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

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

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

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RECEIVED APRIL 23, 1954

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).