REDUCTION OF PERRHENATE[1,2]

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Perrhenates when heated with hydrogen may be reduced to elementary rhenium and if heated with sulfur dioxide to colored compounds of intermediate valence. In solution the result obtained depends not only on the particular reducing agent but also on other factors such as concentration and temperature.

REDUCTION WITH HYDRIODIC ACID

In 1931 Krauss and Steinfeld (15) heated a mixture of potassium perrhenate, potassium iodide, and concentrated hydrochloric acid on a sand bath and crystallized potassium chlororhenate, K_2ReCl_6, from the reaction mixture. They thought that they had evidence that a salt of trivalent rhenium was also produced but Enk (4), who followed the same general procedure, found only the chlororhenate. I and W. Noddack (19) studied the reaction quantitatively by measuring the amount of iodine set free. They found that it represented a decrease in the valence of the rhenium from 7 to 4. Jakób and Jezowska (14) have described a compound of pentavalent rhenium, K_2ReOCl_5, which they obtained by reducing potassium perrhenate with 2 equivalents of hydriodic acid in the presence of hydrochloric acid. In dilute acid this salt, according to these authors (14), undergoes disproportionation to compounds of valence 7 and valence 4:

$$3Re^{+5} = 2Re^{+4} + Re^{+7}$$

Such a disproportionation was noted by Geilmann and Wrigge (7) in the case of rhenium pentachloride.

Jakób and Jezowska (14) found rhenium of valence 4 to be formed when they used 3 equivalents of hydrogen iodide. Young and Irvine (24) carried out the reaction between potassium perrhenate and hydrogen iodide

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in a closed system in an atmosphere of carbon dioxide. They converted iodides to chlorides by successive additions of hydrochloric acid and by subsequent removals of volatile compounds at low temperatures and low pressures. The valence of the rhenium in the final residue was found to be 4.

REDUCTION WITH SOLUTIONS OF CERTAIN OXIDIZABLE SALTS

Hölemann (12) wished to relate the color of a reduced perrhenate solution to the valence of the rhenium. This he was unable to do because the color depends not only on the valence of the rhenium but also on the components of the solution. He studied the reduction potentiometrically and found that ferrous sulfate, stannous sulfate, and titanous sulfate in rather concentrated sulfuric acid solutions caused reduction to valence 5, as did stannous chloride in 15 per cent hydrochloric acid. Chromous sulfate, however, reduced the perrhenate in sulfuric acid to a compound of tetravalent rhenium. This fact was also noted by Turkiewicz (21).

Briscoe, Robinson, and Stoddart (2) obtained a black compound by the action on perrhenate of both hydrazine hydrate and stannous chloride. This they assumed to be the dihydrate of rhenium dioxide. I and W. Noddack (19) also obtained a compound of tetravalent rhenium, K_2ReCl_6, by the latter reagent. The results of Hölemann, of Briscoe, Robinson, and Stoddart, and of I. and W. Noddack seem compatible when it is recalled that compounds of pentavalent rhenium undergo disproportionation readily and that those containing the element in the tetravalent state are easily hydrolyzed. When Hölemann (11) carried out the reduction in hydrochloric acid solution with stannous chloride in the presence of potassium thiocyanate, he found that the rhenium was reduced to valence 4. Druce (3), however, was able to isolate rhenium oxythiocyanate, $ReO(CNS)_4$, from the products of such a reaction.

REDUCTION WITH METALS

The varied results obtained with zinc as the reducing agent may be due in part, at least, to the difference in concentration of the acid. Briscoe, Robinson, and Stoddart (2), using zinc and dilute hydrochloric acid, obtained the dihydrate of rhenium dioxide. They thought this to be the sole product and that the compound could be used in the quantitative determination of rhenium. The material obtained by Geilmann and Hurd (6) by a similar process contained a mixture of the dioxide, lower oxides, and rhenium metal. Young and Irvine (23) found in studying reductions of perrhenic acid with cadmium that, provided the concentration of hydrochloric acid remained above 7 N, chlororhenates were produced almost exclusively, and at concentrations between approximately 7 N and 3 N for the most part chlororhenates and the hydrated dioxide, but at lower concentrations considerable lower oxide was also formed. This latter increased in amount with decreasing acid concentration, and if the hydrochloric acid was less than 0.2 *N* the product consisted of approximately 75 per cent $ReO_2 \cdot 2H_2O$ and 25 per cent $ReO \cdot H_2O$.

Advantage was taken of the solubility of the dioxide in concentrated hydrochloric acid to separate it from the lower oxide. Since the valence of the rhenium in the solution was found to be 4, the absence of Re_2O_3 was proved, as it is also soluble in concentrated hydrochloric acid. The residue was analyzed for rhenium; the valence of the element was obtained by ignition of the compound in oxygen in a closed system over mercury; the amount of water associated with the compound was obtained by reduction with hydrogen. By a similar procedure a lower oxide, $Re_2O \cdot 2H_2O$ was obtained by reduction with zinc. Both lower oxides are black and not readily attacked by dilute alkaline chromate or acid ferric sulfate, but are rapidly attacked by nitric acid and bromine water.

Lundell and Knowles (16) have reported the formation of a rhenide, in which the rhenium possesses a valence of -1, by the passage of a dilute sulfuric acid solution containing perrhenic acid through a Jones reductor.

REDUCTION BY ELECTROLYSIS

Rhenium may be plated out directly on various metals from dilute sulfuric acid solutions of perrhenic acid as has been reported by Fink and Deren (5) and by Lundell and Knowles (16). Compounds of intermediate valence, however, may be obtained if the acid used is at least moderately strong. Jakób and Jezowska (13) were able to obtain rhenium of valence 5 by carrying out the electrolysis in hydrochloric acid of concentration greater than 7 *N*, and lower oxides in a concentrated sulfuric acid solution. With 1 *N* acid they isolated lower oxides. Schmid (20) likewise produced compounds containing rhenium of intermediate valences, 4 and 3, in solutions of 6 *N* hydrochloric acid. Cathodes of both palladium and platinum were used in these investigations.

Hölemann (10, 9) employed an electrolyte of ammonium bifluoride in the hope of obtaining an insoluble fluoride of trivalent rhenium, but the metal was formed directly. With a platinum cathode he obtained both metal and oxide from dilute hydrochloric acid solutions and also from 4 *N* sulfuric acid. By the use of a mercury cathode, however, rhenium amalgam and the dioxide were produced.

REDUCTION OF POTASSIUM CHLORORHENATE

In confirmation of the work of Schmid (20), who obtained an olive-green solution containing Re^{+3} by the electrolytic reduction of perrhenic acid in

6 *N* hydrochloric acid, are the results obtained by Hölemann (10) and by Manchot and coworkers (17, 18) in the reduction of potassium chlororhenate, K_2ReCl_6. Hölemann (10) used a mercury cathode and a solution of hydrochloric acid and obtained rhenium amalgam and an olive-green solution. A green solution was also noted by Manchot and coworkers (18), who employed 1 molar sulfuric acid and both mercury and platinum cathodes. The rhenium in the solution was found by them to be trivalent. The same result was obtained with zinc as the reducing agent, the other factors remaining the same. A compound of trivalent rhenium was not, however, isolated.

Rhenium trichloride produced by the chlorination of rhenium gives a deep red water solution entirely different from the solution described by Manchot and coworkers as containing trivalent rhenium. This may be due to the fact that the anhydrous compound is a dimer, as has been recently found by Wrigge and Biltz (22) from molecular weight determinations in glacial acetic acid. The suggestion of Manchot and Düsing (17) that the rhenium trichloride, produced by Geilmann, Wrigge, and Biltz (8), may have been partially oxidized has been refuted by the latter (1).

SUMMARY

In conclusion, it may be said that the results, in general, described by the various investigators of the reduction of perrhenate show that by the use of the most active reducing agents rhenium metal may be formed, but that compounds containing rhenium of intermediate valences may also be produced, especially at rather high acid concentrations. Such compounds may also be formed by the less active reducing agents. The behavior of perrhenate on reduction coincides with what might be predicted of an element between tungsten and osmium in the periodic classification.

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