrate, no change was observed until after several weeks.)

After about a week the liquid was filtered off, the residue well shaken with dilute sodium hydroxide and ether, and the layers separated. The alkaline solution was acidified, and the precipitate allowed to crystallise once from ether, in which it was very soluble.

It was then recrystallised two or three times from benzene, from which it separated in needles melting at 162°. This substance is readily soluble in ether, ethyl acetate, acetone, or alcohol, but less so in benzene. Analysis and a determination of its molecular weight by the ebullioscopic method showed it to be dithymol, a substance first prepared by Dianin (*J. Russ. Phys. Chem. Soc.*, 1882, **14**, 135). (Found, C = 80·44; H = 9·23. 0·2034, in 9·6 of ether, gave E = 0·16°. M.W. = 286. Calc., C = 80·53; H = 8·72 per cent. M.W. = 298.)

The ethereal solution of the portion insoluble in alkali was evaporated. A brown solid remained, for which no crystallising medium could be found. Although insoluble in cold aqueous sodium hydroxide, it dissolved partly on prolonged heating. To ensure a better effect, it was dissolved in alcohol; sodium hydroxide was then added, and the mixture heated on the water-bath for half an hour. Steam was then blown through to expel the alcohol, and the liquid was filtered. On acidifying the filtrate, a small quantity of dithymol was obtained. The residue was again treated in a similar manner until no more substance would dissolve in alkali. The remainder was a brown, amorphous powder, which is possibly a polymerisation product.

The use of silver nitrate as a catalyst in oxidations of organic substances of various types is being further investigated.

In conclusion, I desire to express my thanks to Professor Inglis for his kind interest in the work.

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