The discrepancy between the observations of the Italian chemists[1] and ours might be caused by the hydrolysis of the compound on solution, in the aqueous ethanol medium which they used. An analogous case is seen in trimethyltin hydroxide in solution[9]. This compound (II) is dimeric in a rigorously anhydrous solvent, but suffers facile hydrolysis in a wet solvent.

Dialkyltin halide oxinates, $XR_2Sn(ox)$ ($X = Cl, NCS$), were prepared by the reaction of dialkyltin dihalide and 8-quinolinol in absolute alcohol or by the reaction of dialkyltin dihalide and dialkyltin dioxinate in absolute alcohol. For example: *dimethyltin chloride oxinate*, (m.p. 135–136.5°. Found: C, 40.41; H, 3.76; Cl, 10.56; N, 4.29; Sn, 35.95. $C_{11}H_{12}ClNOSn$ calcd.: C, 40.24; H, 3.68; Cl, 10.86; N, 4.24; Sn, 36.15 %.), *dimethyltin isothiocyanate oxinate*, (m.p. 123–124°. Found: C, 40.92; H, 3.45; N, 8.16. $C_{12}H_{12}N_2OSSn$ calcd.: C, 41.06; H, 3.45; N, 7.98 %.), or *di-n-propyltin isothiocyanate oxinate* (m.p. 144°. Found: C, 47.39; H, 4.78; N, 6.89; S, 7.63. $C_{16}H_{20}N_2OSSn$ calcd.: C, 47.21; H, 4.95; N, 6.88; S, 7.88 %.), are also yellow crystalline compounds, and may contain a penta-coordinated tin atom.

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The effect of dipolar aprotic solvents on quadrupole splitting of Mössbauer spectral lines of dibutyltin dichloride

In recent years there has been an increasing interest in the effect of solvents on organic reactions. One of the most active areas in this field is the use of dipolar aprotic solvents that strongly solvate cations but poorly (predominantly electrostatically) solvate anions.

Electron-donating aprotic solvents such as dimethylformamide (DMFA), dimethyl sulfoxide (DMSO) and hexamethyltriamidophosphate (HMTAP) do not form hydrogen bonds with anions but interact rather strongly with electron-deficient cations. This results in the poorly solvated anions having very high reactivity in nucleophilic reactions (type S_N2). Reviews dealing with the outstanding role which solvating aprotic solvents play in a great many organic reactions have been published recently[1–3]. Ethers such as tetrahydrofuran (THF) and dimethoxyethane (DME) can be regarded as solvents of this type[3,4]. The solvation effect of THF and DME in metal-organic reactions is rather marked and commensurable with those of DMFA, DMSO, etc.

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It has already been reported that these solvents promote Würtz reactions[5,6], heterolytic exchange[7], metalation[4,8–10], alkylation[10,11] and formation[12–14] of organometallic compounds.

Until the present work, the solvent solvating power has been estimated only by the effect of the solvent on the reaction rate, the realization of reactions that do not take place in other media, and other similar means.

We conceived it to be possible that the strong solvation of a cation (or cationoid portion of the molecule) in the case of a negligibly solvated anion must cause a more or less pronounced distortion of the field symmetry of the metal nucleus, if the positive end of the dipole is the metal. For organotin compounds where the phenomenon of γ-quantum resonance absorption (Mössbauer effect) is well known[15], it was possible to estimate the change of the gradient of the electric field directly by means of the quadrupole splitting of Mössbauer spectral lines. Quadrupole splitting differs from zero value in all organic derivatives of tin in sp^3-hybridization with substituents markedly different in their electronegativities.

To confirm this assumption we have studied the Mössbauer spectra of dibutyltin dichloride in a number of solvating solvents known to be different one from another in their solvating powers. The quadrupole splitting values were measured at different molar ratios of solvent/dibutyltin dichloride. The main results of this investigation are presented in Fig. 1.

It can be seen that quadrupole splitting increases rapidly in the presence of solvating solvents up to solvation saturation state which occurs at a molar ratio of solvent/dibutyltin dichloride of about 3. Further dilution of the solution makes no change in the quadrupole splitting value, Δ, which is a constant characteristic for any one solvent.

It is possible, we believe, to estimate quantitatively the solvating powers of

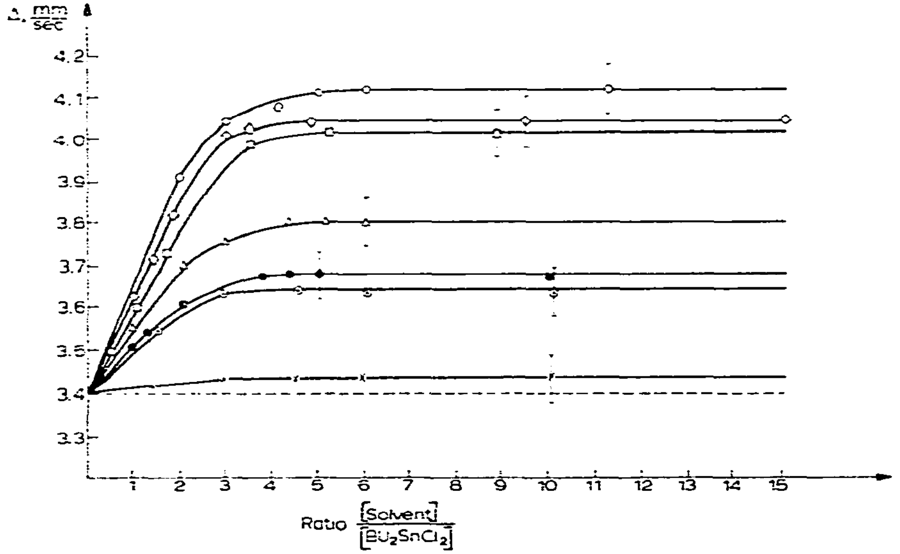

Fig. 1. The quadrupole splitting values measured at different molar ratios of solvent/dibutyltin dichloride. (○) Dimethyl sulfoxide; (◇) dimethylformamide; (□) hexamethyltriamidophosphate; (△) dimethoxyethane; (●) tetrahydrofuran; (⊙) diethoxyethane; (×) diethyl ether.

diethyl ether, THF, DME, DMFA, DMSO and HMTAP towards dibutyltin dichloride by comparing the Δ-values for the different solvents after the saturation state is reached. For example, if the solvating power (P_S) of diethyl ether is taken as 1, the P_S values of THF, DME, HMTAP, DMFA and DMSO should be 7, 10, 15.5, 16 and 18, respectively.

The scale obtained is broadly in accordance with the generally accepted ideas on the capacities of the above solvents for cation solvation. Nevertheless, this method should not be made the basis of any general scale of solvents as regards the solvation of cations as a whole. Solvation degree in any special case is determined by several factors which cannot at present be estimated quantitatively. It is evident that solvation degree with aprotic dipolar solvents is governed not only by their "basicity" in terms of the proton, dipole moments and dielectric constants, but also and to a greater extent by chemical composition and steric conditions[3,4]. At present, some subtle differences in the solvation characteristics of several solvents cannot be explained even qualitatively. For example, the substitution of DME for diethoxyethane (DEE), which differs little from the former in chemical composition and properties, decreases the stability of aromatic anion-radicals[16] and reduces the rates of exchange reactions in $RMgX + R'X$ systems[7]. It is notable that diethoxyethane solvates dibutyltin dichloride to a far less extent than DME.

The correlation between degree of solvation calculated with the help of Mössbauer spectra, and the kinetics of Sn–Cl bond reactions is now being studied.

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