NOTES

The Formation of $K_5W_3Cl_{14}$ During the Reduction of Chlorotungstates with Tin

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In the course of developing a synthesis for tripotassium enneachloro-ditungstate(III), a study of the reduction of WCl_x^{6-x} in concentrated HCl by Sn has been conducted. It has been found that because of the equilibrium

$$3W_2Cl_9^{-3} + Cl^- = 2W_3Cl_{14}^{-5} \qquad (I)$$

either $K_3W_2Cl_9$ or $K_5W_3Cl_{14}$ can be obtained.

The existence of the new compound, $K_5W_3Cl_{14}$, has been strongly indicated by X-ray powder photographs and confirmed by analysis. The equilibrium has been studied spectrophotometrically. The $W_3Cl_{14}^{-5}$ ion gives a deep red solution in water or HCl with an absorption maximum at 515 mμ while $W_2Cl_9^{-3}$ solution is yellow-green with absorption maxima at 462 and 625 mμ. The compound $K_5W_3Cl_{14}$ is a dark green crystalline solid whereas $K_3W_2Cl_9$ is olive or yellow-green. The former is more soluble and more easily oxidized. At equilibrium the concentration of $W_2Cl_9^{-3}$ is several-fold greater than that of $W_3Cl_{14}^{-5}$.

Experimental

The synthesis of $K_5W_3Cl_{14}$ was carried out as follows. To 5 g. of K_2CO_3 in 13 ml. of hot water was added 6.6 g. of H_2WO_4 in small portions. After complete solution was obtained 166 ml. of concentrated HCl was added as HCl gas was bubbled through the warm solution. The precipitated KCl was filtered off and an amount of KCl (0.8 g.) in slight excess of that necessary to form $K_5W_3Cl_{14}$ was added. The solution was poured into a one-liter flask containing 150 g. of mossy (feathered) tin. Reduction was allowed to proceed for 2 hours at 25°. The solution was decanted from the tin, saturated with HCl gas and placed in an ice-bath for 24 hours. Care was taken to minimize air oxidation of the W(III) formed during the reduction. The product was recovered by suction filtration and sparingly washed with cold HCl, cold EtOH and Et_2O. Yields of $K_5W_3Cl_{14}$ were from 35–45% based on the limiting reagent H_2WO_4.

Anal. Calcd. for $K_5W_3Cl_{14}$: K, 15.7; W, 44.4; Cl, 39.9. Found: K, 15.9; W, 43.8; Cl, 39.3.

If the KCl was filtered off and no additional KCl was added, as described above, the product was $K_8W_2Cl_9$ in 45–55% yields. This method for producing $K_3W_2Cl_9$ is a notable improvement over the procedure of Olsson.[1,2]

Results and Discussion

X-Ray powder photographs of $K_5W_3Cl_{14}$ made with a North American Phillips powder camera Straumanis arrangement using Cu Kα radiation showed ten unique strong lines which can be assigned to $K_5W_3Cl_{14}$ and somewhat weaker lines corresponding to the $K_3W_2Cl_9$ and KCl, which arise because of the equilibrium. Powder photographs of $K_3W_2Cl_9$ showed none of the ten unique lines, and confirmed the work of Brossett[3] and Pauling[4] on $K_3W_2Cl_9$.

A study of the equilibrium was carried out by visually noting color changes and by measuring absorption spectra on a Cary automatic recording spectrophotometer. In the experiments described, the concentration of the solutions was 2 g./l. with respect to the tungsten salts and 0.8 g./l. with respect to KCl.

It was found that the equilibrium (I) proceeds easily to the left as indicated by the fact that red $K_5W_3Cl_{14}$ soon turns green on standing and shows high optical densities at 462 and 625 mμ.

Solutions containing $K_5W_3Cl_{14}$ + KCl were red and fairly stable showing the characteristic absorption maximum of $W_3Cl_{14}^{-5}$ at 515 mμ.

Solutions of $K_3W_2Cl_9$ to which KCl was added turned red and showed the characteristic $W_3Cl_{14}^{-5}$ maximum, while solutions of $K_3W_2Cl_9$ were quite stable, green, and had the usual $W_2Cl_9^{-3}$ maxima at 462 and 625 mμ.

It was found that 8 *m* HCl + KCl (0.8 g./l.) was the best medium for forcing the equilibrium (I) to the right and for preserving $K_5W_3Cl_{14}$ solutions. The equilibrium was found to take place in water, HCl solutions, and several organic solvents, notably methyl cyanide. However, complex formation with the solvent was a complicating factor in the non-aqueous systems. The alkali salts of $W_3Cl_{14}^{-5}$ are more soluble than their $W_2Cl_9^{-3}$ analogs.

The correct I.U.C. name for $K_5W_3Cl_{14}$ is pentapotassium tetradecachloro-tritungstate(III).

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[2] O. Olsson, *Ber.*, **46**, 573 (1913).

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[4] L. Pauling, *Chem. Eng. News*, **25**, 2970 (1947).

On the Water Solubilities of Ethers

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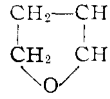
It is common practice to attribute the large differences in water solubilities of low molecular weight alcohols over that of their isomeric ethers to a co-association of the alcohol and water molecules through hydrogen bonds. Apparently the view is taken that water molecules may form hydrogen bonds with ether molecules, but since ethers lack an OH group for reciprocal bonding with water, only one hydrogen bond per molecule may be formed with ethers and this is insufficient to give the ethers an appreciable water solubility. This viewpoint makes it difficult to explain the complete water solubility of tetrahydrofuran.



tetrahydrofuran

Nevertheless, upon comparing the water solubili-