In conclusion, then, it is shown that high yields of tetraethyllead can be obtained by the reaction of tetravalent lead salts with the ethyl derivatives of the electropositive metals. The less reactive ethyl metal compounds, diethylmercury and ethylaluminum sesquibromide, do not produce tetraethyllead but simply reduce the tetravalent lead salt to the divalent lead salt. Metallic lead results in all reactions in which tetraethyllead is produced. The primary factor which determines the yield of tetraethyllead is the stability of the monoethyllead compound produced as the first intermediate. With potassium hexachloroplumbate a secondary reaction can occur to produce tetraethyllead. This reaction involves the ethylation of the by-product lead metal by the ethyl metal compound and the ethyl chloride which is formed on decomposition of the unstable ethyllead trichloride which forms as the first intermediate. Ethyllithium, ethyl Grignard reagent and diethylzinc are the only ethylmetal compounds found to be reactive in this secondary reaction.

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An Electromotive Force Investigation of the Product of the Solution of Antimony in Liquid Antimony Triiodide[1]

BY JOHN D. CORBETT AND FRANK C. ALBERS

RECEIVED AUGUST 5, 1959

Formation of a lower iodide of antimony is strongly suggested by the transport of metal by gaseous SbI_3 and by the solution of the metal in liquid triiodide. The oxidation–reduction process relating the unknown solute and SbI_3 has been investigated at 251° by electromotive force measurements on the cell $C|Sb(N_M{}^0), SbI_3 \vdots Sb(N_M), SbI_3|C$ where the solution of mole fraction "dissolved" metal $N_M{}^0$ in equilibrium with solid metal serves as a reference electrode. Treatment of the results in terms of a general electrode reaction indicates that the solute is formed by a two electron reduction of SbI_3. The assumption that ions derived from the solvent carry the current within the cell is supported by similar results obtained for solutions containing 2 to 5 mole % added KI. The product of the reaction of antimony with liquid SbI_3 appears to be the catenated Sb_2I_4; the alternative, a diamagnetic, solvated SbI, is considered less likely.

Introduction

Although antimony triiodide is the only known iodide of antimony stable in the solid state, there is some evidence that significant amounts of reduction to a lower iodide may occur when the product can exist at low concentrations. The transport of the non-volatile antimony metal by gaseous SbI_3 at 300° is fairly unequivocal evidence for the formation of a subiodide, and the apparent solution of the metal in molten SbI_3, 1.69 mole % at 201° and 5.8% at 400°, also has been attributed to a similar reaction in the liquid state.[2]

In this particular case, application of the technique of acid-stabilization that has allowed the isolation of the lower oxidation states from other such systems[3] has not proved fruitful. The amount of reduction of SbI_3 is essentially unchanged by the addition of either AlI_3 or ZnI_2 to the melt, probably as a result of the small basicity of the molecular SbI_3 toward these acids.[4]

A study of the number of electrons involved in the oxidation–reduction process relating the lower halide (or metal) and the normal, solvent salt (as might be determined from concentration cell measurements) should be a particularly useful means of characterizing the solute in such solutions. This approach to the study of metal–metal halide solutions was pioneered by Karpachev and co-workers.[5–7] Using carbon as oxidation–reduction electrodes, they reported that the dependence of cell voltage on the concentration of "dissolved" metal indicated that molten solutions of $CdCl_2$, $PbCl_2$ and LiCl reacted with the respective metals to form Cd^0[5] (or $Cd_2{}^{+2}$), Pb^+[7] and Li^0 or $Li_2{}^+$[6] as solutes. In addition, the Ce–$CeCl_3$ system recently has been investigated, using a CeCl–Cl_2 reference electrode, by Senderoff and Mellors.[8] The present paper is concerned with a study of concentration cells with solutions of antimony in SbI_3 and the interpretation of the simple dependence of voltage on the amount of "dissolved" metal for this system.

Experimental

Somewhat different techniques than those previously reported[5] are necessary in the present system. The cell found most suitable for the concentration cell measurements is shown in Fig. 1. The electrodes consist of $^1/_2$'' sections of $^1/_8$'' spectroscopic electrodes (National #L3803) drilled $^3/_{16}$'' deep from one end and then heated to 1000° *in vacuo* to remove the binder. These slip over $^1/_{16}$'' tungsten wires which are sealed through the Pyrex cell with uranium glass. The diaphragm is a 10 mm., ultrafine, sintered glass disk; occasionally this was partially fused so as to decrease its area and porosity. Approximate amounts of metal (A. D. MacKay, 99.999%) were placed in the two compartments, with excess in the anode so that the so-called metal-satu-

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[1] Presented at the 135th meeting of the American Chemical Society, Boston, Mass., April 6, 1959. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] J. D. Corbett, S. v. Winbush and F. C. Albers, THIS JOURNAL, **79**, 3020 (1957).

[3] J. D. Corbett and R. K. McMullan, *ibid.*, **78**, 2906 (1956); R. K. McMullan and J. D. Corbett, *ibid.*, **80**, 4761 (1958); J. D. Corbett, W. J. Burkhard and L. F. Druding, to be published.

[4] S. v. Winbush and J. D. Corbett, unpublished.

[5] S. Karpachev and A. Stromberg, *Zhur. Fiz. Khim.*, **13**, 397 (1939).

[6] S. Karpachev and E. Jordan, *ibid.*, **14**, 1495 (1940).

[7] S. Karpachev, A. Stromberg and E. Jordan, *ibid.*, **18**, 43 (1944).

[8] S. Senderoff and G. Mellors, *J. Electrochem. Soc.*, **105**, 224 (1958).

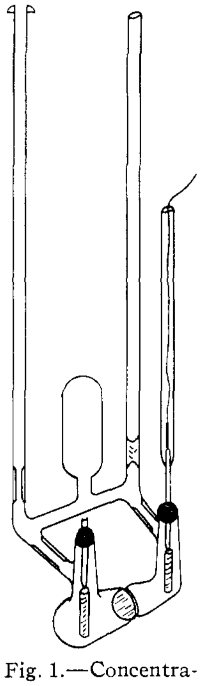

Fig. 1.—Concentration cell.

rated melt served as a reference solution. The SbI_3, m.p. 166.5 ± 0.5°, prepared from the metal and excess iodine in a sealed tube, and vacuum sublimed several times, was melted into the central bulb attached to the cell. The apparatus then was sealed from the line *in vacuo*, the salt melted down into the electrode compartments, and each of these sealed from the bulb by collapsing the connecting tubing. The cell was immersed to above the tungsten seals in a molten $LiNO_3$–$NaNO_3$–KNO_3 bath controlled to 251 ± 1° by an auxiliary heater operated by a West–Gardsman controller. As noted during earlier solubility experiments,[2] equilibration of metal and SbI_3 is quite slow, and 18 to 24 hr. is required to attain a stable potential. A Leeds and Northrup K-2 potentiometer and 2430-A galvanometer are necessary in order to attain an adequate sensitivity, as SbI_3 in the cell has a minimum resistance of about 30 KΩ and this changes insignificantly as metal dissolves. The graphite electrodes appear to reach equilibrium fairly rapidly, as judged from the recovery after intentional polarization. Tungsten electrodes polarize somewhat more readily while Ta and Pt electrodes alloy with antimony. Graphite shows no detectable reaction with pure SbI_3.

Because of the high fluidity and appreciable vapor pressure (*ca.* 25 mm.) of SbI_3, significant flow through the diaphragm occurred during the time necessary for equilibration, and the catholyte concentration therefore could not be determined from the initial amount of metal therein. Multiple additions of metal to the catholyte by means of fragile ampoules sealed within the cell gave unreliable results for the same reason, and changing the catholyte concentration by electrolysis was not practical because of the high resistance of the cell. As a consequence of these factors the voltage–concentration data reported herein were obtained individually from separate cells; after a voltage measurement at equilibrium the cell was quenched with the solutions not in contact with the diaphragm (by means not shown) and the catholyte analyzed as previously described.[2] Further investigation of this method of analysis (volatilization of SbI_3 from the precipitated metal under conditions where metal is neither transported or entrained) with known mixtures showed the error in metal recovery was +0.012 mole % in the range 0.4 to 2.5 mole % metal.

Results and Discussion

The cell investigated can be represented as

$$\overset{-}{C}|Sb(N_{M^0}), SbI_3\vdots Sn(N_M), SbI_3|\overset{+}{C} \qquad (1)$$

where $N_M{}^0$ is the constant mole fraction of metal in the "metal-saturated" reference anode. In order to analyze the data in as general a manner as possible, the electrode reaction will be represented as

$$m\mathrm{SbI_3} + nm\mathrm{e}^- = \mathrm{Sb}_m\mathrm{I}_{m(3-n)} + nm\mathrm{I}^- \qquad (2)$$

a *nm* electron reduction of $m$$SbI_3$ molecules to give a single molecule of product, subiodide or metal. If N_0 and N_r are the respective mole fractions of SbI_3 and $Sb_mI_{m(3-n)}$ and the reference-cell contribution is given by K, then the voltage dependence on concentration is, for ideal solutions

$$E = -RT/nmF(\ln N_r - m \ln N_0) + K \qquad (3)$$

For simplicity, iodide ion is assumed to carry current within the cell; this will be shown later to introduce a negligible error. It is also assumed that in the dilute solutions investigated N_0 is essentially constant. In these dilute solutions N_r is proportional to the measured mole fraction metal N_M as is seen from the general reaction for solution of metal in SbI_3

$$(m - nm/3)\mathrm{SbI_3} + (nm/3)\mathrm{Sb} = \mathrm{Sb}_m\mathrm{I}_{m(3-n)} \qquad (4)$$

so that (3) simplifies to

$$E = -RT/nmF(\ln N_M) + K' \qquad (5)$$

The results of 14 separate measurements over a sixfold concentration range are so shown in Fig. 2.

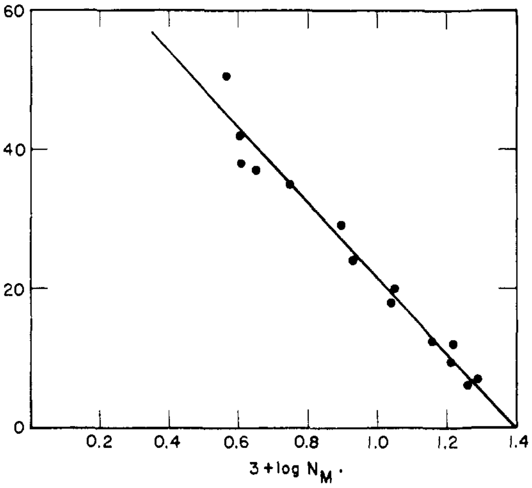

Fig. 2.—E *vs.* N_M for the cell C|Sb($N_M{}^0$), SbI_3|Sb(N_M), SbI_3|C at 251°.

The least-squares line, $E \times 10^3 = 75.3 - 53.8 (\log N_M + 3)$, corresponds to a value of 1.94 ± 0.13 for *nm* and (2.48 ± 0.12) $\times 10^{-2}$ for the intercept $N_M{}^0$. The latter compares very favorably with the value (2.52 ± 0.03) $\times 10^{-2}$ interpolated from direct solubility measurements,[2,9] substantiating the attainment of equilibrium in the cell measurements. Barring a large non-ideality of the solute, the data appear to justify the conclusion that the cathode reaction and, presumably, also the process of solution of the metal, involves a two-electron reduction of SbI_3 to the solute. In view of this result the only likely reduction reactions seem to be, for $m = 1, n = 2$

$$\mathrm{SbI_3} + 2\mathrm{e}^- = \mathrm{SbI} + 2\mathrm{I}^-$$

or, for $m = 2, n = 1$

$$2\mathrm{SbI_3} + 2\mathrm{e}^- = \mathrm{Sb_2I_4} + 2\mathrm{I}^-$$

The formation of Sb_2I_4 is tentatively taken to be correct, as SbI apparently can be eliminated by the observation that these solutions are diamagnetic,[2] whereas SbI would be expected to have two unpaired electrons. The results do *not* allow polymerization of SbI; the possibility of solvation by SbI_3 will be considered shortly.

The approximation of constant solvent concentration in the derivation of eq. 5 has an insignificant effect on the conclusions. If N_r and N_0 are solved for in terms of N_M from eq. 4 with $m = 2$, $n = 1$, substantially the same value of *nm* (1.95) is obtained from the slope of a plot of eq. 3. As for the assumption that iodide is the principal conduction

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(9) Inclusion of the independent value of $N_M{}^0$ in the least-squares treatment gives *nm* = 1.96 ± 0.09 (95% confidence limits). The single value of 2.1 for *nm* has also been obtained at 314°.

species, transport by the perhaps more plausible ions $SbI_2{}^+$ or $SbI_4{}^-$ as well as by I^- affects only the coefficient of the solvent term $\ln N_0$ in eq. 3 and, as has been seen, this is of no consequence. However, it is obvious that conduction by ions derived from the solute would directly obviate the previous conclusions.[10] Although the presence of such ions is not reflected by an appreciable change in the conductivity of SbI_3 on reaction with metal, substantiation of the earlier conclusions regarding the nature of the solute and the fact that the solvent furnishes the conducting ions comes from concentration cell experiments in which 2 to 5 mole % KI had been added to the SbI_3. In this case, concentration changes in the catholyte readily can be produced by electrolysis, since even with 2% KI the conductivity of the melt is 100 times greater than that of pure solvent. Furthermore, from what is known concerning conduction processes in fused salt mixtures, it is highly probable that in this solution the potassium ion carries most if not all of the current (with perhaps a small contribution by iodide), so that the interpretation of the cell data is free of any ambiguity associated with conduction by antimony-containing ions. The data obtained still indicate that *nm* is between 1.9 and 2.5. The results are less accurate than those shown in Fig. 2 as they are affected by a change in $N_M{}^0$ with KI concentration,[11] for which satisfactory corrections can be applied, and by the continuous diffusion through the diaphragm during the 1 to 4 hr. necessary for equilibrium after each electrolysis. Correction of the data with the diffusion equations derived for a constant-composition anolyte gives more consistent results for *nm*, $2.0_5 \pm 0.1$ (average deviation) for three runs with 2% KI and 1.9 to 2.2 for one with 5% KI.

Although it seems certain that each molecule of the product is formed by a two-electron reduction of SbI_3, as noted in the earlier discussion, the method is rather insensitive to changes in the amount of solvent. Hence, it cannot be ascertained with any accuracy *how many* SbI_3 molecules are involved in the two-electron reduction, that is, how the product is solvated. Although $\cdot\overset{\cdot}{\underset{\cdot\cdot}{Sb}}\text{–}I$ is not allowed magnetically, spin pairing as a result of strong coördination by the solvent might be possible, giving, for example, $I_2\underset{\cdot\cdot}{Sb}\text{–}I \rightarrow \overset{\cdot\cdot}{\underset{\cdot\cdot}{Sb}}\text{–}I$. This is considered unreasonable since the relative acidities expected for the two oxidation states involved would not favor a strong interaction. On the other hand, the isomeric $I_2\underset{\cdot\cdot}{Sb}\text{–}\underset{\cdot\cdot}{Sb}I_2$ does have some precedence in the structure known for P_2I_4[12]; the molecular As_2I_4[13] also may be catenated similarly. It is striking that the chemistry of antimony apparently does not resemble that of bismuth in this respect. Reduction of at least bismuth(III) chloride or bromide gives the bismuth(I) halide,[14] for which the structure $X\text{—}\underset{\cdot\cdot}{Bi}\text{=}\underset{\cdot\cdot}{Bi}\text{—}X$ has been suggested.[15]

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[10] For sample, *nm* would equal 4 with $Sb_mI_m{}^{+}{}_{(3-n)-1}$.

[11] At 326°, the temperature of these experiments, $N_M{}^0 = 4.26^2$, 3.6 ± 0.1, and 2.6 ± 0.15 for 0, 2.0 and 5.0 mole % KI in SbI_3, respectively. A compound is formed between KI and SbI_3 with a molar ratio greater than unity.

[12] Y. C. Leung and J. Waser, *J. Phys. Chem.*, **60**, 539 (1956).

[13] F. Jaeger and H. Doornbosch, *Z. anorg. allgem. Chem.*, **75**, 261 (1912).

[14] J. D. Corbett, THIS JOURNAL, **80**, 4757 (1958).

[15] M. A. Bredig, *J. Phys. Chem.*, **63**, 978 (1959).

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Metal–Olefin Compounds. I. The Preparation and Molecular Structure of Some Metal–Olefin Compounds Containing Norbornadiene (Bicyclo[2.2.1.]hepta-2,5-diene)

BY R. A. ALEXANDER, N. C. BAENZIGER, C. CARPENTER AND J. R. DOYLE[1]

RECEIVED JULY 6, 1959

The preparation of a number of metal–olefin compounds containing norbornadiene and either platinum or palladium is described. The physical and chemical properties of these compounds indicate that both olefinic bonds of the hydrocarbon are coördinated to a single metal atom in the *cis* positions of the coördination sphere. In addition, two new compounds formed by the 1,5-homoconjugative addition of mercury salts to norbornadiene are described.

Introduction

Several cyclic polyolefins have been reported to form compounds with platinum, palladium and other metallic halides.[2–8] Physical measurements on a number of these compounds, *i.e.*, 1,3,5,7-cyclooctatetraene–dibromoplatinum(II), dicyclopentadiene–dichloroplatinum(II) and 1,5-cyclooctadiene–dichloroplatinum(II) indicate that the hydrocarbon is chelated to the metal atoms. The resulting compounds, in solution, are monomeric species in contrast with 1,3-bis-(ethylene)-2,4-dichloro-μ-dichlorodiplatinum or 1,3-bis-(ethylene)-3,4-dichloro-μ-dichlorodipalladium.[9–12]

Recent work has shown that norbornadiene will undergo a number of addition reactions, and it was of interest to attempt to prepare and determine the molecular configuration of the products formed by the reactions of norbornadiene and platinum or palladium salts. In addition the relative simplicity of norbornadiene would facilitate X-ray crystal-

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[1] To whom communications concerning this paper should be addressed.

[2] K. A. Hofmann and J. V. Narbutt, *Ber.*, 1625 (1908).

[3] K. A. Jensen, *Acta Chem. Scand.*, **7**, 866 (1953).

[4] J. R. Doyle and H. B. Jonassen, THIS JOURNAL, **78**, 3965 (1956).

[5] J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 2622 (1952).

[6] J. Chatt, L. M. Vallarino and L. M. Venanzi, *ibid.*, 2496 (1957).

[7] J. Chatt, L. M. Vallarino and L. M. Venanzi, *ibid.*, 3413 (1957).

[8] J. Chatt and L. M. Venanzi, *ibid.*, 4735 (1957).

[9] N. C. Baenziger and J. N. Dempsey, THIS JOURNAL, **77**, 4984 (1955).

[10] N. C. Baenziger and J. R. Holden, *ibid.*, **77**, 4987 (1955).

[11] J. A. Wunderlich and D. P. Mellor, *Acta Cryst.*, **7**, 130 (1954).

[12] J. A. Wunderlich and D. P. Mellor, *ibid.*, **7**, 57 (1955).