Organometallic Electrochemistry: On the Couple $Me_3SnSnMe_3/Me_3Sn^+$

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QUANTITATIVE oxidation of organometallic compounds of the R_3MMR_3 type (R = alkyl or aryl; M = Sn or Pb) to R_3M^+ ions is brought about by metallic salts ($AgNO_3$,[1] $AgClO_4$,[2] $Hg_2(NO_3)_2$,[3] $HgCl_2$[4]). It seems reasonable to write the reaction in the following form:

$$R_3MMR_3 = 2R_3M^+ + 2e.$$

Such an interpretation can be suggested on the basis of observations that the above reaction takes place in a galvanic cell consisting of a platinized platinum electrode immersed in a methanolic solution of ditin compounds and of a silver electrode dipping in a silver nitrate solution,[5] both with $LiNO_3$ (2M) as supporting electrolyte.

We report that, under equilibrium conditions, an electron-transfer concerning hexamethylditin and trimethyltin ions may formally be compared with the system,

$$H_2 \leftrightarrows 2H^+ + 2e.$$

In a half-cell consisting of a platinized platinum electrode (platinum foil, 2·5 × 2 cm.) immersed in methanol and $LiNO_3$ (0·5 M) solution (previously degassed with dry nitrogen), a known quantity of hexamethylditin was oxidized to trimethyltin ions; silver ions being produced electrolytically by means of a silver anode dipped in the same half-cell. In such a way the assumed equilibrium potentials of the platinum electrode against S.C.E. could be measured at 25° for several mixtures of hexamethylditin and trimethyltin ions.

Five runs have been carried out, each employing ten mixtures of the two species performed from an initial concentration (*c*) of hexamethylditin of 1·223, 0·930, 0·820, 0·555, and 0·450 × 10^{-3}M. The corresponding five plots obtained by plotting the equilibrium potential *E*-values against $\log \frac{x^2}{1-x}$ (*x* represents the percentage of organoditin oxidized; in all runs about 60%) gave slopes of 0·0302 ± 0·0007v in good agreement with the relation:

$$E = E_0 + 0{\cdot}0296 \log 4c + 0{\cdot}0296 \log \frac{x^2}{1-x}.$$

The best value of E_0 from all the calculated values for the fifty mixtures studied is assumed to be $-0{\cdot}141 \pm 0{\cdot}004$ v against S.C.E., neglecting the unknown junction potential.

The same value was obtained from other measurements on mixtures of the two species without oxidation of the organoditin compound by silver ions. This shows that the platinized platinum electrode efficiency was not affected in the previous runs by the finely precipitated metallic silver.

In addition, two concentration-cell experiments were performed [solvent, methanol: $LiNO_3$(0·5 M)] in which the two compartments, equipped with platinized platinum electrodes of the same size, contained the same amount of organoditin compound while trimethyltin ions were in the ratios 1 to 10 and 1 to 20 respectively. The observed e.m.f. values at 25° were 0·030 and 0·039 v respectively, compared with calculated values 0·0296 and 0·0385.

In order to test the efficiency of this system under dynamic conditions, we made use of the biamperometric technique. By adding hexamethylditin to trimethyltin ions or trimethyltin ions to hexamethylditin, with a constant potential difference (50, 70, or 100 mv) applied through two platinized platinum wire electrodes (12 mm. long, 1 mm. diameter), the current increased linearly, reaching a maximum constant values in all cases when the molar ratio hexamethylditin: trimethyltin ions was equal to 0·5.

Since the above results could not be obtained when smooth platinum or mercury electrodes were used, we suggest that the reversibility of the system is connected with the ability of the platinized platinum to form trimethyltin radicals at the electrode–solution interface. The presence of triphenyltin radicals has already been proposed by Dessy *et al.*[2] to justify the existence of redox peaks for the species $Ph_3SnSnPh_3$, Ph_3Sn^+, and Ph_3Sn^- submitted to triangular voltammetry.

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