[CONTRIBUTION FROM THE HAYDEN MEMORIAL LABORATORIES OF NORTHEASTERN UNIVERSITY]

Acids and Bases. VI. Aluminum Chloride, Ferric Chloride and Stannic Chloride as Acid Catalysts in the Reaction of Metals with Thionyl Chloride[1,2]

BY R. A. HUBBARD, 2ND, AND W. F. LUDER

Calcium, zinc and lead do not react appreciably in boiling thionyl chloride. Sodium reacts very slowly. Antimony reacts rapidly. Aluminum, magnesium, iron, tin, bismuth and mercury react more slowly. The products are sulfur and sulfur dioxide, $AlCl_3$, $SbCl_3$, $MgCl_2$, $FeCl_3$, $SnCl_4$, $BiCl_3$ and $HgCl_2$.

The presence of acids increases the rate: slightly with stannic chloride, markedly with aluminum chloride and ferric chloride. The explanation offered by the electronic theory of acids and bases is that the acid catalysts, by displacement, increase the concentration of the acidic solvent cation which is reacting with the metal. This catalysis is another illustration of one type of acidic behavior: the displacement of an acid by another.

I. Introduction

According to the electronic theory of acids and bases, the presence of acids such as aluminum chloride, ferric chloride and stannic chloride should increase the reaction rate of metals with ionizing solvents.[3]

Although this behavior is a familiar one in aqueous solutions, little work has been done with nonaqueous solvents. In this investigation thionyl chloride was chosen as a convenient solvent that contains no protons.

By coördinating with the chloride ion, acids should displace the acidic portion of the thionyl chloride molecule, thus increasing the concentration of solvent cations. This higher concentration of acidic ions should result in a faster reaction with metals. Such a prediction was made in 1946[3]; work to test it has now been completed.

II. Experimental

Materials.—Eastman Kodak Co. thionyl chloride was distilled from quinoline, followed by fractional distillation from linseed oil.[4] The boiling point was 76.0° at 760 mm. As needed the thionyl chloride was distilled, in an all-glass apparatus protected from water vapor, directly into a weight buret.

Aluminum chloride and ferric chloride (C.P. anhydrous) were taken from fresh bottles, stored over phosphorus pentoxide, and weighed in piggies fitted with ground caps. After each sample was weighed it was placed over phosphorus pentoxide *in vacuo* for at least 12 hours before it was used. Stannic chloride (C.P. anhydrous) was distilled through a ground joint directly into the buret from which it was weighed.

Tin (20 mesh) was screened through a Taylor standard sieve series to a particle size range of 0.598–0.883 mm. Aluminum dust was screened to 0.298–0.417 mm. range. Mercury and the other metals used were taken from a fresh container, except for sodium which was taken from storage under kerosene and cut for fresh surfaces immediately prior to testing.

Apparatus and Procedure.—Rate experiments were performed in an all-glass apparatus fitted with interchangeable ground joints and protected from the entrance of water vapor. A 50-ml. flask was connected through a vertical, water-jacketed condenser to eudiometer tubes filled with mercury. Reaction rates were measured in terms of milliliters of sulfur dioxide per minute evolved at the boiling point of the solutions used.

Because both sulfur dioxide and thionyl chloride react rapidly with mercury, silicone oil (General Electric 9981 L.T.N.V.) at a depth of 1 cm. was used as a protective layer in the eudiometer. Although the silicone oil did not stop the reaction completely, it did prevent the small amount of scum formed from sticking to the glass and thus interfering with the accuracy of the readings.

Despite performing the experiments in boiling solutions ($SOCl_2$ hydrolyzes to SO_2 and HCl) considerable difficulty was experienced in keeping the reagents and apparatus moisture-free. The procedure finally adopted was as follows. In addition to weighing out the catalysts as mentioned previously, before each run dry air was passed through the reaction flask while it was being heated to a high temperature with an open flame for 10 minutes; and during the addition of reagents a slow stream of dry air was kept flowing out the opening. Thionyl chloride, or a catalyst solution, was pumped in from a weight buret through a side-arm on the reaction flask. After the liquid was refluxing steadily, a weighed amount of metal was added through a ground joint carrying a drying tube at the top of the condenser. The drying tube was replaced for 15 seconds, to permit steady refluxing to be re-established; then it was quickly removed, the cap was put back on, and the time was recorded.

Because aluminum stuck in the condenser tube it was added in a different manner. The sample was placed in a depression blown into the lower side of a short piece of glass tubing. One end of the tubing was fitted by means of a ground joint to the side-arm of the reaction flask while a stream of dry air flowed into the other end. When the tube was turned 180° the aluminum dropped into the air stream and was blown into the flask.

III. Results

Before rate experiments were made, the products of reaction were determined by standard qualitative methods. Earlier studies of the reaction between metals and thionyl chloride[5] were carried out at temperatures above the boiling point of thionyl chloride. Depending upon various factors, different products were obtained, including both chlorides and oxides of the metals, sulfur monoxide, sulfur dioxide, sulfur monochloride and sulfur dichloride.

In our work, run at the boiling point of the liquid, the reactions always followed the same course. Sulfur, sulfur dioxide and the chloride were formed. For example, the equation for the reaction of tin with thionyl chloride at the boiling point is

$$Sn + 2SOCl_2 \longrightarrow SnCl_4 + S + SO_2$$

Sodium reacts very slowly with boiling thionyl chloride, and its rate apparently slows down with time. Possibly this behavior, which is to be investigated further, is caused by the presence of a coating of oxide or chloride. Calcium, zinc and lead do not react appreciably. Aluminum reacts rapidly, antimony very rapidly; magnesium, iron, tin,

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[1] Abstracted from a thesis submitted by R. A. Hubbard, 2nd, to the faculty of Northeastern University in partial fulfillment of the requirements for the M.S. degree, June, 1950.

[2] Presented as a part of the Symposium on Acids and Bases at the Chicago meeting of the American Chemical Society, September 6, 1950.

[3] W. F. Luder and S. Zuffanti, "The Electronic Theory of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 54.

[4] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1935, p. 399.

[5] North and Hageman, THIS JOURNAL, **34**, 890 (1912); Schenk and Platz, *Z. anorg. Chem.*, **215**, 113 (1933).

bismuth and mercury react more slowly. Analyses showed that the chlorides formed were: $AlCl_3$, $SbCl_3$, $MgCl_2$, $FeCl_3$, $SnCl_4$, $BiCl_3$ and $HgCl_2$.

Mercury, tin and aluminum were selected as most convenient for further investigation. Runs were made with 10 to 12 g. of thionyl chloride. Concentrations were calculated as molalities.

The results are shown graphically in the figures. The volume of sulfur dioxide is corrected to standard conditions. Time is given in minutes. All runs were checked at least three times.

IV. Discussion

Much of the work on reactions of metals with aqueous solutions of acids has been done with rotating plates or cylinders. Under these conditions the reactions are usually first order. Hurst and Jermyn[6] noted that at low speeds the reaction was zero order, and that the order increased to one at high speeds. As is to be expected, our reactions are zero order. The velocity constant k, given at the bottom of each figure, is equal to the slope of the straight line.

In Fig. 1, the lowest line is for the reaction of tin used after taking it from the bottle without making any attempt to clean it or to remove an oxide coating that might be present. The top lines show the increased rate (k changed from 0.445 to 1.832) after the tin had been cleaned and etched successively with dilute sodium hydroxide and hydrochloric acid solutions 10 minutes each and rinsed with alcohol and ether.

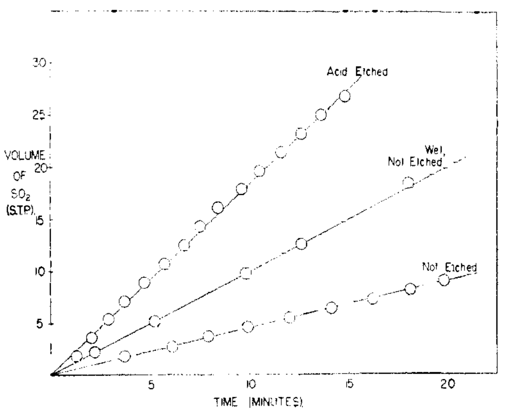

Fig. 1.—Tin and thionyl chloride: k as calculated from the curves (3.0 g. Sn, 12 g. $SOCl_2$): Sn not etched, $SOCl_2$ not dried: 1.005; Sn not etched, $SOCl_2$ dried: 0.445; Sn etched, $SOCl_2$ dried: 1.832.

The effect of traces of water in the thionyl chloride is shown by the middle line of Fig. 1, which was obtained with thionyl chloride distilled and weighed in the open.

Figures 2 and 3 show the results of adding the three acids to untreated and treated tin.

The reaction of mercury (untreated) is so much slower that the graph is plotted on a different scale in Fig. 4.

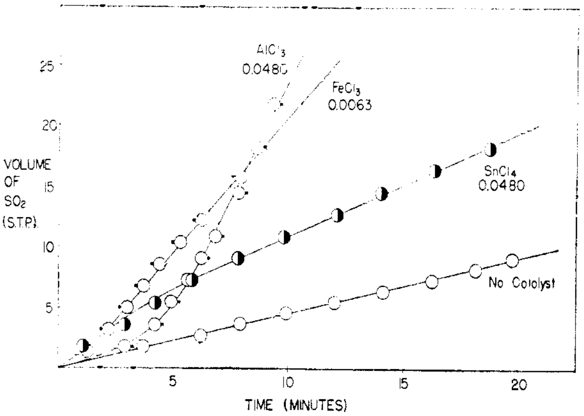

Fig. 2.—Tin and thionyl chloride (tin not etched): k as calculated from the curves (3.0 g. Sn, 12 g. $SOCl_2$): no catalyst, 0.445; $SnCl_4$, 0.860; $FeCl_3$, 2.22; $AlCl_3$, 4.00.

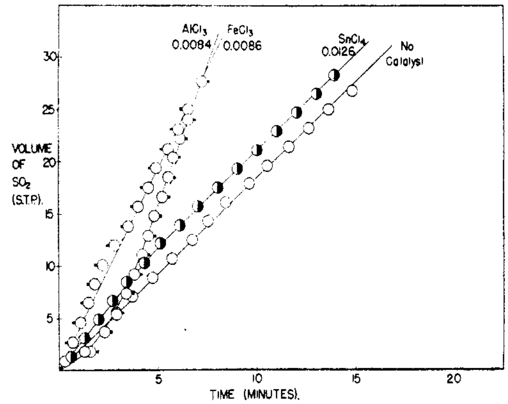

Fig. 3.—Tin and thionyl chloride (tin etched): k as calculated from the curves (3.0 g. Sn, 10 g. $SOCl_2$): no catalyst, 1.832; $SnCl_4$, 1.875; $FeCl_3$, 3.90; $AlCl_3$, 5.41.

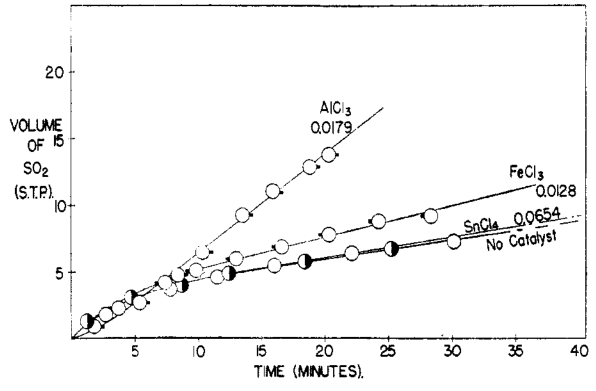

Fig. 4.—Mercury and thionyl chloride: k as calculated from the curves (5.0 g. Hg, 12 g. $SOCl_2$): no catalyst, 0.142; $SnCl_4$, 0.157; $FeCl_3$, 0.237; $AlCl_3$, 0.750.

Aluminum (Fig. 5) reacts slowly at first, then speeds up to a constant high rate. Apparently this behavior is caused by the presence of the well-known oxide coating, which was present on the untreated metal.

At the beginning of the investigation, the possibility was considered that the rates might be affected by changes in temperature of the boiling liquids caused by the presence of the solutes or by changes in atmospheric pressure. Assuming a conservatively high value for the activation energy of the reaction, the calculated effects caused by the observed small temperature changes are entirely

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[6] Hurst and Jermyn, *J. Chem. Soc.*, 158 (1950).

negligible compared to the large increases in rate caused by the presence of the acids.

Apparently the marked effects observed can be explained according to the electronic theory of acids and bases. For example, using tin and aluminum chloride to illustrate, the reaction is

$$Sn + 2SOCl_2 \longrightarrow SnCl_4 + S + SO_2$$

Although in a solvent having as low a dielectric constant as that of thionyl chloride the secondary ionization must be slight, the equations look simpler, and the result is the same, if they are abbreviated as follows.

Ionization of the solvent may be represented as

$$SOCl_2 \longrightarrow SO^{+2} + 2Cl^{-1}$$

The reducing action of the metal with solvent cations may be written

$$\begin{array}{l} Sn + 2SO^{+2} \longrightarrow Sn^{+4} + 2SO \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad S + SO_2 \end{array}$$

The acid increases the concentration of the reactive cations by combining with the basic chloride ions

$$2AlCl_3 + SOCl_2 \longrightarrow 2AlCl_4^{-1} + SO^{+2}$$

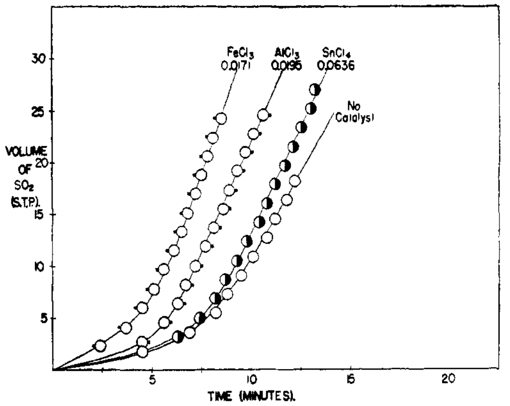

Fig. 5.—Aluminum and thionyl chloride: k as calculated from the curves (0.27 g. Al, 12 g. $SOCl_2$): no catalyst, 3.34; $SnCl_4$, 4.05; $FeCl_3$, 5.35; $AlCl_3$, 4.55.

Further investigations are under way in this laboratory involving: (1) the effect of variation in concentration of the catalysts, (2) conductimetric titrations, (3) the behavior of indicators in thionyl chloride.

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[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

The Action of Alkanols on Tetrafluoroethylene[1,2]

BY J. D. PARK, M. L. SHARRAH, W. H. BREEN AND J. R. LACHER

Saturated fluorinated alkyl ethers, RO—CF_2—CF_2H, have been prepared by adding alkanols to $CF_2{=}CF_2$ under autogenous pressure, and in the presence of a base. These ethers are quite stable. Attempts to prepare them by bubbling the olefin through a sodium alkoxide solution at atmospheric pressure failed. Their structure was proved by hydrolysis to CHF_2COOR with sulfuric acid and silica gel. Physical properties, including infrared and ultraviolet absorption spectra, are given.

Some fluorinated alkyl ethers were previously prepared and a review of the literature was reported in previous papers.[3-7]

The present paper deals with the addition of alkanols to tetrafluoroethylene under autogenous pressure in the presence of a base at temperatures below 38°: $CF_2{=}CF_2 + ROH \xrightarrow{\text{base}} R\text{-}O\text{-}CF_2\text{-}CF_2H$.

Preparation of Ethers.—The methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl alcohols were added to tetrafluoroethylene following the procedure described below for the preparation of 1,1,2,2-tetrafluoroethyl *n*-butyl ether.

Exactly 100 g. (43% excess) of a 10% sodium butoxide solution and 2 g. of du Pont "Terpene B"[8] (polymerization inhibitor) was placed in a 500-cc. capacity Parr hydrogenation bomb equipped with an auxiliary valve. The bomb was then cooled in Dry Ice, evacuated, and 75 g. of C_2F_4 transferred into it. The bomb was then allowed to come to room temperature under mechanical agitation. Reaction started at about 0°, and the temperature rose to about 35–38°. No heat must be supplied at this stage; otherwise a violent explosion may occur (due to the C_2F_4 undergoing polymerization and disproportionation to C and CF_4). After about five hours, the contents of the bomb were poured into water, the excess alcohol removed and the heavier ether layer separated, dried over calcium chloride, and subsequently fractionated under reduced pressure. About 112 g. (yield 81%) of *n*-butyl 1,1,2,2-tetrafluoroethyl ether was obtained.

Attempts to prepare the ethers by bubbling the olefin through the sodium alkoxide solution under atmospheric pressure were unsuccessful due apparently to the low solubility of the olefin in the alkoxide solution. It was also necessary to distil the *n*-butyl and *n*-amyl adducts under reduced pressure to prevent decomposition of the products.

The structure of these alcohol adducts was proved by hydrolysis[3,7] of the ether to $CHF_2C{\genfrac{}{}{0pt}{}{/\!\!/O}{\diagdown OR}}$ in the presence of sulfuric acid and silica gel. The mechanism of this addition of alcohols to tetrafluoroethylene has been previously postulated by Miller, *et al.*[5]

Physical Properties.—Some of the physical properties of the ethers are listed in Table I. The boiling points, densities and refractive indices are in line with what one might expect for an homologous series. The atomic refraction for fluorine is reasonable for compounds of this type.

The ultraviolet absorption spectra were mea-

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[1] This paper represents part of a thesis submitted by Marion L. Sharrah to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the degree Doctor of Philosophy, August, 1948.

[2] This work was supported in part by a grant from the Office of Naval Research, Contract N6-onr-231, Task Order 6, project No. NR-056-105.

[3] J. D. Park, D. K. Vail, K. R. Lea and J. R. Lacher, THIS JOURNAL, **70**, 1550 (1948).

[4] J. D. Park, M. L. Sharrah and J. R. Lacher, *ibid.*, **71**, 2337 (1949).

[5] W. T. Miller, Jr., E. W. Fager and P. H. Griswold, *ibid.*, **70**, 431 (1948).

[6] J. A. Young and P. Tarrant, *ibid.*, **72**, 1860 (1950).

[7] W. E. Hanford and G. W. Rigby (to du Pont), U. S. Patent 2,409,274 (Oct. 15, 1946).

[8] A terpene fraction consisting principally of dipentene and terpenolene boiling at 176–196° and having refractivity and density values of n^{22}_D 1.470–1.478 and $d^{15.8}_4$ 0.855–0.870.