Substitution at Saturated Carbon. Part 22.[1] Rate Constants for the Substitution of Tetraethyltin by Mercury(II) Carboxylates in t-Butyl Alcohol, Acetonitrile, Acetone, and Ethyl Acetate

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Rate constants are reported for the reactions between tetraethyltin and mercury carboxylates [$Hg(O_2CR)_2$] in t-butyl alcohol, acetonitrile, acetone, and ethyl acetate. When the group R contains a −*I* group (R = CH_2Cl, CH_2OMe, or CH_2CH_2Cl) the rate constants are greater in all solvents than with R = Me. When R = Et or Bu^t rate constants are generally lower than with R = Me except in acetonitrile. It is suggested that in all the above solvents, as well as in methanol, there is dominant electrophilic attack of the mercury(II) carboxylate on the tetraethyltin.

THERE have been but few reported studies of the rates of aliphatic electrophilic substitutions in a variety of solvents. Tagliavini *et al.*[2] and Gielen and Nasielski[3] obtained rate constants for iododemetallation of tetra-alkyl-leads in several solvents, and data are available also for halogenodemetallations of tetra-alkyltins[4-6] (see also ref. 7). For these various halogenodemetallations, it is generally considered[5,7] that there is a change of mechanism with change of solvent from the quite polar solvents such as methanol and dimethylformamide to the relatively nonpolar solvents such as chlorobenzene and carbon tetrachloride. For example, in the reaction of tetra-alkyltins with bromine, the value of $k(Et_4Sn)/k(Me_4Sn)$ changes from 0.46 in dimethylformamide to 0.83 in acetic acid, 12.3 in chlorobenzene, and 95.0 in carbon tetrachloride.[7] Again, in the reaction of tetraethyltin with bromine and with iodine, $k(Br_2)/k(I_2)$ changes from 1.0×10^2 in acetic acid to 1.4×10^4 in chlorobenzene.[7]

We have studied a number of substitutions of tetra-alkyltins by mercury(II) salts in polar solvents, and have concluded that the reaction involves dominant electrophilic attack of the mercury(II) salt on the tetra-alkyltin.[7] In the course of this work, we showed[8] that in methanol reaction (1) was accelerated by electron withdrawing

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[4] M. Gielen and J. Nasielski, *Bull. Soc. chim. belges*, 1962, **72**, 32; S. Boué, M. Gielen, and J. Nasielski, *J. Organometallic Chem.*, 1967, **9**, 443.

[5] M. Gielen and J. Nasielski, *Bull. Soc. chim. belges*, 1962, **71**, 601; *J. Organometallic Chem.*, 1963, **1**, 173.

[6] M. H. Abraham and P. L. Grellier, *J.C.S. Perkin II*, 1975, 623.

[7] M. H. Abraham, ' Electrophilic Substitution at a Saturated Carbon Atom,' in ' Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1973, vol. 12.

[8] M. H. Abraham and D. F. Dadjour, *J.C.S. Perkin II*, 1974, 233.

($-I$) groups in R, as indeed should be the case if the tetraethyltin were acting as an electron donor in a traditional S_E2 reaction.

$$\mathrm{Et_4Sn + Hg(O_2CR)_2 \longrightarrow EtHgO_2CR + Et_3SnO_2CR} \quad (1)$$

The only comparable investigation is that of Dessy,[9] who found that in reaction (2) electron-withdrawing groups in R retarded the reaction. This was explained[9] as due to an initial co-ordination in which the triethylboron functioned as an electron acceptor. Dessy's studies were carried out with the rather nonpolar solvent bis-(2-methoxyethyl) ether, and it occurred to us that we might use the substituent effect of the group R in reaction (1) as a mechanistic probe, since a change of mechanism in the less polar solvents could result (*cf.* the work of Dessy) in $-I$ groups now retarding reaction (1). Following our earlier studies with methanol, we chose t-butyl alcohol (dielectric constant $\varepsilon^{30} = 11.6$) as an alcoholic solvent of only moderate polarity, and selected the solvents acetonitrile, acetone, and ethyl acetate as a series of aprotic solvents covering quite a wide range of polarity.

Rate constants[a] and relative rate constants [with respect to mercury(II) acetate] for the substitution of tetraethyltin by mercury(II) carboxylates [$\mathrm{Hg(O_2CR)_2}$] at 30 °C

	Solvent	R: $\mathrm{Bu^t}$	Et	Me	$\mathrm{ClCH_2CH_2}$	$\mathrm{MeOCH_2}$	$\mathrm{ClCH_2}$
k_2	MeOH[b]	26.7	52.2	71.5	89.3	233	329
	$\mathrm{Bu^tOH}$	0.18	0.67	1.14[c]	1.27	3.96	20.8
	MeCN	10.5	9.3	10.7	33.0	50.0	(Fast)
	MeCOMe	1.17	1.22	1.44	7.71	10.59	(Fast)
	$\mathrm{MeCO_2Et}$[d]	0.19	0.25	0.30[e]	2.24		
k_2^{rel}	MeOH	0.37	0.73	1	1.25	3.26	4.60
	$\mathrm{Bu^tOH}$	0.15	0.58	1	1.11	3.47	18.25
	MeCN	0.98	0.87	1	3.08	4.67	(Large)
	MeCOMe	0.81	0.85	1	5.35	7.35	(Large)
	$\mathrm{MeCO_2Et}$[d]	0.63	0.83	1	7.47		

[a] Values of k_2 in l mol^{-1} min^{-1}. [b] Ref. 8. [c] This value is appreciably higher than those we have found before [0.49 at 26.5 °C (ref. 15) and 0.503 at 30 °C (ref. 12)] but we use it here for consistency. [d] At 25 °C. [e] Estimated value.

$$\mathrm{Et_3B + RCO_2H \longrightarrow EtH + Et_2BO_2CR} \quad (2)$$

Kinetics were followed by our usual method in which unchanged $\mathrm{Hg(O_2CR)_2}$ is converted into $\mathrm{HgI_3^-}$ with an excess of iodide ion, and the concentration of $\mathrm{HgI_3^-}$ is determined spectrophotometrically. Because of the presence of the various solvents in the final solutions for analysis, separate calibration experiments were carried out for each solvent. In nearly all cases, reactions followed clean second-order kinetics, first-order in each reactant. The two exceptions involved reactions of $\mathrm{Hg(O_2CCH_2Cl)_2}$ in acetonitrile and acetone, in which an initial process, too fast to be followed, gave way to a slower process over the last 25% of reaction.* As in the case of reactions in methanol,[8] we found that in t-butyl alcohol, acetonitrile, and acetone, addition of the corresponding carboxylic acid first led to an increase in the rate constant and then to a decrease. We interpret these variations as before: suppression of slight solvolysis of the mercury(II) carboxylates results in an increase in the observed rate constant to the correct value, and the subsequent decrease is due to a slight solvent effect. In ethyl acetate, however, there is monotonic increase in rate constant with added carboxylic acid, perhaps due to a lesser amount of solvolysis and a greater solvent effect. In the latter case we therefore took the observed rate constant at low added carboxylic acid concentration as the correct value. The various observed rate constants are collected in the Table; each rate constant represents about six kinetic runs. In the Table are also given the rate constants relative to mercury(II) acetate as unity. The effect of substituents (R) on the rate constant is qualitatively similar in the cases of methanol and t-butyl alcohol, but quantitatively larger for the less polar t-butyl alcohol. There is no indication of any reversal in substituent effect with change of solvent, and the enhanced effect of substituents in t-butyl alcohol can be explained as due to a larger reaction parameter in the less polar solvent (this has often been observed in the case of the Hammett ρ value; see for example ref. 10).

Substituent effects amongst the three aprotic solvents are also qualitatively similar and increase quantitatively in the sense MeCN < MeCOMe < $\mathrm{MeCO_2Et}$; again in accord with the expected solvent effect on a reaction parameter. Even in the least polar solvent we have studied, ethyl acetate ($\varepsilon^{25} = 6.02$), $-I$ groups in R still accelerate the reaction. Although the effects in the three aprotic solvents are qualitatively slightly different from those in the alcohols, the general effect is the same. Thus in all solvents, the mercury(II) salt functions as an electrophile and the tetraethyltin as an electron donor.

Kochi[11] has suggested that in processes taking place *via* a rate-limiting electron-transfer step [equation (3)], steric effects of the cleaved alkyl group should be absent; the cleaved alkyl group effect would then be influenced primarily by electron release leading to the following sequence of reactivity in the cleaved alkyl

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* In the other solvents, good second-order plots were obtained for $\mathrm{Hg(O_2CCH_2Cl)_2}$.

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[10] T. M. Krygowski and W. R. Fawcett, *Canad. J. Chem.*, 1975, **53**, 3622.

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group R: $Bu^t > Pr^i > Et > Me$. Thus in the reaction of tetra-alkyl-leads with hexachloroiridate(IV), the data of Kochi lead to values of $k(Et\text{-}PbEt_3)/k(Me\text{-}PbEt_3)$ of 42 (in MeCN) and 14 (in HOAc) and $k(Et\text{-}PbMe_3)/k(Me\text{-}PbMe_3)$ of 100 (in MeCN) and 9 (in HOAc). On the other hand, we have found [12,13] for reaction with mercury(II) acetate in methanol that $k(Et\text{-}SnPr^i_3)/k(Me\text{-}SnPr^i_3)$ is only 0.002 3; for the same reaction the (less

$$R\text{-}M + E^+ \xrightarrow{\text{slow}} R\text{-}M^{\cdot+} + E \xrightarrow{\text{fast}} R\text{-}L + M^+ \quad (3)$$

diagnostic) overall value of $k(Et_4Sn)/k(Me_4Sn)$ is 0.004 4 in methanol and 0.009 2 in t-butyl alcohol, yet $k(Et_4Pb)/k(Me_4Pb)$ is *ca.* 2×10^3 for the hexachloroiridate(IV) reaction in both acetonitrile and acetic acid.[11]

We therefore favour a simple two-electron transfer from the tetraethyltin to the mercury(II) carboxylates, and from the data shown in the Table suggest that reaction (1) proceeds by an S_E2 (open) mechanism in all the alcoholic and aprotic solvents we have used so far. This is in marked contrast to results on the halogenodemetallation of tetra-alkyl-tins and -leads,[2-7] from which it is clear that there is a fundamental change in mechanism with change of solvent from polar to relatively nonpolar.

The data in the Table also indicate that the transition state in reaction (1) is quite polar, since there are appreciable rate reductions on transfer from methanol to the less polar t-butyl alcohol, and on transfer from acetonitrile to acetone to ethyl acetate. Thus the S_E2 transition state in reaction (1) must carry a moderate-to-large separation of charge.

EXPERIMENTAL

The mercury(II) carboxylates, tetraethyltin, methanol, and t-butyl alcohol were as described before.[8,14,15] Acetonitrile was purified by repeated treatment with P_2O_5 followed by distillation. Acetone was allowed to pass slowly through a 60 cm column of Linde molecular sieves (4 Å; 1.6 mm pellets) and then fractionally distilled. The middle constant-boiling fraction was collected and used immediately after distillation. G.l.c. analysis showed that this procedure reduces the water content of the acetone to less than 0.005% by weight. We did not store the acetone over molecular sieves, since we observed that on prolonged contact decomposition took place with formation of mesityl oxide. Ethyl acetate was treated similarly to acetone; the water content of the purified solvent was 0.035% by weight.

Kinetic measurements were carried out essentially by the method previously described.[8,14] The calibrations obtained before for solvents methanol,[14] t-butyl alcohol,[15] and acetonitrile [16] were used, and for the solvents acetone and ethyl acetate new calibrations were prepared. This was necessary because of the presence of the solvent in the quenched solutions for analysis; preliminary experiments had shown that the extinction coefficient of HgI_3^- in methanol was affected by the presence of quite small quantities of acetone and ethyl acetate.

Apart from the insolubility of a number of mercury(II) salts in ethyl acetate, the only difficulty we found was with the solvent t-butyl alcohol. Our observed rate constants (Table) were self-consistent and reproducible, yet the present value of the rate constant for the mercury(II) acetate reaction at 30 °C is twice the value we have found before.[12,15] The solvent was dried and purified by the same method as used previously, but it is possible that the resulting solvent is slightly different from the batches of solvent used before. The rate constants for t-butyl alcohol in the Table were all determined in the present work, so that the comparative substituent effects should be valid even though the absolute values of the rate constants are not well reproduced from year to year.

We thank the British Council (D. F. D.) and the Iranian Ministry of Science and Higher Education (D. F. D. and M. R. S.-H) for support, and the S.R.C. for a grant.

[6/2190 *Received, 29th November, 1976*]

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