[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, No. I, 32]

STUDIES RELATING TO METALLO-ORGANIC COMPOUNDS. I. INTRODUCTION. II. THE EQUIVALENT CONDUCTANCE OF TRIMETHYLSTANNYL CHLORIDE IN ETHYL ALCOHOL

BY CHARLES A. KRAUS AND CONRAL C. CALLIS

RECEIVED SEPTEMBER 8, 1923

Introduction

The metallo-organic compounds, that is, compounds in which metallic elements appear united with carbon groups, have attracted marked attention within recent years after having passed through a long period of neglect. But even now efforts are directed chiefly towards the preparative side, while the physicochemical properties of these compounds remain largely undetermined. It might be expected that in the metallo-organic compounds the metallic elements function in a manner analogous to carbon in ordinary carbon compounds and that here, if anywhere, substances might be formed which should serve to bridge the gap between inorganic and organic compounds. The present series of investigations was undertaken for the purpose of supplying further knowledge in this field, particularly in relation to the constitution and physicochemical properties of certain of these compounds.

The metallo-organic compounds may be divided into several classes: first, the derivatives of the normal elements of the fifth, sixth and seventh groups; and second, the derivatives of the normal elements of the first, second, third and fourth groups and of certain of the heavier elements of other groups.

The members of the first class of substances are, in general, more stable than those of the second. They may be looked upon as organic derivatives of the normal hydrides of the elements in question, although the hydrides, as a rule, are much less stable than the corresponding organic derivatives.

The elements of this group form mixed compounds in which the valences of the central element may be partially satisfied by hydrogen and partially by hydrocarbon groups. Other mixed compounds may also be formed in which a portion of the valences may be satisfied by electronegative elements or groups. These latter compounds are not, as a rule, very stable, particularly with respect to water, which hydrolyzes them readily. They do not appear to possess salt-like properties in a marked degree. Some of the elements of this group are metallic and others non-metallic and there is nothing to indicate that any marked distinction exists between compounds derived from metallic and those derived from non-metallic elements.

A remarkable property of the members of this group of substances is their power of combining with acids and with the organic halides to form stable compounds of the formula $M''R_{n+1}X$, in which n is the normal valence of the element with respect to hydrogen, R is a univalent organic group or hydrogen, and X is an electronegative element. These compounds, which are well known, being represented by the substituted ammonium, sulfonium and iodonium salts, exhibit marked electrolytic properties, in that they are highly ionized in water as well as in practically all other solvents of higher dielectric constant, are conductors of electricity in the fused condition, and yield strong bases. Thus, the substituted ammonium, sulfonium and iodonium bases, as well as the bases of other elements of these groups, are practically as strong as the hydroxides of the alkali metals.

The second group of compounds, derived from the elements of the first, second, third and fourth groups, as well as from certain other heavy elements, may likewise be looked upon as organic derivatives of the hydrides of these elements. But while the hydrides have a relatively low stability, particularly in the case of the less electropositive elements, the corresponding organic derivatives are comparatively stable. These may be divided into two sub-groups, depending upon whether the element in question is strongly electronegative or strongly electropositive. In the case of the strongly electropositive elements such as sodium, the compounds are solids at ordinary temperatures, and exhibit, to some degree at least, electrolytic properties resembling those of the corresponding hydrides in this respect.[1] The corresponding compounds of the less electronegative elements are, as a rule, mobile liquids at ordinary temperatures, having low freezing points and exhibiting no electrolytic properties. In a few instances mixed compounds are known in which hydrogen and organic groups both occur. In many instances, too, mixed compounds containing organic groups and strongly electronegative elements or groups of elements are formed, many of which are comparatively stable. However, those compounds containing two or more electronegative elements or groups show a considerable tendency to hydrolyze in the presence of water or other similar solvents.

The most interesting representatives of this series of compounds are those corresponding to the formula $M^nR_{n-1}X$, in which a single valence of the central element is satisfied by a strongly electronegative element or group. These compounds have ordinarily been looked upon as salts, and indeed they exhibit numerous properties common to salts. Thus, solutions of these compounds in water or the alcohols conduct the electric current,[2] while they yield corresponding bases of the type $M^nR_{n-1}OH$, which exhibit marked alkaline properties in aqueous solution. It should be pointed out, however, that these bases are weak when compared with bases of the

---

[1] Hein, *Z. Elektrochem.*, **28**, 469 (1922).

[2] (a) Bredig, *Z. physik. Chem.*, **13**, 303 (1894). (b) Zelinsky and Krapiwin, *ibid.*, **21**, 47 (1896).

type $M^{n}R_{n+1}OH$. Thus, the ionization constant[2a] of trimethyl tin hydroxide at 25° is 1.7×10^{-7}.

While the compounds of the type $M^{n}R_{n-1}X$ have ordinarily been classed among the electrolytes or the salts, their behavior, even in solution in various solvents, would appear to indicate that they are not true salts. Thus Zelinsky and Krapiwin have determined the equivalent conductance of triethyl tin iodide in methyl alcohol[2b] and have found that the solutions are not as highly ionized as are the corresponding solutions of typical salts, while at the same time they conform approximately to the law of mass action. The same is true of diethyl tin di-iodide in the same solvent, which here, however, appears to behave like a binary electrolyte.

The physical properties of the pure compounds do not correspond with those of salts. The mere fact that most of these substances have comparatively low melting points and are comparatively volatile at ordinary temperatures would appear to indicate that they are not true salts. Perhaps the most typical example of substances of this type is trimethyl tin iodide, which is a liquid boiling at about 170° and melting slightly above 0°. The properties of the corresponding bromide and chloride are similar to those of the iodide, the boiling points being somewhat lower and the melting points somewhat higher.

These compounds are characterized by their ready solubility in a great variety of liquids. At ordinary temperatures, trimethyl tin iodide, for example, is miscible (in all proportions) with water, alcohol, ether, acetone, petroleum ether, benzene, toluene, etc. Only in the case of ammonia and various amines does a solid phase appear. In this case, the solid phase consists of a compound between trimethyl tin iodide and the solvent. The nature of the compound here involved will be discussed more fully subsequently.

Compounds of this class do not conduct the electric current in the pure liquid condition. Thus the specific conductance of trimethyl tin iodide is below 0.3×10^{-5}. What the true value of the conductance of this substance is cannot readily be determined, owing to the fact that traces of impurity have a strong influence on its conductance and the purification of these substances is not readily accomplished. The other halides of the trimethyl tin group exhibit properties corresponding to those of trimethyl tin iodide. So, also, amyl mercury iodide in the fused state is a poor conductor of the current. It is probable that all substances of this type are non-electrolytes in the fused condition.

In solution in various solvents the compounds of this type exhibit marked divergence from ordinary salts. In Table I are given approximate values of the conductance of trimethyl tin iodide in different solvents.

An examination of this table will show that while trimethyl tin iodide conducts the current fairly readily in certain solvents, in other solvents it is virtually a non-conductor. Furthermore, there is no relation between the conductance of the solutions and the dielectric constant of the solvent medium. Thus the conductance in nitrobenzene and nitromethane, of dielectric constants 36 and 39, respectively, is little higher than that in ether or benzene. In other words, dissolved in these solvents, trimethyl tin iodide is not an electrolyte. On the other hand, in acetone, pyridine, and the alcohols, trimethyl tin iodide conducts the current fairly readily, the ionization in general being higher, the higher the dielectric constant of the medium, with the exception of acetone, in which solvent the conductance is markedly lower than even in amyl alcohol although the fluidity of acetone is much higher than that of amyl alcohol. It would appear that the electrolytic properties of solutions of trimethyl tin iodide are due to some specific interaction with the solvent medium. Apparently, those solvents containing basic oxygen or nitrogen atoms form electrolytic solutions. On the other hand, solvents which do not contain basic oxygen or nitrogen atoms yield non-conducting solutions, irrespective of the value of the dielectric constant.

TABLE I

CONDUCTANCE OF TRIMETHYL TIN IODIDE IN VARIOUS SOLVENTS

Specific cond. of $(CH_3)_3SnI = 0.3 \times 10^{-5}$

Solvent	Dielectric const.	Dilution	Specific cond.	Equiv. cond.
Benzene	2.3	0.271	2.21×10^{-6}	...
Ether	4.4	0.677	1.27×10^{-5}	...
Nitrobenzene	36	0.948	1.02×10^{-5}	...
Nitromethane	39	0.948	5.70×10^{-5}	...
Benzonitrile	26	0.271	1.58×10^{-4}	...
Methyl salicylate	8.8	0.406	3.68×10^{-6}	...
Ethyl acetate	6.1	0.406	7.37×10^{-5}	...
Acetone	22	0.271	4.42×10^{-3}	0.120
		92.5	2.48×10^{-5}	0.229
Amyl alcohol	16	0.271	1.44×10^{-2}	0.390
		8.67	5.84×10^{-5}	0.503
Benzyl alcohol	13	0.271	8.86×10^{-2}	2.40
		8.67	3.81×10^{-3}	3.30
Pyridine	13	0.215	7.03×10^{-2}	1.51
		13.72	1.92×10^{-3}	2.65
Ethyl alcohol	26	0.271	4.41×10^{-2}	1.20
		1.084	2.22×10^{-2}	2.41

It may be surmised that the electrolytic properties of solutions in the amines and the alcohols and similar compounds are due to the formation of compounds of the ammonium and oxonium type. That this is actually the case will be shown in other numbers of this series.

The Equivalent Conductance of Trimethyl Tin Chloride in Ethyl Alcohol

The work of Zelinsky and Krapiwin, as well as our own preliminary measurements, indicates that the trimethyl tin halides are ionized in alcoholic solution, although less than are the corresponding typical salts. It appeared of interest to determine the true degree of ionization of one of these compounds in alcohol, as well as to determine whether or not the law of mass action is here applicable.

Materials and Apparatus.—Trimethyl tin chloride was prepared by chlorinating tin tetramethyl which had previously been purified by treating with ammonia vapor to precipitate any halide present, leaving behind the tin tetramethyl.[3] Chlorination is readily effected by leading dry chlorine through tin tetramethyl cooled in ice water with the exclusion of daylight. The trimethyl tin chloride is separated from any excess tin tetramethyl by fractional distillation and is finally purified by successive recrystallizations from low-boiling petroleum ether at low temperatures. The last traces of petroleum ether are removed by means of a vacuum pump.

Trimethyl tin chloride crystallizes in the form of needles melting at 37°.

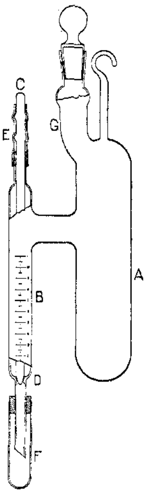

Fig. 1
Weight buret

Absolute alcohol was prepared by dehydrating 95% alcohol with lime in the usual way. This product was then treated with freshly dehydrated copper sulfate, 1 kg. of copper sulfate for 6 liters of alcohol, the whole being heated under a reflux condenser for several days, with a slow stream of air passing through the apparatus. The alcohol was then vaporized with a stream of pure dry air passing through it; about $^3/_4$ of the vapor was condensed and collected for use, the remainder passing by and being later condensed and rejected. By this method, alcohol having a specific conductance of 3.0×10^{-8} was obtained.

The conductance apparatus and thermostat employed were similar to those earlier employed in this Laboratory and described elsewhere in THIS JOURNAL.[4]

The cell employed was that previously used by Kraus and Kurtz[5] in this Laboratory; its constant was found to be 0.018286 ± 1. All measurements were carried out at 25.00 ± 1°.

For the preparation of dilute solutions of known concentration, a stock solution was made up by introducing a known weight of trimethyl tin chloride into a known weight of alcohol contained in a special weight buret, shown in Fig. 1. A is the body of the buret containing the solution. G is a side arm carrying a ground-glass stopper through which the constituents of the solution are introduced. B is an arm graduated in cc., the bottom of which is closed by means of the rod C, which is ground and polished into its seat at D. The rod C is attached to the upper end of the side tube B by means of the short length of pure rubber tubing E. The delivery tube of the buret is closed by the tube F. The solution in the buret at no time comes in contact with a lubricated surface. Approximately the desired amount of solution is introduced into the side arm B, after which the end of the buret is introduced into the cell and the liquid in B is allowed to run out by raising the rod C. When all the liquid has run out, the buret is removed from the cell and the cap F replaced, and the amount of solution introduced into the cell is determined by reweighing the buret. This apparatus has been found extremely useful in handling liquids which dissolve stopcock lubricant.

The cell was removed from the bath after each addition of solution, and the contents were thoroughly mixed. The cell was then returned to the thermostat and conductance

---

[3] Werner and Pfeiffer, *Z. anorg. Chem.*, **17**, 82 (1898).

[4] Kraus and Parker, THIS JOURNAL, **44**, 2429 (1922).

[5] Kraus and Kurtz, *ibid.*, **44**, 2463 (1922).

measurements made at intervals until a constant value was reached. This procedure was repeated until check readings were obtained. At the lower concentrations, a slow change in the value of the conductance took place with time, which rendered these observations somewhat uncertain. At higher concentrations, this effect was not observed; it was greatly accentuated in case the specific conductance of the alcohol was high. In the case of the iodide the effect was much more pronounced than in that of the chloride and could not be overcome at the time.

Experimental Results.—In Table II are given the results of a series of measurements with trimethyl tin chloride at 25°. The specific conductance of the solution given in the second column has been corrected for the specific conductance of the solvent, whose value is given at the head of the table. The equivalent conductance is given in the third column and the mass-action function, $K \times 10^4$, in the last column.

Table II

Conductance of Trimethyl Tin Chloride in Absolute Alcohol at 25°

347.37 g. of absolute alcohol. Specific conductance, l, of alcohol $= 0.305 \times 10^{-7}$. Cell constant, 0.018286. Solution added contained 4.83% of $(CH_3)_3SnCl$ by weight

Concn. $\times 10^3$	Specific Cond. $l \times 10^7$	Equivalent cond. Λ	$K \times 10^4$
0.1566	17.88	11.42	0.346
0.2600	24.16	9.29	.344
0.3178	27.56	8.67	.356
0.6219	40.09	6.45	.350
1.0441	53.36	5.11	.349
1.8773	72.91	3.89	.347
3.0545	94.55	3.10	.349
4.9749	122.58	2.46	.350
8.9449	167.47	1.87	.356
16.5707	234.09	1.41	.369

Discussion.—The results are shown graphically in Fig. 2, values of $1/\Lambda$ being plotted as ordinates and values of the specific conductance as abscissas. If the law of mass action is applicable, the experimentally determined points, according to this plot, should lie on a straight line, the intercept of which on the axis of ordinates yields the value of $1/\Lambda_0$ and the slope of which gives the value of K/Λ_0^2, from which the value of K may be determined.

An examination of the plot will show that, with the exception of two or three determinations at higher concentrations, the points lie on a straight line practically within the limits of the experimental error. This is also indicated by the value of the mass-action constant as given in the last column of Table II. The plot yields for Λ_0 the value 30.8, and for K the value 0.349×10^{-4}.

It is evident that the law of mass action holds very nearly up to a concentration of 10^{-3} equivalents per liter, while at higher concentrations there is a slow deviation in the same direction as in the case of ordinary electrolytes in solvents of higher dielectric constant. This electrolyte in alcohol, therefore, resembles moderately weak acids and bases in water and moderately strong acids in alcohol. This is a striking fact, inasmuch as it is practically the first instance of an electrolyte, other than an acid or a base, which has been shown to conform to the law of mass action in solvents of higher dielectric constant.

Heretofore, the only weak electrolytes known have been the acids and bases. It appears, however, that, in general, compounds of the type $M^nR_{n-1}X$ are comparatively weak electrolytes.

Actually, the compounds of this type have many properties in common with the acids. As has already been pointed out, in the pure liquid state they are indifferent conductors of the electric current. In solution they act as electrolytes only when dissolved in solvents of the basic type, such as ammonia, water, etc. This is also true of the acids. In the case of the acids, the conductance is accounted for on the assumption that a compound of the type $M^nH_{n+1}X$ is formed between the acid and the solvent. As will later be shown, the compounds of the type $M^nR_{n-1}X$ likewise combine with solvents of the ammonia and water type to form new compounds of the type $M^nR_{n+1}X$. These compounds, therefore, so far as their physicochemical properties are concerned, may be classed with the acids.

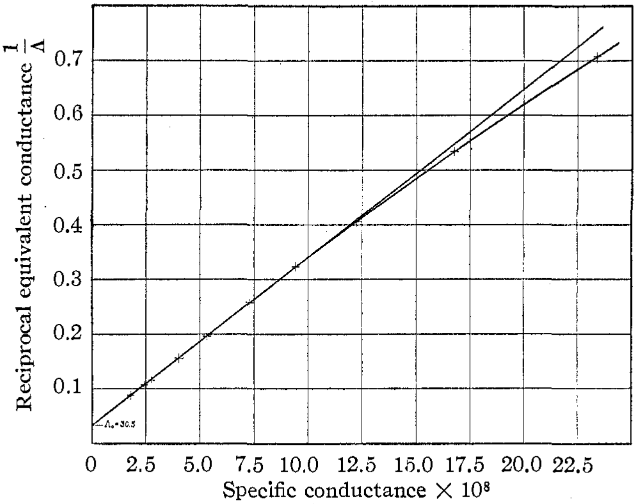

Fig. 2.—Approach of conductance values to the mass-action relation of solutions of $(CH_3)_3SnCl$ in absolute alcohol

That this should be the case is not unexpected, as has been pointed out by one of the authors.[6] The behavior of an element, or a group of elements, in its compounds with other elements or groups, is determined by its position in the potential series. A strongly electropositive group combined

---

[6] Kraus, *Rec. trav. chim.*, **42**, 588 (1923).

with a strongly electronegative element or group yields an electrolyte, that is, a compound which is ionized in the pure state as well as in solution. As the electropositive constituent becomes less electropositive, the electrolytic properties of the resulting compound become less pronounced, the specific conductance of the pure substance in the liquid condition diminishes and its ionization in solution, under otherwise comparable conditions, likewise diminishes. When the electropositive constituent lies somewhere near the middle of the potential series, in other words, when its position corresponds with that of hydrogen, the compound will exhibit practically no electrolytic properties, or only weakly electrolytic properties in the pure state and, in general, will not exhibit electrolytic properties in solution. Only in case the group is capable of associating itself with the solvent, or some added substance, to form a new and more electropositive group will solutions of these compounds exhibit electrolytic properties.

That a group of the type of the trimethyl tin group lies intermediate in the potential series is further shown by the fact that this group forms a stable negative as well as positive ion. In fact, compounds in which this group acts electronegatively are probably true salts. Thus, compounds of the type $(CH_3)_3SnNa$ may readily be formed, and these compounds exhibit marked electrolytic properties in solution and in general behave like salts. Such compounds will be discussed more fully in a succeeding article.

Summary

1. The metallo-organic compounds corresponding to the formulas $M^{n}\mathbf{R}_{n+1}X$ and $M^{n}\mathbf{R}_{n-1}X$ exhibit electrolytic properties, but only the members of the first class are true electrolytes. The members of the second class exhibit electrolytic properties only under particular conditions.

2. Data are given for the conductance of trimethyl tin iodide in the pure state and in solution in various solvents. The pure compound is a poor conductor, while solutions of this compound in solvents of the non-basic type are likewise poor conductors, even though the dielectric constant of the solvent may be high. Solutions in the alcohols and the amines are relatively good conductors.

3. The equivalent conductance of trimethyl tin chloride in absolute alcohol at low concentrations has been measured. From these measurements the value 30.8 is deduced for Λ_0. Up to a concentration of 10^{-3} N, the conductance values conform to the law of mass action within the limits of the experimental error. The mass-action constant has the value 0.349×10^{-4}.

4. The properties of compounds of the type of trimethyl tin chloride are discussed. It is suggested that the electrolytic properties of solutions of this and similar compounds in the alcohols and the amines are due to

the formation of a more electropositive group by combination of the trimethyl tin group with the solvent. It is pointed out that the properties of trimethyl tin chloride correspond closely to the properties of methyl iodide and more particularly to those of the halogen acids.

5. The properties of the trimethyl tin group and of its compounds may be accounted for on the basis of the electro-affinity of this group. The analogy which this group bears to hydrogen is pointed out.

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 32]

THE FREE ENERGY AND HEAT OF FORMATION OF LEAD MONOXIDE

BY DAVID F. SMITH[1] AND HUBERT K. WOODS

RECEIVED SEPTEMBER 11, 1923

Introduction

The purpose of this investigation was to determine the change in the free energy and heat content when lead oxide (PbO) is formed from its elements at 25°.

Apparently no measurements have yet been made from which the free energy of lead oxide may be accurately obtained. High-temperature equilibria would doubtless be complicated by the formation of other oxides of lead and always involve a more or less unreliable extrapolation to standard temperature on account of inaccurate heat data. Lewis and Randall[2] have attempted to calculate the free energy of lead monoxide from solubility measurements and molal free energies but obtain a very uncertain value. As the results of Berl and Austerweil[3] show, in solutions of lead monoxide there is considerable formation of complex ions such as $PbOH^+$, so that the activity of the lead ion would be difficult to estimate even in very dilute solutions. Lewis and Randall[2] have also pointed out the probable uncertainty in the thermochemical value of the heat of formation of lead monoxide and the excessive discrepancy between their approximate value of its free energy and that obtained by using low-temperature specific-heat data, heats of reaction, and the constant entropy principle (the so-called "third law of thermodynamics").

Since lead oxide is only slightly soluble in dilute alkaline solutions, a measurement of the electromotive force of cells such as $H_2(g) \mid$ dil. alkaline solution $\mid PbO(s) + Pb(s)$ should give directly a measure of the free-energy change in the reaction $H_2(g) + PbO(s) = Pb(s) + H_2O(l)$. A combina-

---

[1] National Research Fellow in Chemistry.

[2] Lewis and Randall, "Thermodynamics," McGraw-Hill Co., New York, **1923**, p. 497.

[3] Berl and Austerweil, *Z. Elektrochem.*, **13**, 165 (1907).