XCI.—*The Reduction of Potassium Per-rhenate.*

By Henry Vincent Aird Briscoe, Percy Lucock Robinson, and Eric Maurice Stoddart.

Noddack (*Z. anorg. Chem.*, 1929, **181**, 1) found that the yellow oxide of rhenium, Re_2O_7, when heated in sulphur dioxide, was reduced to a blue oxide of indefinite composition, and this, when heated in hydrogen, gave a black oxide to which was ascribed the formula ReO_2. Further, on evaporating to dryness a per-rhenate solution containing hydrazine hydrochloride, he obtained a black oxide which he believed to be identical with that already mentioned. Noddack does not appear to have obtained this black substance when employing milder reducing agents; these yielded a yellow solution which when made alkaline with barium hydroxide gave a yellow precipitate believed to be barium rhenate. He concluded that the yellow solution was rhenic acid and considered this the main product of the reduction, stating that " in acid aqueous solutions this reduction," *i.e.*, to black ReO_2, " does not take place." Krauss and Steinfeld (*ibid.*, 1930, **193**, 385), however, who reduced per-rhenate in aqueous solution with various reagents, obtained this black material with several of them. They state that a yellow colour is first produced, which changes through " gelb, gelbgrün, blauviolett," the final result being the separation of a black precipitate; but they were uncertain whether this precipitate was the metal itself or an oxide.

The present communication deals with a reinvestigation of this reduction, showing that the first and light-coloured product is a colloidal suspension of the black material which it subsequently yields. This proves to be $ReO_2,2H_2O$ and can be obtained quantitatively from the per-rhenate, a reaction reminiscent of that by which $OsO_2,2H_2O$ is produced.

No evidence of the formation of rhenic acid or the precipitation of barium rhenate has been obtained.

EXPERIMENTAL.

Reduction of the Per-rhenate.—Qualitative experiments. Several reducing agents were tried, all of which gave yellow solutions.

Zinc. A solution of per-rhenate in N-hydrochloric acid, on treatment with fine zinc filings, quickly turned yellow and then threw down a black precipitate. With $0{\cdot}5N$-acid, precipitation was much slower, and after filtration, a yellow solution was obtained which when centrifuged (2500 r.p.m.) deposited the black material and became almost colourless. A little aqueous sodium phosphate added to the nearly neutralised yellow solution accelerated flocculation, and centrifuging rendered a solution so treated colourless. When 0·25N-acid was used, very little black material was deposited in the first instance, but after standing over-night the yellow colour was much reduced and a black deposit had formed.

Calcium. No reduction effects were observed in neutral per-rhenate with calcium, but acidification caused a slight yellow coloration.

Magnesium. This metal had no effect, even on boiling, until the solution was acidified, whereupon, even with acetic acid, there was an immediate blackening of the solution.

Devarda's alloy. In warm 5N-caustic soda solution there was no reduction, but with 0·5N-hydrochloric acid darkening occurred.

Hydrazine hydrate. Aqueous per-rhenate treated with this reagent went yellow after a period, the colour gradually deepened through brown to black, and subsequently a precipitate slowly separated. The phenomena were compatible with the formation of a colloidal suspension followed by its flocculation.

Contrary to the findings of Krauss and Steinfeld, who observed blackening under such conditions, faintly acid per-rhenate gave no evidence of reduction with hydrazine even after 24 hours. Possibly they either added sufficient of the reagent to render the solution alkaline, or they boiled the mixture, which causes reduction as already reported by Noddack (*loc. cit.*).

By using a large excess of hydrazine hydrate, reddish brown solutions stable enough for the cataphoresis experiments described below were obtained.

Stannous chloride. The black material was deposited immediately from acid solutions by this reagent.

The concentration of potassium per-rhenate normally employed in these experiments was 0·5%. Difference in concentration affects only the time taken by the reactions, and from none of the concentrations used have we been able to obtain the "blaüviolett" observed by Krauss and Steinfeld (*loc. cit.*).

Quantitative experiments. 0·25 G. of potassium per-rhenate was dissolved by warming in 10 c.c. of water, and about 0·3 g. of zinc was added, followed by 5N-hydrochloric acid sufficient to dissolve it. The contents of the flask were kept warm and reduction took about 45 mins., all the zinc being then dissolved, and the solution acid. The acidity was reduced by the careful addition of more zinc, as faintly acid conditions were necessary for quantitative precipitation. The solution was diluted to 25 c.c. and allowed to cool; the black precipitate then settled, leaving a clear supernatant liquor from which it was quantitatively separated by filtration on an asbestos mat in a tared Gooch crucible. The prepared crucible had been dried over phosphoric oxide in a vacuum desiccator, and the product was similarly dried and subsequently weighed (Table I). The mean ratio of the weight of the product to the potassium per-rhenate was 0·8740; whereas the calculated value for the ratio $ReO_2,2H_2O/KReO_4$ is 0·8786 if one uses Re = 186·3 (Hönigschmid, *Z. anorg. Chem.*, 1930, **191**, 309). Thus the black material was $ReO_2,2H_2O$.

This hydrate, on being heated at 250° for 12 hours in an evacuated tube connected to a drying train containing phosphoric oxide, gave the anhydrous oxide (Table I).

TABLE I.

Expt.	$KReO_4$, g.	Product, g.	Calc. for $ReO_2,2H_2O$, g.	Anhydrous product, g.	Calc. for ReO_2, g.
1	0·2946	0·2553	0·2589	0·2192	0·2191
2	0·2603	0·2280	0·2288	0·1962	0·1957
3	0·3335	0·2901	0·2931	0·2494	0·2490
4	0·2040	0·1785	0·1793	0·1539	0·1532
5	0·2295	0·2011	0·2017	0·1730	0·1726
6	0·2705	0·2375	0·2377	0·2047	0·2039
7	0·2345	0·2058	0·2061	0·1771	0·1766

The Alleged Rhenic Acid and Rhenates.—Noddack (*loc. cit.*) states that dissolution of the metal, of rhenium disulphide, or of a lower oxide in nitric acid yields rhenic acid, which is precipitated as the yellow barium salt when the solution is made alkaline with barium hydroxide. This procedure was repeated with both the metal and the disulphide, but in neither case was any yellow colour observed, and, further, when neutralised by caustic potash the solutions behaved exactly as though a per-rhenate were present. Noddack also obtained a yellow solution, believed to contain rhenic acid, by the reduction of a per-rhenate. On repeating this, using zinc in hydrochloric acid solution as the reducing agent, we obtained on addition of baryta water a white precipitate which proved to be entirely zinc hydroxide. Other reducing agents gave solutions from which no rhenate could be precipitated.

Colloidal Rhenium Dioxide.—It has been shown that the first products of reduction of a per-rhenate with zinc or hydrazine hydrate are colloidal, and that from these solutions the black hydrated dioxide may be separated by centrifuging, especially in the presence of an electrolyte. The yellowish-brown solution thus obtained was stabilised by means of gelatin and used for a cataphoresis experiment. In this way, although the colloid moved very slowly under a *P.D.* of 240 volts, its charge was shown to be positive.

If per-rhenate be reduced with zinc in fairly concentrated (5*N*) hydrochloric acid, a dark yellow solution is obtained, which, when well diluted, deposits some dioxide and leaves a brownish colloidal solution. The complete removal of acid by the addition of alkali, however, results in the deposition of dioxide. This hydrated dioxide is soluble in concentrated hydrochloric acid to a dark yellow solution, which on dilution yields a dark colloidal solution : probably the tetrachloride is first formed and is hydrolysed by water, giving the hydrated dioxide stable as a colloid only in the presence of some acid and completely precipitated from nearly neutral solution.

Summary.

The reduction of a per-rhenate yields first a yellow colloidal solution, most probably of hydrated dioxide, followed by the precipitation of $ReO_2,2H_2O$. This material can be quantitatively precipitated and may be dehydrated without decomposition.

No evidence of the formation of intermediate products has been observed.

Grateful acknowledgment is made to the Research Committee of this College for a grant for the purchase of rhenium.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE.
[*Received, February* 13*th*, 1931.]