

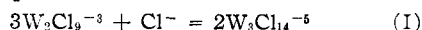
NOTES

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

BY ROBERT A. LAUDISE AND RALPH C. YOUNG

RECEIVED MAY 14, 1955

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



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 $m\mu$ while $W_2Cl_9^{-3}$ solution is yellow-green with absorption maxima at 462 and 625 $m\mu$. 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 $K_3W_2Cl_9$ 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 $Cu K\alpha$ 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 Brossett³ and Pauling⁴ on $K_3W_2Cl_9$.

(1) O. Olsson, *Z. anorg. Chem.*, **88**, 49 (1914).

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

(3) C. Brossett, *Arkiv. Kemi. Mineral Geol.*, **12A**, No. 4, 8 (1935).

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

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 $m\mu$.

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

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 $m\mu$.

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).

Acknowledgment.—The authors wish to thank Prof. D. P. Shoemaker and Mr. N. E. Weston for their assistance in taking powder pictures.

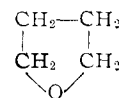
DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.

On the Water Solubilities of Ethers

BY LLOYD N. FERGUSON

RECEIVED MAY 28, 1955

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-

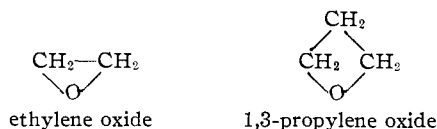
ties of the dialkyl ethers, starting with diethyl ether, with those of their isomeric normal alcohols, it is observed that the water solubilities are quite similar.

Ether	Water solubility ^a near room temp.	Isomeric <i>n</i> -alcohol	Water solubility ^a near room temp.
Diethyl	7.5%	<i>n</i> -Butyl	9%
Ethyl <i>n</i> -propyl	Slightly soluble	<i>n</i> -Pentyl	2.7
Di- <i>n</i> -propyl	Slightly soluble	<i>n</i> -Hexyl	0.6
Diisopropyl	0.2	<i>n</i> -Hexyl	0.6
<i>n</i> -Propyl isopropyl	0.5	<i>n</i> -Hexyl	0.6
Di- <i>n</i> -butyl	0.05	<i>n</i> -Octyl	Slightly sol.

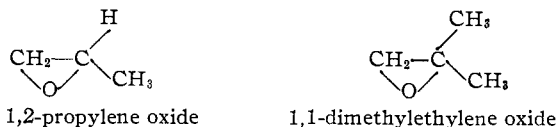
^a "Lange's Handbook of Chemistry," 6th edition, Handbook Publishers, Inc., Sandusky, Ohio.

Only the first three alcohols, methyl, ethyl and propyl, are water soluble, which can be attributed to co-association with water through hydrogen bonds. The desolubilizing effect of the larger alkyl groups of the higher homologs outweighs the solubilizing effect of hydrogen bonding. It appears that the low solubility of the first few dialkyl ethers is due to a steric effect. If one attributes the infrared frequency shift of the H-Cl bond, upon solution in various solvents, to hydrogen bonding with the solvent molecules, the frequency-shift will be affected by the basicity of the solvent and steric factors. The steric factor should be negligible with HCl, so that it is not unreasonable to correlate the basicity of the ethers with observed frequency shifts,¹ which is in the order diisopropyl ether > diethyl ether = dibutyl ether > dioxane. This is about what one would expect considering electrical effects alone.² Toward a larger acid, the steric effect should upset this order. This is indeed the case, for the reported³ relative basicities of ethers toward BF₃ decreases in the order tetrahydrofuran, dimethyl ether, diethyl ether, diisopropyl ether. In the absence of steric effects, one would expect the opposite order, with tetrahydrofuran being about the same as diethyl ether.

Considering water solubility again, tetrahydrofuran and dioxane are completely soluble, as also are ethylene oxide and 1,3-propylene oxide.



This is not due to their having cyclic structures because the water solubility of 1,2-propylene oxide is only 33% and for 1,1-dimethylethylene oxide it is only 5.8%.



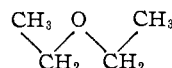
(1) W. Gordy and P. C. Martin, *J. Chem. Phys.*, **7**, 99 (1939).

(2) The steric effect begins to show up when methyl alcohol is the acid. The frequency shift of the O-D band of CH₃OD in different ethers is in the order, diethyl ether > diisopropyl ether > ethyl *n*-butyl ether > di-*n*-butyl ether > dioxane (W. Gordy and S. C. Stanford, *ibid.*, **8**, 170 (1940)).

(3) H. C. Brown and R. M. Adams, *THIS JOURNAL*, **64**, 2557 (1942).

Apparently liquid water can offer an appreciable steric hindrance to association with its molecules. This is not hard to believe when one regards liquid water as large polymeric aggregates of H₂O molecules. Sterically unhindered ethers can associate with the polymers to make them water soluble, just as can small alcohol molecules. Therefore, when attributing the low water solubility of small dialkyl ethers, in comparison to their isomeric alcohols, to a lack of association or hydrogen bonding, attention should be focused upon the steric factor. In its absence, the ethers would be water soluble, similarly as are tetrahydrofuran, dioxane, ethylene oxide and 1,3-propylene oxide.

The steric effect in dimethyl ether is surprising but not so in diethyl ether. Based on its dipole moment and other factors,⁴ the most stable form of diethyl ether is



in which the methyl groups partially shield the oxygen atom. Fisher-Hirschfelder models of dimethyl ether do not reveal much interference from the methyl groups but evidently it is sufficient to prevent its solubilization by water. The same spatial interference from the methyl groups is found in 1,1-dimethylethylene oxide, which has a low water solubility. In tetrahydrofuran and in dioxane, the alkyl chains are held back away from the oxygen atoms to permit association with water and complete water solubility.

(4) H. A. Stuart, "Molekülstruktur," J. Springer, Berlin, 1934, p. 101.

CHEMISTRY DEPARTMENT
HOWARD UNIVERSITY
WASHINGTON 1, D. C.

The Density of Pentaborane

By PAUL S. GAKLE AND STANLEY TANNENBAUM

RECEIVED MAY 13, 1955

The present literature contains two values for the density of pentaborane at 0°: 0.61 g./ml. reported by Stock,¹ and Smith and Miller's² value of 0.643 g./ml. In this research a range of densities *vs.* temperatures was measured from -8 to 25°, and the value at 0° was found to be 0.637 ± 0.002 g./ml. The equation for the density-temperature curve is: $d = -0.000733t + 0.637$, where t is in degrees centigrade. The maximum deviation of any measured point from the curve was ±0.05% over a 30° range in temperature.

Experimental

The density of pentaborane was measured in a straight tube pycnometer similar to that described in ref. 3. The unit was calibrated with distilled water in a 0° ice-bath. The calibration was checked with toluene (J. T. Baker Analyzed Reagent Grade) and agreed within 0.2% with the values from Timmerman.⁴

(1) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(2) S. H. Smith, Jr., and R. R. Miller, *THIS JOURNAL*, **72**, 1452 (1950).

(3) S. Tannenbaum, S. Kaye and G. Lewenz, *ibid.*, **75**, 3753 (1953).

(4) J. Timmerman, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950.