[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

Phase Studies on the Binary Systems of Tin Tetrabromide, Tin Tetraiodide and Trichlorosilane with Some Aliphatic Ethers

BY HARRY H. SISLER, EDW. E. SCHILLING[1] AND WARREN O. GROVES

Diethyl ether and tin tetrabromide form an addition compound of low stability which melts at about 12°. The formula is probably $SnBr_4 \cdot 2(C_2H_5)_2O$. Tin tetrabromide forms the solid compounds $SnBr_4 \cdot 2C_4H_8O$ and $SnBr_4 \cdot 2C_5H_{10}O$ with tetrahydrofuran and tetrahydropyran, respectively. These products melt at about 120°. Similar addition compounds with tin tetraiodide were not obtained. Trichlorosilane shows no tendency to form an addition compound with diethyl ether, but forms a 1:1 compound with tetrahydrofuran. This compound melts at −91° and is considerably dissociated at its melting point. Some theoretical implications of these data are discussed.

Recent studies[2,3] in this Laboratory have shown that, whereas tin tetrachloride readily forms stable molecular addition compounds in the solid state with various ethers, silicon and germanium tetrachlorides do not exhibit this tendency. The formation of the tin tetrachloride addition compounds was interpreted as resulting from Lewis acid–base reactions in which the tin atom expands its valence shell by accepting a pair of electrons from each of two molecules of ether to form compounds of the type of $SnCl_4 \cdot 2R_2O$. The failure of silicon and germanium tetrachlorides to form such compounds was attributed to the size of the chlorine atom being such as to cause four of these atoms to so completely fill the coördination sphere of the silicon or germanium atom, as to effectively prevent any reaction with the ether molecules.

It was, therefore, decided to determine what would be the effect on the tendency for tin tetrachloride to react with ethers of changing the chlorine atoms for the larger bromine or iodine atoms and also to study the effect of exchanging one of the chlorine atoms in silicon tetrachloride for a hydrogen atom. Therefore, the following systems were studied: $SnBr_4$–$(C_2H_5)_2O$, $SnBr_4$–C_4H_8O, $SnBr_4$–$C_5H_{10}O$, SnI_4–C_4H_8O, SnI_4–$C_5H_{10}O$, $SiHCl_3$–$(C_2H_5)_2O$, and $SiHCl_3$–C_4H_8O [C_4H_8O = tetrahydrofuran and $C_5H_{10}O$ = tetrahydropyran].

Experimental Method

Preparation of Materials.—Tin tetrabromide was prepared by the direct action of bromine on reagent grade mossy tin. The tetrabromide was obtained as a water-white liquid freezing at 30° by fractional distillation from over an excess of tin. Tin tetraiodide manufactured by C. A. F. Kahlbaum was purified by repeated recrystallization from pure carbon tetrachloride and drying at 120°. The purity was checked by tin analysis. Found: Sn, 18.84, 18.92, 18.94. Calcd. for SnI_4: Sn, 18.95. The tin tetraiodide melted at 145.0°. The trichlorosilane was obtained from the Anderson Chemical Company and distilled through a 3-foot heated column packed with spiral helices, a constant boiling middle fraction being retained. The fraction retained froze at −126.8°.

Tetrahydrofuran and tetrahydropyran for use in these studies were contributed by the Electro-Chemicals Division of E. I. du Pont de Nemours and Co. and, after standing over sodium, were fractionally distilled through a packed column. In each case a constant boiling middle fraction was used. Diethyl ether, C.P. grade, obtained from Merck and Co., Inc., was purified in the same manner. No system was completed from a single batch of material, and, in some systems, the data were obtained using materials from several different batches.

Procedure.—The freezing points for the systems $SnBr_4$–$(C_2H_5)_2O$, $SiHCl_3$–$(C_2H_5)_2O$, and $SiHCl_3$–C_4H_8O were obtained by means of cooling curves, recorded automatically by a Leeds–Northrup Micromax temperature recorder with a copper–constantan thermocouple. The method used is discussed in detail in a previous publication.[3] The data thus obtained are believed to have an accuracy of ±1.5° except at very low temperatures where the estimated limit of error is ±2°.

Most of the freezing points in the tin tetraiodide systems were detected visually rather than by breaks in cooling curves. This was desirable because of the tendency for mixtures in these systems to supercool and also because the change in slope of the cooling curve at the freezing point for many of the compositions in these systems was very slight and therefore difficult to detect.

The tin tetrabromide–tetrahydrofuran and tin tetrabromide–tetrahydropyran compounds were prepared by adding, in an atmosphere of dry nitrogen, either component to an excess of the other component dissolved in dry petroleum ether, and cooled in an ice-bath. The solid which precipitated in each case was washed repeatedly with petroleum ether and filtered under a positive pressure of dry nitrogen. The product was then dried in a stream of nitrogen and transferred to a weighing bottle and placed in a desiccator over phosphorus pentoxide.

Method of Analysis of the Tin Tetrabromide–Ether Compounds.—The compositions of the solid addition compounds which formed with tin tetrabromide and tetrahydrofuran or tetrahydropyran were checked by bromide analysis. Samples were weighed by difference into glass stoppered erlenmeyer flasks. Several potassium hydroxide pellets were added to each sample. Each flask was then tilted so that 25–30 ml. of distilled water could be added without wetting the sample. The flask was quickly stoppered, to prevent loss of HBr formed during hydrolysis, and throughly agitated until complete solution was accomplished. The solution was then acidified with acetic acid and was titrated with silver nitrate solution using eosin adsorption indicator.

Results

The Tin Tetrabromide–Diethyl Ether System.—The data for the tin tetrabromide–diethyl ether system are recorded graphically in Fig. 1. Open circles represent freezing points, solid circles eutectic temperatures. Freezing point curves for both forms of diethyl ether were obtained but only the higher eutectic was detected. This eutectic lies at about 0.3 mole % tin tetrabromide and −118°. Another eutectic occurs at about 52 mole % of the tetrabromide at 7°. Compound formation in this system is evident but the exceedingly flat nature of the maximum in the curve indicates a high degree of dissociation at the melting point of the compound and, in general, a low degree of stability. The solid which separates in the region between the two eutectics is light yellow in color as is also the solution formed when it melts. When cooled to about −30° the solid becomes colorless. Attempts were made to isolate the compound but were unsuccessful be-

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[2] Sisler, *et al.*, THIS JOURNAL, **70**, 3818 (1948).

[3] Sisler, *et al.*, *ibid.*, **70**, 3821 (1948).

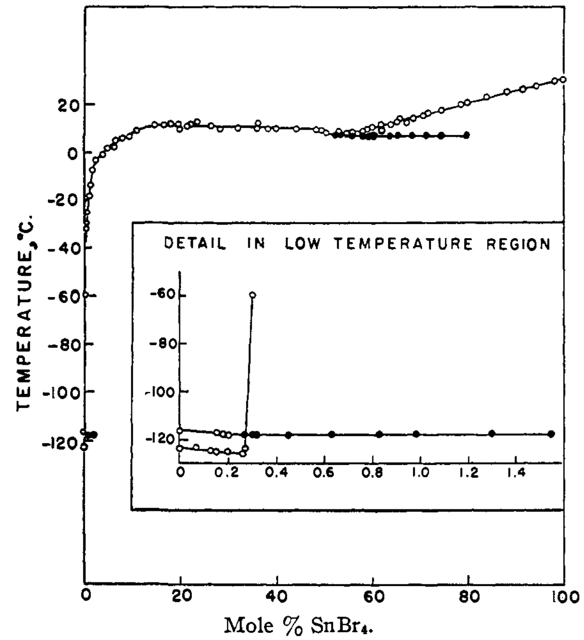

Fig. 1.—The SnBr$_4$–(C$_2$H$_5$)$_2$O system.

cause of its instability. The maximum in the curve is so flat that the composition of the compound is not precisely indicated. In view of the known behavior of tin tetrahalides toward aliphatic ethers, particularly the data reported below, the formula SnBr$_4$·2(C$_2$H$_5$)$_2$O seems a logical guess.

The Tin Tetrabromide–Tetrahydrofuran and Tin Tetrabromide–Tetrahydropyran Systems.—It was found that tin tetrabromide reacts with both tetrahydrofuran and tetrahydropyran at room temperature to form solid products. These reactions were carried out, using the methods described above, both in the presence of an excess of the ether and in the presence of an excess of the tetrabromide. With each of the ethers tin tetrabromide forms the same product regardless of which component is in excess. The compositions of the solid products were checked by bromide analysis, and found to correspond to the formulas SnBr$_4$·2C$_4$H$_8$O and SnBr$_4$·2C$_5$H$_{10}$O, respectively. Typical analytical results follow:

With tetrahydrofuran: Found: Br, 54.87, 53.83, 54.63 (product obtained from excess SnBr$_4$); 54.56, 54.61, 54.60 (product obtained from excess ether). Calcd. for SnBr$_4$·2C$_4$H$_8$O: Br, 54.87.

With tetrahydropyran: Found: Br, 52.10, 52.04, 52.02 (product obtained from excess SnBr$_4$); 52.06, 52.49, 52.09 (product obtained from excess ether). Calcd. for SnBr$_4$·2C$_5$H$_{10}$O: Br, 52.35.

The compound SnBr$_4$·2C$_4$H$_8$O as obtained is a tan colored, crystalline substance which melts with charring and vaporizes at around 120°. The solid is not extremely hygroscopic as compared to SnCl$_4$·2C$_4$H$_8$O[3] and has the odor of tetrahydrofuran. It is quite soluble in absolute alcohol, chloroform and acetone, is less soluble in diethyl ether and carbon disulfide and only slightly soluble in carbon tetrachloride and paraffin hydrocarbons. The solutions obtained vary in color from dark amber to light yellow depending upon the concentration.

The compound SnBr$_4$·2C$_5$H$_{10}$O is a pale yellow, crystalline substance which melts at about 125°, with less charring than with the tetrahydrofuran compound. It also volatilizes at about the same temperature. The tetrahydropyran compound is slightly less soluble in the various solvents tested than is the tetrahydrofuran compound. Both compounds are decomposed in aqueous solution.

The Trichlorosilane–Diethyl Ether System.—Data for the system SiHCl$_3$–(C$_2$H$_5$)$_2$O are represented graphically in Fig. 2. Because of a strong tendency toward supercooling and the low temperatures involved, complete data for this system were not obtained. However, the data which were obtained would seem to indicate that no compound formation occurs in this system. The two black circles are believed to indicate the eutectic temperature since the extrapolated freezing point curves for the two components intersect at about that temperature. Points lying on the freezing point curves for both forms of diethyl ether were obtained.

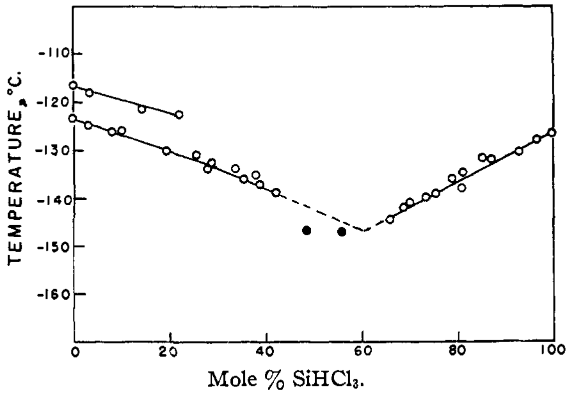

Fig. 2.—The SiHCl$_3$–(C$_2$H$_5$)$_2$O system.

The Trichlorosilane–Tetrahydrofuran System.—Data obtained for the system SiHCl$_3$–C$_4$H$_8$O are represented graphically by Fig. 3. Eutectics

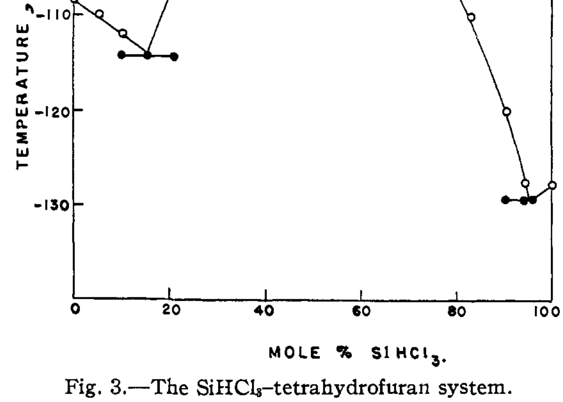

Fig. 3.—The SiHCl$_3$-tetrahydrofuran system.

occur at 96.2% mole % $SiHCl_3$ and −129.3° and at 15.3 mole % $SiHCl_3$ and −114.3°. Compound formation is indicated; the composition of the compound is apparently $SiHCl_3 \cdot C_4H_8O$ and its melting point is −91.0°. From the nature of the maximum in the freezing point curve one would conclude that the compound is considerably dissociated in the liquid state at its melting point.

The Tin Tetraiodide–Tetrahydrofuran System.—Data for this system are represented graphically in Fig. 4. The single eutectic obtained in this system contains very little tin tetraiodide and the eutectic temperature, therefore, is almost the same as the freezing point of pure tetrahydrofuran. There is a break in the freezing point curve at between 4 and 5 mole % of SnI_4 and −35°. It is not clear whether this represents formation of a compound which melts incongruently or whether it merely indicates a phase transition temperature between two forms of tin tetraiodide. The usual methods for distinguishing between these two possibilities are not readily applicable in this instance. We consider phase transition between two forms of tin tetraiodide to be the more likely possibility, however. The color of the solid phase which separates above −35° is yellow, and it is coarsely crystalline. The solid obtained below −35° is finely divided and is red in color.

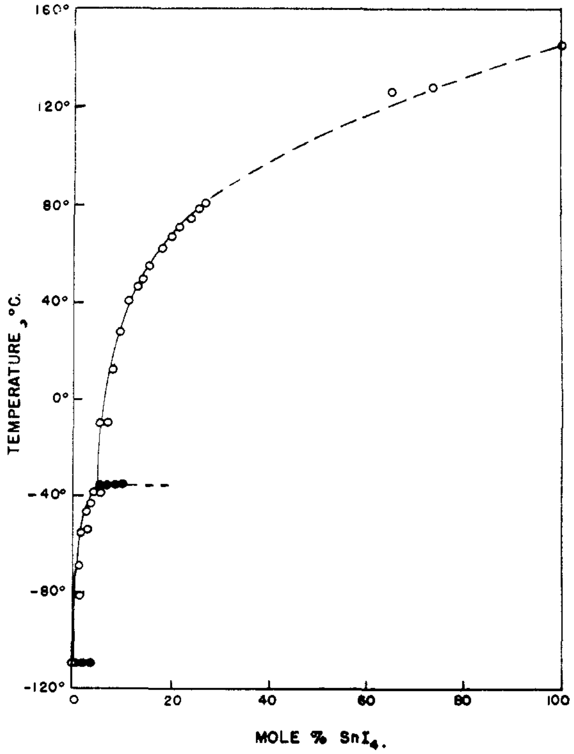

Fig. 4.—The SnI_4–tetrahydrofuran system.

Because of the high vapor pressure of ether over the mixture, freezing points in the range of about 27 to 100 mole % SnI_4 were not readily obtainable by our technique. However, the distribution of points indicates that the curve is probably continuous in this region.

The Tin Tetraiodide–Tetrahydropyran System.—Data for this system are represented graphically in Fig. 5. The single eutectic obtained in this system occurs at −51.0° and about 0.9 mole % of tin tetraiodide. Because of the high vapor pressure of ether over the mixture, the freezing point curve in the range of about 44 to 100 mole % of SnI_4 could not be determined by our technique. However, the distribution of the points which were obtained indicates that the curve from the eutectic to 100 mole % SnI_4 is probably a smooth curve. In any case, there is no positive evidence of compound formation in the system.

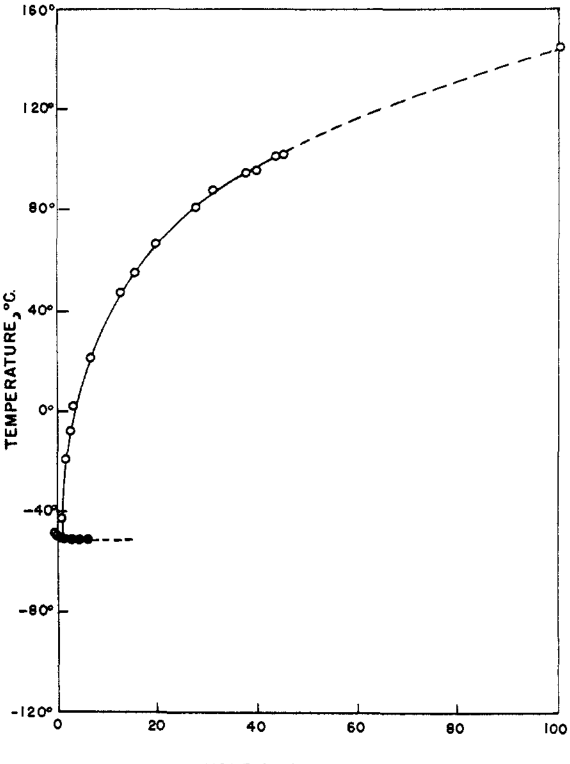

Fig. 5.—The SnI_4–tetrahydropyran system.

Discussion

Pfeiffer[4] observed the fact that the apparent ability of tin tetrahalides to form addition compounds with ethers decreases greatly with increasing size of the halide. This observation is in line with our suggestion that steric effects explain the failure of silicon and germanium tetrachlorides to form such compounds. The results reported herein support this point of view.

The addition compound of tin tetrachloride with diethyl ether $SnCl_4 \cdot 2(C_2H_5)_2O$, is stable under ordinary conditions and has a melting point of about 83°.[4] The tin tetrabromide–diethyl ether addition compound is thermally unstable at ordinary conditions and dissociates very readily under reduced pressure. Tin tetrachloride reacts vigorously with tetrahydrofuran and tetrahydropyran to yield products having no noticeable vapor pressure of ether. These reactions liberate large quantities of heat. In the corresponding tetrabromide reactions, however, little heat is evolved and the solid products obtained have noticeable

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[4] Pfeiffer, *Z. anorg. Chem.*, **87**, 335 (1914).

vapor pressures of the corresponding ethers. The melting points of the tetrabromide compounds are approximately 60° lower than those of the tetrachloride products. The study of systems involving tin tetraiodide revealed little or no tendency for the tetraiodide to form addition compounds with tetrahydrofuran and tetrahydropyran.

The replacement of one of the chlorine atoms in silicon tetrachloride by a hydrogen atom does not cause addition compound formation with diethyl ether. With tetrahydrofuran a 1:1 compound of low stability is obtained. This compound, however, may be the result of weak hydrogen bonding between the silicon and oxygen or some other process, rather than coördination between the silicon and oxygen.

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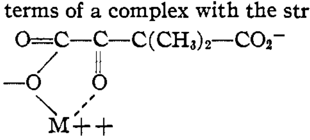
[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Metal Ion-catalyzed Decarboxylation: A Model for an Enzyme System[1]

BY RUDOLPH STEINBERGER[2] AND F. H. WESTHEIMER

A study of the decarboxylation of dimethyloxaloacetic acid, A, $RO_2C—CO—C(CH_3)_2—CO_2H$ (R = H) has shown that the first product of decarboxylation is the enol form of α-ketoisovaleric acid. Similarly, the monoethyl ester of A, ($R = C_2H_5$) yields the enol form of ethyl α-ketoisovalerate. The enols have been identified spectroscopically and by bromine titration. The decarboxylation of dimethyloxaloacetic acid is catalyzed by heavy metal-ions, whereas that of the mono ester is not. The *p*H-rate profiles for these decarboxylation reactions show that the anion of the ester, the mono and dianions of the diacid, and a complex of the diion with metal ions, undergo decarboxylation. The effect of metal ions, M, on the decarboxylation reaction has been interpreted in terms of a complex with the structure

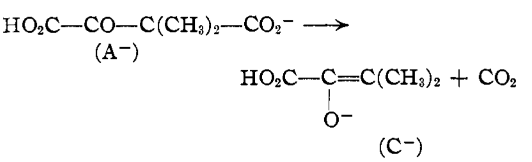


The results obtained with dimethyloxaloacetic acid have been compared with those for the enzymatic and non-enzymatic decarboxylation of oxaloacetic acid itself, and a tentative hypothesis has been formulated to account for the role of the protein in the enzymatic process.

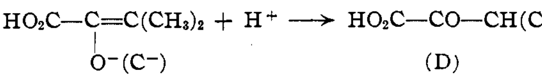
Introduction

In a recent communication, the authors[3] outlined a synthesis of dimethyloxaloacetic acid, A, $HO_2CCOC(CH_3)_2CO_2H$ and of its monoethyl ester, B, $C_2H_5O_2CCOC(CH_3)_2CO_2H$; they further showed that the decarboxylation of the acid is catalyzed by heavy metal ions, whereas the monoethyl ester is essentially unaffected by these ions. From these facts it was concluded that the metal ion which catalyzes the decarboxylation of dimethyloxaloacetic acid (and by analogy of oxaloacetic acid) must be coördinated with that carboxyl group of the diacid which is not lost during the reaction.

The present paper gives in detail a proposed mechanism by which metal ions catalyze certain decarboxylations. The proposed mechanism for the decarboxylation of A^-, the monoanion of dimethyloxaloacetic acid, is shown in equations (1) and (2)



$$\underset{(\mathrm{A}^-)}{\mathrm{HO_2C{-}CO{-}C(CH_3)_2{-}CO_2^-}} \longrightarrow \mathrm{HO_2C{-}}\underset{\underset{(\mathrm{C}^-)}{\mathrm{O}^-}}{\mathrm{C}}\mathrm{{=}C(CH_3)_2 + CO_2} \quad (1)$$



$$\mathrm{HO_2C{-}}\underset{\mathrm{O^-\,(C^-)}}{\mathrm{C}}\mathrm{{=}C(CH_3)_2 + H^+} \longrightarrow \underset{(\mathrm{D})}{\mathrm{HO_2C{-}CO{-}CH(CH_3)_2}} \quad (2)$$

The intermediate first formed is the enol, C, or enolate ion, C^-, of α-ketoisovaleric acid, D; this ion is stable enough to be identified both spectroscopically and by bromine titration. During the catalyzed decarboxylation, a metal ion complex of the diion is probably formed. The effect of various complex-forming agents upon the rate of the catalyzed decarboxylation is interpreted, and a possible role for the enzyme in an enzyme-catalyzed decarboxylation of oxaloacetic acid is discussed.

Experimental

Kinetic Method

Apparatus.—Most of the kinetic determinations were made in a manometric apparatus of a familiar type.[4] The reaction rate was followed by measuring the amount of carbon dioxide evolved at various stages of the reaction. The sample of β-keto acid was introduced into the reaction mixture by means of a platinum bucket, which was suspended from the ground glass stopper of the reaction vessel; the bucket was dropped into the reaction mixture by rotating the stopper. Both reaction flask and manometer were immersed in a thermostat held at 25.00 ± 0.02°. Readings were taken through a window in the bath.

In most of the reactions here reported the reaction flask was shaken at a rate of 240 to 310 oscillations per minute. Slower rates were sometimes satisfactory; but in concentrated buffer solutions the slower shaking rate failed to bring about the prompt evolution of CO_2, even from creased flasks, and apparent induction periods, as long as an hour, were observed.

Retention of CO_2.—The manometric method just mentioned was used with solutions having a $pH < 6$. There is undoubtedly some retention of CO_2 by solutions where the $pH > 5$; this effect, however, is quite small and the amount of CO_2 evolved corresponds almost quantitatively to that shown in equation (1). In general, the evolution of CO_2 is somewhat slow at the beginning of an experiment, but reaches the first-order rate before the reaction has proceeded 5% to completion.

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(1) Presented at the 118th Meeting of the American Chemical Society, at Chicago, September, 1950.

(2) Atomic Energy Commission Predoctoral Fellow, 1949-1950.

(3) R. Steinberger and F. Westheimer, THIS JOURNAL, **71**, 4158 (1949).

(4) J. Brönsted and C. King, *ibid.*, **47**, 2523 (1925).