**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.

**Acknowledgment.**—The authors express their appreciation to Professor Eugene G. Rochow of Harvard University, to Professor Charles A. Brown of Western Reserve University and to Dr. E. H. de Butts of the Hercules Powder Company for their advice, assistance and encouragement through various stages of this work.

SCHENECTADY, N. Y.
CAMBRIDGE, MASS.

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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).

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# NOTES

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

BY GUNTHER L. EICHHORN AND ISAAC M. TRACHTENBERG

RECEIVED APRIL 15, 1954

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 $\tau$ 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.

COATES CHEMICAL LABORATORY
LOUISIANA STATE UNIVERSITY
BATON ROUGE, LOUISIANA

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

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## 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).

TABLE I

UNIT CELL DIMENSIONS OF RARE EARTH OXYFLUORIDES, RHOMBOHEDRAL LaOF STRUCTURE TYPE[a]

| | $a$ in Å. | $\alpha$ in deg. | Fluorine, % Found | Fluorine, % Theor. | Metal, % Found | Metal, % Theor. |
|---|---|---|---|---|---|---|
| LaOF[a] | 7.132 ± 0.001 | 33.01 ± 0.01 | | | | |
| LaOF | 7.132 ± .001 | 32.99 ± .01 | 10.80 | 10.93 | 79.68 | 79.87 |
| PrOF | 7.016 ± .004 | 33.03 ± .03 | 10.26 | 10.80 | 80.68 | 80.10 |
| NdOF | 6.953 ± .001 | 33.04 ± .01 | 10.54 | 10.60 | 80.21 | 80.43 |
| SmOF | 6.865 ± .002 | 33.07 ± .02 | 10.00 | 10.25 | 81.77 | 81.13 |
| EuOF | 6.827 ± .002 | 33.05 ± .02 | | | | |
| GdOF | 6.800 ± .001 | 33.05 ± .01 | 9.75 | 9.90 | 82.03 | 81.76 |
| TbOF | 6.758 ± .011 | 33.02 ± .09 | | | | |
| CeOF[b] | 6.985 ± .001 | 33.56 | 9.59 | 10.85 | 80.01 | 79.00 |
| CeOF | 5.703 ± .001 | Cubic, face-centered | | | | |
| CeOF[c] | 5.66 ± .01 to 5.73 ± 0.01 | | | | | |

[a] See reference 3. [b] Rhombohedral cell dimensions corresponding to the face-centered cubic cell actually observed. [c] See reference 4.

dimensions of a series of rare earth oxyfluorides were obtained and are listed in Table I together with values previously found by other investigators. All the oxyfluorides examined with the exception of cerium oxyfluoride had the rhombohedral structure found by Zachariasen[3] for lanthanum oxyfluoride. The cubic cell dimensions found for cerium oxyfluoride are within the range of values reported by Finkelnburg and Stein[4] who found that the cell constant of the fluorite type structure varied with the amount of fluorine in the lattice.

The oxyfluorides of lanthanum, praseodymium, neodymium, samarium, europium and gadolinium were made by hydrolysis of the anhydrous fluoride by heating at about 800° in a current of moist air. In the case of praseodymium some higher oxide also was formed. Cerium and praseodymium oxyfluorides were prepared by hydrolysis in a moist ammonia stream at 800°. Hydrolysis in air led to cerium dioxide. Terbium oxyfluoride was formed accidentally as the result of fluorination of $Tb_4O_7$ followed by hydrolysis in a stream of undried hydrogen.

The cell dimensions were determined from the back reflection lines of films exposed in a Debye-Scherrer type powder camera (rad. = 5.73 cm.) using Cu K$\alpha$ or Fe K$\alpha$ radiation. The data were treated using Cohen's[5] analytical extrapolation method. The errors listed are the standard errors from one determination.

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(3) W. H. Zachariasen, *Acta Cryst.*, **4**, 231 (1951).

(4) W. Finkelnburg and A. Stein, *J. Chem. Phys.*, **18**, 1296 (1950).

(5) E. R. Jette and F. Foote, *ibid.*, **3**, 605 (1935).

DEPARTMENT OF CHEMISTRY
STATE UNIVERSITY OF IOWA
IOWA CITY, IOWA

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# Isomer, Neutron Energy and Radiation Dosage Effects on Reactions Activated by Radiative Neutron Capture in Organic Bromides

BY J. C. W. CHIEN AND J. E. WILLARD

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Capron and co-workers[1] have shown recently that the $Br^{79}$ $(n,\gamma)$ $Br^{80m}$ (4.4 hr.) process gives higher organic yields[2] in propyl bromides, bromobenzene[3] and bromoform[4] than the $Br^{79}$ $(n,\gamma)$ $Br^{80}$ (18 min.) process, when commercial reagents are used without further purification. They have reasoned that impure reagents should give isomer effects similar to pure organic compounds even though the absolute values of the organic yields are different. Fox and Libby[5] and Rowland and Libby[6] have reported, however, that the organic yields for $Br^{80m}$, $Br^{80}$ and $Br^{82}$ produced by the $(n,\gamma)$ process in highly purified liquid propyl bromides are identical. They have pointed out that if impurities were present which could react with inorganic bromine ($Br_2$ or HBr) to return it to organic combination, these might increase the apparent organic yield of the 4.4 hr. isomer relative to that of the 18 min. isomer because of its longer radioactive lifetime in solution.[7] The experiments summarized below were designed to determine whether the reported isomer effects can be obtained reproducibly. Related information on reported neutron energy effects and on the effect of $\gamma$-ray dosage on organic yields is also given.

### Experimental

Several methods of purification and irradiation similar in type to those reported previously[8-13] were used.

The organic yield due to the $Br^{79}$ $(n,\gamma)Br^{80}$ (18 min.) process was determined independently of that due to the $Br^{80m}$ (4.4 hr.) $\rightarrow$ $Br^{80}$ (18 min.) isomeric transition process by two methods. In the first, advantage was taken of the fact that, for a 2 min. irradiation, the 18 min. activity produced by the isomeric transition was negligible (*ca.* 2%) compared to that produced by the $(n,\gamma)$ process. In the second method the organic yields of both the 18 min. and

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(1) P. C. Capron and E. Crevecoeur, *J. Chem. Phys.*, **21**, 1843 (1953).

(2) The "organic yield" is the fraction of the $(n,\gamma)$ events which lead to organically bound radiobromine.

(3) P. C. Capron and E. Crevecoeur, *J. chim. phys.*, **49**, 29 (1952).

(4) P. C. Capron and Y. Oshima, *J. Chem. Phys.*, **20**, 1403 (1952).

(5) M. S. Fox and W. F. Libby, *ibid.*, **20**, 487 (1952).

(6) F. S. Rowland and W. F. Libby, *ibid.*, **21**, 1495 (1953).

(7) The average age of the 18 min., 4.4 hr. and 36 hr. atoms produced by a 1 hr. neutron irradiation and present at the end of the irradiation is 19.3, 29.2 and 29.9 min., respectively; the average ages after a 6 hr. bombardment are 25.8, 160 and 176 min. The usual irradiation time used by Capron and Crevecoeur was three hours. They did one experiment with a one hour irradiation which they felt showed that the isomer effects which they observed could not be due to the different average lifetimes of $Br^{80}$ and $Br^{80m}$.

(8) E. G. Bohlman and J. E. Willard, THIS JOURNAL, **64**, 1342 (1942).

(9) R. S. H. Chiang, S. Goldhaber and J. E. Willard, *ibid.*, **73**, 2271 (1951).

(10) S. Goldhaber and J. E. Willard, *ibid.*, **74**, 318 (1952).

(11) G. Levey and J. E. Willard, *ibid.*, **74**, 6161 (1952).

(12) J. F. Hornig and J. E. Willard, *ibid.*, **75**, 461 (1953).

(13) J. C. W. Chien and J. E. Willard, *ibid.*, **75**, 6160 (1953).