requirements and the steric limitations. These structures are represented by formulas V and VI in Table I. According to either structure, the *3:3* UCit, UMal and UTar trimers would have charges of -8, -5 and -5, respectively.

The *3:2* Trimer.—The most reasonable view of the 1.5:1 complexes, revealed by the spectrophotometric results, is that they are trinuclear, containing three uranium atoms and two organic groups; *i.e.*, they are *3:2* trimers.

A titration curve of a 1.5:1 UCit mixture has its second inflection point at about *p*H 8 where the OH/U ratio is equal to $3^2/_3$. Since spectrophotometric studies showed that this mixture was composed almost entirely of the 1.5:1 complex, it is obvious that the formation of *3:2* trimer from three uranyl ions and two citric acid molecules required eleven hydroxyl ions.

Six plausible structures, represented by formulas VII through X in Table I, can be written for the *3:2* UCit trimer. In view of the resistance of (U=O) bonds to mere hydration, it is believed that structures VIIb and IXb are improbable since they are merely the hydrated forms of VIIa and IXa. The *3:2* UCit trimer would thus bear a -5 charge.

Titrations of 1.5:1 UTar and UMal mixtures did not yield definite inflection points, a fact undoubtedly connected with the precipitation noticed in these mixtures. If one assumes, however, that *3:2* UTar and UMal trimers are similar in structure to the *3:2* UCit trimer, then nine hydroxyl ions would be required for the formation of one *3:2* UMal or UTar trimer from three uranyl ions and two organic acid molecules. Such *3:2* UMal and UTar trimers would each have a -3 charge.

Relative Stabilities of *3:3* and *3:2* Trimers.—The stoichiometry indicates that the equilibrium between *3:3* and *3:2* trimers can be represented as

$$1 \text{ mole } 3:3 \text{ trimer} \rightleftarrows 1 \text{ mole } 3:2 \text{ trimer} + 1 \text{ mole anion, R}$$

The forward reaction involves the replacement of an organic R′ group by a hydroxyl ion, but the R′ ion immediately attaches a hydrogen ion, re-forming the original alcohol group, to produce the free anion, R. Therefore, the hydroxyl ion does not enter the over-all stoichiometric equation.

This is the reason that the second inflection point in the titration curve of 1:1 mixtures (Fig. 1) occurs when OH/U equals $1^2/_3$ plus the number of carboxyl groups in the original carboxylic acid regardless of the fact that the ratio of *3:3* trimer to *3:2* trimer varies in the three systems studied, UCit, UMal and UTar.

The previously mentioned fact that the ratio of the stability of the 1:1 complex to the 1.5:1 complex at slightly alkaline *p*H decreases in the order UMal > UTar > UCit might suggest that the relative stability of *3:3* and *3:2* trimers depends on the size of the R′ group on the central uranium atom in the *3:3* trimer. However, molecular models indicate that the extra (CH_2COO^-) group of the citrate groups do not add a considerable amount of steric hindrance to that already existing in *3:3* UMal and UTar complexes. It is more likely that electrostatic repulsions by the (CH_2COO^-) groups are responsible for the stability differences. The reason for the time factor in the titration of a 1:5 UMal mixture (see Fig. 5) is not evident at present.

Uranyl–Lactate System.—The occurrence of the inflection point at OH/U = $2^2/_3$ near *p*H 6, just before precipitation occurs, in the titration curve of the 1:1 uranyl–lactate mixture may be considered evidence for the formation of a ULact trimer in the light of the previous interpretation of the factor, $^2/_3$. This, of course, implies the previous formation of dimer. However, the failure to obtain a titration break at OH/U = 2 suggests that trimer formation begins before dimer formation is complete.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY AND THE DEPARTMENT OF CHEMISTRY OF HARVARD UNIVERSITY]

The Chlorination of Metals in the Presence of a Donor Solvent[1]

BY ROBERT C. OSTHOFF AND ROBERT C. WEST

RECEIVED APRIL 3, 1954

A method for the low temperature chlorination of cobalt, nickel, manganese, zinc and chromium, in several donor solvents, is described. Several methods for the isolation of relatively pure anhydrous metal halides or coördination compounds of the anhydrous halides have been established. It is shown that the halogenation of the metals in the presence of donor solvents is a rather general one; and that it must involve coördination of the solvent to the metal, for these reactions do not occur in non-polar solvents.

I. Introduction

Pure anhydrous chlorides of metals are customarily prepared by passing chlorine gas over the pure metals at elevated temperatures,[2] since the procedure of drying the hydrated chlorides ordinarily leads to a certain amount of hydrolysis and loss of chlorine. This procedure is in certain cases unsatisfactory; for example, cobalt(II) chloride cannot be conveniently prepared in this way since it does not sublime appreciably at 500°, and the cobalt surface merely becomes covered with the chloride and the reaction ceases. However, iron(III)

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[1] Presented before the Division of Physical and Inorganic Chemistry, 125th Meeting of the American Chemical Society, Kansas City, Mo., March, 1954.

[2] L. Vanino, "Handbuch der Präparativen Chemie," Vol. I, Edwards Bros., Ann Arbor, Mich., 1943, pp. 489, 494, 544, 594 ff.

chloride may be prepared readily from the elements at relatively low temperatures.[3]

Ducelliez and Raynaud[4,5] have prepared the bromides of cobalt, nickel, manganese, zinc and magnesium by bromination of the various metals in diethyl ether at room temperature. In each case, the intermediate complex $MBr_2 \cdot Et_2O$ was isolated.[6,7]

Raynaud later extended this work by preparing the tri- and pentabromides of antimony by the same method.[8] His most conclusive paper, however, recorded his experiments with zinc and bromine in water, diethyl ether, benzene, carbon tetrachloride, octane and petroleum ether. Only in water and ether did reaction take place within three months. As a result of his investigations, Raynaud concluded that a solvent promotes the bromination of a metal only if it dissolves both bromine and the bromide which is formed, and only if it forms a complex compound with the bromide. He proposed as a reaction mechanism that the bromine attacks the solvent with the production of HBr, which is the active agent in brominating the metal.[9]

Rowley, *et al.*, have prepared magnesium bromide etherate from magnesium and bromine in diethyl ether[10] and have recently suggested this reaction as a convenient method for preparing pure anhydrous magnesium bromide.[11] By similar procedures, $CrCl_3 \cdot 3C_2H_5OH$ has been prepared by treatment of metallic chromium with hydrogen chloride in anhydrous ethanol.[12] However, there appear to be no literature references to the preparation of anhydrous metal halides by chlorination of metals in the presence of donor solvents.

II. Experimental

In the present investigation a general procedure was used in the preparations of the various anhydrous metal halides. A 300-ml. round-bottom flask was equipped with a reflux condenser bearing a drying tube filled with calcium chloride or alternatively a dry nitrogen gas by-pass; and with a gas inlet tube extending to within 3 cm. of the bottom. The flask was also equipped with a stirrer and all connections were made with ground glass joints. The various metal powders were introduced into the flask and covered with 60–200 ml. of solvent. A moderately fast stream of dry chlorine gas was then bubbled through the mixture. The mixture was agitated constantly during the course of each experiment to bring the metal particles into contact with the solvent. In cases in which the heat of reaction was not sufficient to cause the solvent to boil, the flask was heated on a steam-bath to maintain refluxing.

The reaction mixtures were worked up by decanting the solutions through a suction filter in a stream of dry nitrogen and extracting any residue with a sufficient portion of boiling solvent to dissolve all but traces of the salt or complex which had formed. The filtrate was evaporated and the products isolated as indicated under the specific experiments listed below. The metallic residue was washed on to the filter with further quantities of solvent and then washed well with water, then with ethanol and ether, and finally dried and weighed.

Preparation of Cobalt(II) Chloride.—Metallic cobalt powder, 5.8 g., was suspended in the reaction flask in 60 ml. of anhydrous ethanol. Chlorine gas was then passed through the suspension. At the start of this run the heat of reaction was sufficient to maintain reflux for the first hour. After this time, the mixture was warmed on a steam-bath to maintain gentle refluxing. The total reaction time was 140 minutes. After filtration the ethanol solution was allowed to stand in a vacuum desiccator over concentrated sulfuric acid. The bright blue crystals[13] which were formed were transferred under dry nitrogen and recrystallized from absolute ethanol. The crystals were pumped on a vacuum line for four hours during which time the temperature was gradually raised to 100°. A light blue powder of $CoCl_2$ in 84% yield remained; about 4% of unreacted metal was recovered. The remainder of the cobalt presumably may be accounted for by mechanical losses and by virtue of its solubility in ethanol. *Anal.* Calcd. for $CoCl_2$: Cl, 54.6. Found: Cl, 54.2. Cobalt(II) chloride was also formed by a similar procedure when ether was substituted for ethanol. However, the reaction in diethyl ether is less vigorous than in ethanol and under more or less comparable conditions only 33% or approximately one third as much halide is formed in ether as in ethanol. Longer reaction times give essentially quantitative yields of cobalt(II) chloride which is practically insoluble in the ether. This fact allows one to wash the cobalt(II) chloride with anhydrous ether and obtain a product suitable for use in coupling Grignard reagents, for example. This washing is necessary since chlorination of solvent invariably accompanies the reaction of the metal with chlorine, and these chlorine-containing compounds would react with the Grignard reagents.

Preparation of Nickel(II) Chloride.—The reaction flask which was charged with 8.0 g. of nickel and 100 ml. of ethanol was warmed gently to maintain refluxing throughout this chlorination. A yellowish-white precipitate started to form after 25 minutes, and the reaction mixture soon became thick and pasty. An additional 40 ml. of ethanol was added to keep the mixture liquid, during the entire reaction time of 150 minutes. After filtration of the yellowish-green ethanolic solution, the product was isolated by distilling off the alcohol. The mixture was heated on a steam-bath until distillation became slow; the bright yellow precipitate which formed was filtered with suction from the remaining ethanol and washed with anhydrous ether, all under a stream of nitrogen. The product was dried in a vacuum drying pistol at 100° for two hours and the yield was 39%. *Anal.* Calcd. for $NiCl_2$: Cl, 54.7. Found: Cl, 54.0.

When the crude precipitate was taken up in anhydrous ethanol and the ethanol allowed to evaporate in a desiccator over sulfuric acid, long brilliant yellow needles were formed. These had a chlorine content corresponding to a dialcoholate. *Anal.* Calcd. for $NiCl_2 \cdot 2C_2H_5OH$: Cl, 32.0. Found: Cl, 32.1. This compound has not been previously described although Dolian and Briscoe[14] have noted refractometric evidence for the probable formation of this compound in ethanol solutions of nickel(II) chloride. The compound was extremely hygroscopic and turned green in a few seconds in moist air. The crystals lose alcohol slowly at room temperature in an anhydrous atmosphere, and rapidly and completely when heated to 100° *in vacuo*.

Preparation of $NiCl_2 \cdot C_4H_8O_2$.—In order to facilitate the isolation of a nickel compound from the crude reaction mixture, the ethanol solution was filtered through a sintered glass funnel, and three times the volume of the solution of purified 1,4-dioxane was slowly added. A fine powder precipitated and this was allowed to stand for 15 hours at room temperature. The product was washed with anhydrous ether, filtered and dried in a vacuum desiccator over phosphorus(V) oxide. The pale yellow-orange product which formed was stable and not appreciably hygroscopic. *Anal.* Calcd. for $NiCl_2 \cdot C_4H_8O_2$: Cl, 32.6. Found: Cl, 32.3. Anhydrous nickel(II) chloride could not be isolated from the addition compound as such, for only 17% of the total dioxane was lost on heating to 100° in high vacuum for six hours. The addition compound was not completely decomposed after heating to 160° at 2 mm. for four hours.

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[3] B. R. Tarr, "Inorganic Syntheses," Vol. III, McGraw–Hill Book Co., Inc., New York, N. Y., 1950, p. 191 *et seq.*

[4] F. Ducelliez and A. Raynaud, *Compt. rend.*, **158**, 2002 (1914).

[5] F. Ducelliez and A. Raynaud, *ibid.*, **158**, 578 (1914).

[6] F. Ducelliez and A. Raynaud, *Bull. soc. chim.*, **15**, 599 (1914).

[7] F. Ducelliez and A. Raynaud, *ibid.*, **15**, 727 (1914).

[8] A. Raynaud, *ibid.*, **27**, 411 (1920).

[9] A. Raynaud, *Compt. rend.*, **181**, 1069 (1925).

[10] W. V. Evans and H. H. Rowley, THIS JOURNAL, **52**, 3523 (1930).

[11] H. H. Rowley, *ibid.*, **72**, 3305 (1950).

[12] J. Koppel, *Z. anorg. Chem.*, **28**, 461 (1901).

[13] This was probably $CoCl_2 \cdot 2C_2H_5OH$ (*cf.* L. Lloyd, *et al.*, *J. Chem. Soc.*, 662 (1928). *Anal.* Calcd. for $CoCl_2 \cdot 2C_2H_5OH$: Cl, 31.9. Found: Cl, 32.3.

[14] F. F. Dolian and H. T. Briscoe, *Proc. Indiana Acad. Soc.*, **45**, 110 (1935).

Preparation of Manganese(II) Chloride.—Powdered manganese metal was chlorinated in anhydrous ethanol. During the first hour the heat of the reaction was sufficient to reflux the solvent, but during the second hour the reaction flask had to be heated. At the end of the run, the alcohol was distilled off and the pearly white manganese(II) chloride in 65% yield was obtained after drying *in vacuo* in a drying pistol. *Anal.* Calcd. for $MnCl_2$: Cl, 56.3. Found: Cl, 56.0.

When the manganese chloride was dissolved in an excess of ethanol and the solution was allowed to stand in a vacuum desiccator for one month over sulfuric acid, pink transparent crystals of the dialcoholate, $MnCl_2 \cdot 2C_2H_5OH$,[15] formed. *Anal.* Calcd. for $MnCl_2 \cdot 2C_2H_5OH$: Cl, 32.5. Found: Cl, 32.1. Like the corresponding nickel compound all of the alcohol could be removed in a vacuum drying pistol at 100°.

An alternative procedure for isolation of a manganese salt, involved conversion of the chloride to the dioxane addition compound.[16] When the manganese(II) chloride was taken up in excess ethanol, and about three times the volume of anhydrous 1,4-dioxane added, a fine powdered solid which was not hygroscopic was obtained. *Anal.* Calcd. for $MnCl_2 \cdot C_4H_8O_2$: Cl, 33.1. Found: Cl, 33.2. Unfortunately, this compound was too stable to be used in the isolation of anhydrous manganese chloride, since $MnCl_2 \cdot C_4H_8O_2$ was not affected by heating to 100° in high vacuum for 6 hours.

Preparation of Chromium(III) Chloride.—A suspension of 10 g. of chromium metal in 150 ml. of ether was chlorinated for 340 minutes at room temperature. At the end of this time the blue solution was filtered and the crystals of chromium(III) chloride were isolated in approximately 42% yield by heating to 80° *in vacuo*. *Anal.* Calcd. for $CrCl_3$: Cl, 67.2. Found: Cl, 67.0. However, the pure anhydrous halide was isolated only with great difficulty.

Preparation of $ZnCl_2 \cdot C_4H_8O_2$.—A suspension of 10 g. of powdered zinc in 150 ml. of anhydrous ether was chlorinated for 150 minutes at room temperature. The heat of the reaction maintained refluxing for the entire reaction period. At the end of the chlorination a two-phase liquid system resulted. The lower layer was treated with three times its volume of anhydrous 1,4-dioxane and a fine white powder of $ZnCl_2 \cdot C_4H_8O_2$ was isolated in 80% yield. *Anal.* Calcd. for $ZnCl_2 \cdot C_4H_8O_2$: Cl, 31.6. Found: Cl, 31.6. Pure anhydrous zinc chloride was not readily obtained from the dioxane addition compound.

Discussion

The chlorination of metals in the presence of a donor solvent seems to be a rather general reaction, although no reaction was found to take place with tungsten, molybdenum or silicon in the presence of ether. No reaction is observed if a non-polar solvent such as benzene is substituted for the oxygenated solvents. Thus, one might expect that the role of the solvent is to coördinate with the metal chloride and keep removing the chloride from the surface of the metal, as indicated in the equations

$$\underset{\text{(surface)}}{MCl_x} + Et_2O \rightleftarrows MCl_x{:}OEt_2 \rightleftarrows MCl_x + Et_2O$$

One would thus predict that any Lewis base could be used as a solvent in these reactions. There is, unfortunately, no experimental evidence to support this.

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[15] O. E. Zvyagintsev and A. Z. Chkhenkeli, *J. Gen. Chem.* (*U.S.S.R.*), **11**, 791 (1941).

[16] H. Rheinboldt, A. Luyken and M. Schmittman, *J. prakt. Chem.*, **149**, 30 (1937).

NOTES

The King Method for First-order Rate Determinations Modified for Fast Reactions

BY GUNTHER L. EICHHORN AND ISAAC M. TRACHTENBERG

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King[1] has reported a method for the determination of first-order reaction rate constants based upon the equation

$$D_t - D_{t+\tau} = l\,(A)_0(1 - e^{-k\tau})(\epsilon_A - \epsilon_B)e^{-kt}$$

A plot of the logarithm of the difference in optical density of two reaction mixtures, in which the reaction has been initiated τ seconds apart, *versus* time t gives a straight line with a slope $-k$, the rate constant.

This method is very useful for reactions requiring several hours to go to completion. For faster reactions it becomes awkward, because $D_t - D_{t+\tau}$ may become very small, and because large changes in the zero adjustment of the instrument are required during the course of the reaction.

It is possible to eliminate these difficulties by employing only one reaction mixture, instead of two, and by reading the optical density *vs.* the pure solvent, as in conventional spectrophotometric measurements. The differences in optical density required in the above equation are then calculated from the optical densities observed on the same sample at times t and $t + \tau$. When the logarithms of these differences are plotted *vs.* t, straight lines with slopes equal to $-k$ are obtained.

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[1] E. L. King, THIS JOURNAL, **74**, 563 (1952).

Unit Cell Dimensions of Some Rare Earth Oxyfluorides

BY N. C. BAENZIGER, J. R. HOLDEN, G. E. KNUDSON[1] AND A. I. POPOV

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In connection with the preparation and study of some rare earth fluorides and oxyfluorides[2] the cell

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[1] Chemistry Department, Luther College, Decorah, Iowa.

[2] A. I. Popov and G. E. Knudson, THIS JOURNAL, **76**, 3921 (1954).