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The Preparation of Two Lower Oxides of Rhenium

BY RALPH C. YOUNG AND JOHN W. IRVINE, JR.

The chemistry of rhenium in its lower valencies has not as yet been clarified. I. Noddack and W. Noddack[1] have described a solid containing rhenium of valence 2 and a solution, rhenium of valence 1. No analyses other than that of the valence was given. Lower oxides mixed with the hydrated dioxide or metal or both have been reported by Holemann[2a] and also by Geilmann and Hurd.[2b] Lundell and Knowles[2c] obtained in solution rhenium of valence -1 and also of $+1$ in which the element exhibited the characteristics of a halogen. In the present report a method is given for the preparation of two lower oxides of rhenium, $Re_2O \cdot 2H_2O$, and $ReO \cdot H_2O$ in yields of about 25% by the reduction of perrhenate with zinc and with cadmium in hydrochloric acid solution. The method by which these oxides are formed and their chemical and physical characteristics are in accord with what might be expected of an element between tungsten and osmium.

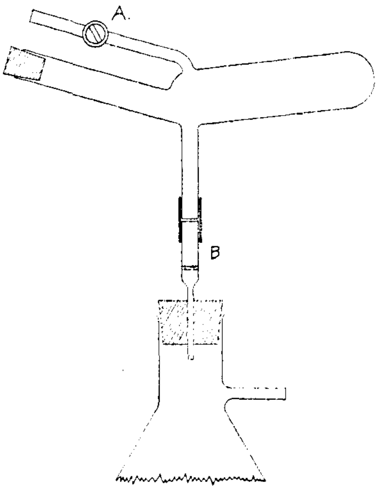

Fig. 1.

In a series of preliminary experiments on the reduction of perrhenate by zinc it was found that the more dilute the hydrochloric acid the greater was the percentage of lower oxide formed. For its preparation, therefore, a low acidity was maintained although not a constant one. The procedure is described below and the results summarized in Table I.

Perrhenic acid, 0.5 to 1.5 milliequivalents in 350 cc. of a 0.2 *N* solution of hydrochloric acid, was allowed to react with 100 milliatoms of C. P. zinc, 6 pieces of about 1 g. each cut from a rod of zinc, in an apparatus which provided for the exclusion of air. Six cc. of 12 *N* hydrochloric acid was added every twenty-four hours until effervescence ceased. The black insoluble reduction product was filtered by means of suction on a Jena fritted glass micro-filter tube connected by rubber tubing to the side arm of the reaction flask. During the filtration and subsequent washing with water the solid was kept from contact with air by carbon dioxide. The small amount of rhenium in the filtrate was found to be present as perrhenate. The micro-tube and contents were dried for twenty-four hours at room temperature in a tube connected with a high vacuum pump and the weight of the reduction product was then obtained. The solid was next placed in an apparatus, Fig. 1, with 40 cc. of 12 *N* hydrochloric acid, heated gently for two minutes and then allowed to remain twenty-four hours in contact with the reagent with occasional shaking. During the entire operation the products were protected from the air by carbon dioxide. The solution should contain rhenium of valence 4 and rhenium of valence 3 if oxides of corresponding valence had been present. Approximately 75% of the solid dissolved in the acid. The rhenium was present in the solution as a hydrogen chlororhenate. This was ascertained by filtration on the micro-filter, B, which was attached to the side-arm of the apparatus by rubber tubing, and by the subsequent determination of the valence of any soluble rhenium compounds by the method of Geilmann and Wrigge.[3] During the filtration and subsequent washing with concentrated hydrochloric acid the solution and solid were protected from the air by carbon dioxide entering the apparatus at A. The rhenium content of the solution was finally obtained by precipitation of Re_2S_7, oxidation of this sulfide by an alkaline solution of hydrogen peroxide, and by precipitation of perrhenic acid as a nitron derivative, according to the procedure of Geilmann and Weibke.[4]

In a separate experiment it was found that no hydrogen was evolved by the treatment with hydrochloric acid. Carbon dioxide was directed over the acid and into a eudiometer tube containing a 25% solution of potassium hydroxide. No insoluble gaseous product was noted.

The micro-tube and contents were dried by the method described previously and the weight of the black product obtained. It was soluble in nitric acid and in bromine water, but not readily attacked by dilute alkaline chromate nor acid ferric sulfate. To determine the percentage of rhenium a weighed sample was converted to perrhenate by heating with excess bromine in a solution containing

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[1] I. Noddack and W. Noddack, *Z. anorg. allgem. chem.*, **215**, 129 (1933).

[2] (a) Holemann, *ibid.*, **211**, 195 (1933); (b) Geilmann and Hurd, *ibid.*, **214**, 260 (1933); (c) Lundell and Knowles, *J. Research Nat. Bur. Standards*, **18**, No. 5, 629 (1937).

[3] Geilmann and Wrigge, *Z. anorg. allgem. Chem.*, **222**, 56 (1935).

[4] Geilmann and Weibke, *ibid.*, **195**, 289 (1930).

sodium bromide slightly more than equivalent to the perrhenate. After the oxidation, the bromide and bromate were decomposed by the usual method and the rhenium content of the solution was then determined accurately with nitron. The excess nitron was removed from the solution by nitric acid and tests were made for zinc by precipitation as $ZnNH_4PO_4$. It was found present to the extent of less than 0.2%. Separate samples were analyzed for chlorine. Less than 1% of the halogen was found. The X-ray diffraction photograph[5] gave the pattern of a typical amorphous material and conclusions could not be drawn as to the presence or absence of rhenium metal. Rhenium sesquioxide was eliminated as a possible constituent as on heating a sample with a solution of 50% sodium hydroxide no hydrogen was evolved and in fact no change at all was apparent. According to Geilmann and Wrigge,[6] hydrogen is evolved when the sesquioxide is subjected to these conditions.

TABLE I

REDUCTION OF PERRHENATE BY CADMIUM AND ZINC IN SOLUTIONS OF HYDROCHLORIC ACID OF LOW CONCENTRATION

				Solid reduction product			
				Part sol. in 12 *N* HCl		Part insol. in 12 *N* HCl	
Reducing agent, g.	$HReO_4$ calcd. as g. of Re	Rhenium in filtrate calcd. as g. of Re	Rhenium reduced, %	Wt. of the part sol. in 12 *N* HCl, g.	Valence of rhenium in part sol. in 12 *N* HCl	Wt. of residue insol. in 12 *N* HCl, g.	% Re in residue insol. in 12 *N* HCl
Zn, 6.5	0.0940	0.0114	87.7	0.0857	4.44	0.0257	87.90
Zn, 6.5	.1880	.0080	95.7	.1776	4.03	.0527	85.95
Zn, 6.5	.2820	.0105	96.2	.2817	4.12	.0715	87.80
Zn, 6.5	.2727	.0069	97.4	.2700	4.26	.0601	86.89
Zn, 6.5	.2727	.0065	97.6			.0685	86.70
Cd, 10	.2820	.0081	97.1	.2713	4.28	.0828	85.85
Cd, 10	.2820	.0098	96.5	.2659	4.05	.0832	85.03
Cd, 10	.2820	.0099	96.4	.2683	4.27	.0632	86.12
Cd, 10	.2970	.0099	96.6			.0913	83.20

The valence of the rhenium in the residue insoluble in hydrochloric acid was obtained by measuring the oxygen absorbed when the material was heated in oxygen in a closed glass system with mercury manometer and the rhenium was oxidized to the heptavalent state. In a preliminary experiment 1 milliatom of rhenium metal was found to absorb 3.51 milliatoms of oxygen. The oxide formed was dissolved in water and the rhenium determined by titration of the perrhenic acid by standard alkali and by precipitation of the nitron derivative of perrhenic acid. Results are given in Table II, and indicate a valence of +1 for the rhenium.

The ratio of Re:H_2O given in Table III was obtained when a sample was reduced with hydrogen at 500°. The water was collected in a tube containing anhydrous calcium chloride and the residual metal was weighed and then oxidized to perrhenate by bromine water and the rhenium obtained as the nitron derivative. From the analysis then can be derived the formula $Re_2O \cdot 2H_2O$.

TABLE II

DETERMINATIONS OF THE VALENCE OF THE RHENIUM IN THE LOWER OXIDES PRODUCED BY REDUCTION OF PERRHENATE WITH (A) ZINC AND (B) CADMIUM

	Rhenium oxide, g.	Millimols of oxygen absorbed	Rhenium found, g.	Milliatoms of oxygen absorbed per milliatom of rhenium	Valence of rhenium
A	0.0522	0.370	0.0453	3.04	0.92
	.0681	.463	.0598	2.89	1.21
	.0527	.355	.0453	2.92	1.16
B	.0612	.350	.0525	2.49	2.02
	.0487	.245	.0405	2.26	2.48
	.0931	.490	.0762	2.39	2.22

TABLE III

REDUCTION BY HYDROGEN AT 500° OF LOWER OXIDES PRODUCED BY THE USE OF (A) ZINC, (B) CADMIUM

	Sample, g.	Water collected, g.	Residue, g.	Rhenium in residue, %	Ratio Re:H_2O
A	0.0606	0.0078	0.0523	98.63	2.00:3.11
	.0532	.0070	.0478	98.95	2.00:3.06
B	.0521	.0072	.0425	96.54	1.00:1.81

Reductions of perrhenate with cadmium were carried out in a manner similar to those with zinc and the results are summarized in the several tables. The solid obtained was a mixture of the hydrated dioxide and a black inactive oxide, $ReO \cdot H_2O$. The latter was obtained in larger yields than was the oxide formed by reductions with zinc, and it was also found to be produced at higher concentrations of hydrochloric acid. The water which it contained is very firmly held as was shown by the following experiment. When 0.0613 g. of the oxide was heated at 100° at 0.1 mm. pressure for two hours, the loss in weight was 0.0018 g., and after being heated an additional two hours at 200° at the same pressure 0.0009 g. more was lost. Only a trace of cadmium and chlorine was found in the product. It was not affected by hydrochloric acid nor by concentrated solutions of alkali in the absence of air. Alkaline chromate and acid ferric sulfate did not readily attack it. It did dissolve in nitric acid and in bromine water, and was slowly oxidized by the oxygen of the air.

Summary

A method has been given for the formation of two lower oxides of rhenium, $Re_2O \cdot 2H_2O$, and $ReO \cdot H_2O$ and for their separation from the hydrated dioxide. Neither oxide is obtained in the

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[5] The authors wish to thank Prof. B. E. Warren and Dr. J. Morgan for their work in obtaining and interpreting the X-ray photographs.

[6] Geilmann and Wrigge, *Z. anorg. allgem. Chem.* **214**, 239 (1933).

pure state. The oxide of valence 1 was formed in the reduction of the perrhenate in dilute hydrochloric acid with zinc and that of valence 2 with cadmium. Both lower oxides are black in color, insoluble in hydrochloric acid, and not readily attacked by dilute alkaline chromate nor acid ferric sulfate, and not by concentrated solutions of alkali. They are dissolved by nitric acid and by bromine water.

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A Crystalline Boric Oxide

BY L. McCULLOCH

This paper announces the discovery by chance of a crystalline boric oxide. Until recently boric oxide has been known as a glass which has resisted efforts to cause it to crystallize.

Taylor and Cole[1] have reported a crystalline oxide made by heating boric acid below 225° in vacuum, having the form of opaque pseudomorphs of the boric acid crystals. From its X-ray pattern they judged their product to be crystalline, and from its quiet fusion they believed it to be anhydrous. They placed its melting point at 294°, and its density at 1.805.

Morey and Merwin[2] were unable to duplicate these results. They also attempted to cause boric oxide to crystallize by aid of " 'mineralizers' other than water," and concluded that "the crystallization of boric oxide is yet to be proved."

More recently, von Stackelberg, Quatram and Dressel[3] have contributed a diagram of the system B_2O_3–H_2O, and a study of the vapor phase. They found only the crystalline solids H_3BO_3 and HBO_2, and a glassy liquid of variable water content.

The attempts at preparation of a crystalline oxide were made with the intentional exclusion of water. It was not anticipated that a crystalline oxide would separate from an aqueous liquid.

This reaction was discovered while the writer was working with boric acid fused in loosely covered quart "tin cans" under atmospheric pressure and kept in an oven between 225 and 250°. Under these conditions the escape of water vapor was retarded and the liquids contained from 8 to 15% water. Occasionally the fused acids were stirred. The boric acid was not of high purity, but was of a good technical grade. It was found that the liquid did not remain clear indefinitely, but after a period of days it became clouded, then in a few hours it thickened and became pasty, and reached finally the state of a stone-like solid. Its combined water had escaped, and from its opaque whiteness the substance was considered to be finely crystalline in structure. In one experiment this reaction acquired "volcanic violence," bubbling out steam and filling the air with white fumes.

Later experiments showed that after prolonged periods of time, boric acid also in glass bottles and in Pyrex flasks would crystallize spontaneously. Impurities seem to shorten the "induction period." A boric acid of "technical" grade became crystalline in seven days, while one of "chemical purity" took fourteen days (fifty-gram samples in Pyrex bulbs at 225°). The first crystals appear as small spheroids (0.3 mm. diameter) upon the glass walls.

By the addition of "seed" from crystalline oxide previously obtained, boric acid fusions can be induced to crystallize immediately. By this method the oxide can be prepared in large quantities. The oxide so prepared is a white, stony substance, with a coarse foam-structure left by the escape of steam. It is so hard and strong that it can only with difficulty be shattered by a hammer. The hardness on the scale of minerals is about 4.

The density is 2.42, by weighing in transformer oil after removal of air in vacuum. The density of boric oxide glass is given as 1.84. This is a remarkable shrinkage in volume on crystallization.

The composition was found by the simple method of analysis given below to be essentially anhydrous boric oxide. One of the products analyzed was a solid cake (1000 g.) from a loosely covered "tin can" of "seeded" boric acid which had been held at 250° for three days. A fragment of this weighing 16.22 g. yielded 28.62 g. H_3BO_3; another weighing 6.48 g. yielded 11.43 g. Hence the analyses give 99.36 and 99.33% B_2O_3. There is one molecule of water to at least 50 molecules of boric oxide. Such an amount might be held in films within a mass of very minute boric oxide crystals.

The melting point is between 460 and 470° for another specimen found after fusion in a sealed glass tube to contain 99.6% B_2O_3. These crystalline granules (10 g. from chemically pure boric acid, crystallized in Pyrex glass) had been sealed within a Pyrex bulb under high vacuum after baking to 400°. The change of the granules to the glassy state was detected easily by observing the sintering and the acquired transparency. That there had been actual fusion was borne out also by tests of the power of

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[1] N. W. Taylor and S. S. Cole, THIS JOURNAL, **56**, 1648 (1934); *J. Am. Ceramic Soc.*, **18**, 55–61 (1935).

[2] G. W. Morey and H. E. Merwin, THIS JOURNAL, **58**, 2248–2254 (1936).

[3] M. von Stackelberg, F. Quatram and Jutta Dressel, *Z. Elektrochem.*, **43**, 14–28 (1937).