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Preliminary communication

The mechanism of reaction of tetraalkyltins with mercuric carboxylates in methanol

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SUMMARY

In the reaction of mercuric carboxylates with tetraalkyltins in methanol, rate constants for attack of the species $(RCO_2)_2Hg$ increase along the series R = t-Bu < Et < Me < Ph < $ClCH_2CH_2$ < $MeOCH_2$ < $ClCH_2$ which suggests an open transition state for these S_E2 substitutions.

Mercuric acetate has often been used as an electrophile in kinetic studies of bimolecular substitutions at saturated carbon[1], but there is little information on the exact mechanism of these S_E2 reactions. It is possible that one or both of the species $MeCO_2Hg^+$ and $(MeCO_2)_2Hg$ could be the active electrophile (Schrauzer[2] has suggested, without giving details, that in water the species $MeCO_2Hg^+$ is the electrophile that attacks alkylcobal-

TABLE 1

RELATIVE RATE CONSTANTS, k_{rel}^{obs}, FOR THE SUBSTITUTION OF TETRAALKYLTINS BY MERCURIC CARBOXYLATES IN METHANOL[a] AT 30°

R in $(RCO_2)_2Hg$	k_{rel}^{obs}		*Acid pK_a in water*
	for n-Bu_4Sn	*for Et_4Sn*	
t-Bu	34	37	5.03
Et	57	73	4.87
Me	100	100	4.76
Ph	150	120	4.21
$ClCH_2CH_2$	160	125	3.99
$MeOCH_2$	–	330	3.57
$ClCH_2$	490	460	2.86

[a] In presence of the corresponding carboxylic acid, to avoid solvolysis of the mercuric salt.

oximes) and for the neutral species $(MeCO_2)_2Hg$ there is also the possibility that reaction might take place via a 6-centered cyclic transition state in preference to an open transition state[3,4].

We have determined second-order rate constants, k^{obs}, for reaction of a series of mercuric carboxylates with Et_4Sn and with n-Bu_4Sn in methanol; relative rate constants with respect to the acetate as 100 are in Table 1. Values of k^{obs} decrease slightly with increase in the initial concentration of mercuric carboxylate, and also on addition of sodium acetate (in the case of reaction of mercuric acetate). Both of these effects can be explained by the presence of a small quantity of the highly reactive species RCO_2Hg^+. Approximate calculations show, however, that 60–80% reaction takes place via the neutral species $(RCO_2)_2Hg$. Rate constants for attack on Et_4Sn are always in the order $k[(RCO_2)_3Hg^-] < k[(RCO_2)_2Hg] < k[RCO_2Hg^+]$ with ratios about $0/1/10^2$. Furthermore, for three salts we find that $k[\text{t-BuCO}_2Hg^+] < k[MeCO_2Hg^+] < k[MeOCH_2CO_2Hg^+]$ and that $k[(\text{t-BuCO}_2)_2Hg] < k[(MeCO_2)_2Hg] < k[(MeOCH_2CO_2)_2Hg]$. The relative rates in the latter series, 42 ($R = \text{t-Bu}$) < 100 ($R = Me$) < 340 ($R = MeOCH_2$) are very close to the average values of k_{rel}^{obs} (see Table 1), so that the values given in Table 1 can be taken as relative rate constants for attack of the species $(RCO_2)_2Hg$ on the tetraalkyltins.

Dessy *et al.*[5] have shown that in the acidolysis of triethylboron by carboxylic acids, electron-attracting substituents in the carboxylic acid retard reaction and electron-donating substituents aid reaction. Accordingly, a mechanism was proposed[5] in which there is prior nucleophilic coordination of the carboxylic acid to the metal atom in the substrate. Our results, on the other hand, suggest that there is predominate electrophilic attack of the $(RCO_2)_2Hg$ species on the tetraalkyltin, and that reaction takes place through an open transition state. The present results thus seem to have yielded the first direct evidence that S_E2 reactions of the species $(RCO_2)_2Hg$ can take place by the S_E2 (open) mechanism rather than by the S_E2 (cyclic) mechanism.

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