Aromatic Substitution. Part 1. Kinetics of Reaction of Phenyltriethyltin with Mercury(II) Salts in Methanol

By **Michael H. Abraham** and **Mohammad Reza Sedaghat-Herati**, Department of Chemistry, University of Surrey, Guildford, Surrey GU2 5XH

Reaction of $PhSnEt_3$ with mercury(II) salts in methanol follows second-order kinetics, first-order in each reactant, and yields only PhHgX and Et_3SnX. It is shown that the reactivity order in the mercury(II) species is $HgI_3^- \ll HgI_2 < HgCl_2 < Hg(OAc)_2$. Under the investigated conditions, mercury(II) chloride reacts only *via* the covalent species $HgCl_2$ and not *via* species such as $HgCl^+$. Comparison with related aliphatic substitutions shows that a phenyl group is cleaved from tin by mercury(II) halides some 4×10^2 times as fast as a methyl group and 1×10^5 times as fast as an ethyl group. Added water mildly accelerates reaction of $PhSnEt_3$ with $HgCl_2$, whilst inert salts retard reaction; the activation energy is quite low, and it is suggested that reaction takes place *via* an intermediate π-complex through a transition state that is not particularly polar.

AROMATIC electrophilic substitution is one of the most widely studied types of organic reaction. Even so, the number of reported investigations on salt effects and solvent effects on aromatic substitutions is quite small, mainly because the conditions under which most aromatic substitutions take place are not suitable for such studies. In general, it seems as though rather mild electrophilic reagents are to be preferred, so that it is necessary to use reactive aromatic substrates in order to avoid drastic experimental conditions. Organometallic substrates with an aryl–metal bond that is readily cleaved by weak electrophiles have been studied on numerous occasions (see refs. 1—3), especially with regard to protodemetallation and halogenodemetallation. More suitable for studies of salt effects and solvent effects is the metal-for-metal exchange, and we report now our results on the substitution of phenyltriethyltin by mercury(II) salts in methanol. This reaction was chosen because we have already devised, in connection with our studies on aliphatic electrophilic substitution, a method of following the kinetics of reaction,[4] and because we have already accumulated thermodynamic data on mercury(II) salts that could be relevant to the aromatic substitution.[5] In addition, there was the interest in possible comparisons with related mercury-for-tin exchanges in the aliphatic series.

Reutov *et al.*[6] have reported that the analogous reaction of phenytrimethyltin with mercury(II) chloride in methanol proceeds very rapidly with cleavage of only the phenyl group. Our own product analyses confirm equation (1; X = Cl) as representing the stoicheiometry of reaction; we were able to isolate phenylmercury(II) chloride in 93% yield. Kinetics of reaction (1; X = Cl)

$$PhSnEt_3 + HgX_2 \longrightarrow PhHgX + XSnEt_3 \qquad (1)$$

were straightforward: in each kinetic run, the normal second-order rate equation was followed, and the observed second-order rate constant was reasonably invariant over a range of initial concentrations of reactants (Table 1). When mercury(II) iodide was the reactant, reaction (1; X = I) was followed by a fast equilibrium (2), entirely analogous to the equilibria observed in ali-

$$Et_3SnI + HgI_2 \rightleftharpoons Et_3Sn^+ + HgI_3^- \qquad (2)$$

phatic substitutions.[7] We used the same computer program as before[8] to obtain the second-order rate constants for reaction (1; X = I). Both reaction (1; X = Cl) and reaction (1; X = I) are very fast, and, even when initial concentrations were reduced to *ca.* 3×10^{-5}M, have half lives of only a few minutes at 298 K. We therefore used a special reaction vessel that was able to deliver 5 ml aliquot portions of the reaction mixture at

TABLE 1

Second-order rate constants for the substitution of phenyltriethyltin by mercury(II) salts in methanol[a]

T/K	$10^5[PhSnEt_3]$/M	$10^5[HgX_2]$/M	k_2/l mol^{-1} s^{-1}
A With $HgCl_2$			
273.15	6.0	4.0	26.2
273.15	8.0	4.0	29.8
273.15	10.0	4.0	30.4
273.15	8.0	3.5	27.2
273.15	8.0	4.0	29.8
273.15	8.0	4.5	27.2
273.15	8.0	5.0	25.7
273.15	8.0	6.0	26.0
273.15	8.0	4.0	29.83[b]
283.15	8.0	4.0	48.58[b]
298.15	4.0	2.0	103.4[b]
308.15	4.0	2.0	156.1[b]
B With HgI_2			
273.15	8.0	4.0	4.12[b]
298.15	8.0	4.0	23.88[b]
308.15	8.0	4.0	42.40[b]
318.15	8.0	4.0	46.86[b]

[a] Rate constants uncorrected for solvent contraction or expansion from 298 K; all runs carried out in duplicate unless shown otherwise. [b] Average values from between 2 to 8 separate runs.

---

[1] O. A. Reutov and I. P. Beletskaya, ' Reaction Mechanism of Organometallic Compounds,' North-Holland Press, Amsterdam, 1968.

[2] R. Taylor in ' Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, vol. 13, 1972.

[3] R. Taylor, in 'Aromatic and Heterocyclic Chemistry,' Chemical Society Specialist Periodical Reports, 1973, **1**, 176; 1974, **2**, 217; 1975, **3**, 220; 1976, **4**, 227.

[4] M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1970, 188, 193.

[5] M. H. Abraham, R. J. Irving, and G. F. Johnston, *J. Chem. Soc.* (*A*), 1970, 199; M. H. Abraham, J. F. C. Oliver, and J. A. Richards, *ibid.* 203; M. H. Abraham and F. J. Dorrell, *J.C.S. Perkin II*, 1973, **444**; M. H. Abraham and P. L. Grellier, *ibid.*, 1975, 1856.

[6] A. N. Kashin, I. P. Beletskaya, A. Ts. Malkhasyan, and O. A. Reutov, *Zhur. Org. Khim.*, 1972, **9**, 1098.

[7] M. H. Abraham and T. R. Spalding, *J. Chem. Soc.* (*A*), 1968, 2530.

[8] M. H. Abraham, P. L. Grellier, M. J. Hogarth, T. R. Spalding, M. Fox, and G. R. Wickham, *J. Chem. Soc.* (*A*), 1971, 2972.

25 s intervals. Several sets of kinetic experiments showed that from run to run, the percentage standard deviation in the rate constant was *ca.* 3—4.

Influence of the Substrate and Reactant.—Rate constants for reaction (1; X = Cl and I) at various temperatures in methanol are in Table 1. The value at 298 K for reaction (1; X = Cl), 103 l mol^{-1} s^{-1}, compares quite well with that found by Reutov *et al.*[6] for reaction of $PhSnMe_3$ with $HgCl_2$ in methanol, *viz.* 135 l mol^{-1} s^{-1}. Thus the leaving group effect is quite small with k(Ph–$SnMe_3$)/k(Ph–$SnEt_3$) being only 1.3; this compares with values for k(Me–$SnMe_3$)/k(Me–$SnPr^i_3$) of 1.6 and k(Et–$SnEt_3$)/k(Et–$SnPr^i_3$) of 3.1 for reaction with mercury(II) acetate in methanol,[9] and k(Me–$SnMe_3$)/k(Me–$SnBu^n_3$) of 0.83 for reaction with mercury(II) iodide in 96% methanol.[10] The (rather small) leaving group effect is common to both aromatic and aliphatic substitutions. This contrasts with the effect of the cleaved group, and in Table 2 are values for a number of substitutions in which cleavage of a phenyl–metal bond may be compared with that of a methyl- or ethyl–metal bond, when the leaving entity is kept constant. As can be seen, a phenyl group is cleaved from tin by mercury(II) halides in methanol *ca.* 400—500 times as rapidly as a methyl group and *ca.* 1 × 10^5 times as rapidly as is an ethyl group. Other substitutions (Table 2) generally result in lower factors. The comparatively low reactivity of phenylcobaloximes may be due to severe steric effects, but the extraordinary low rate factors in the SO_2 insertion reaction (Table 2) suggest that these insertions are not necessarily simple electrophilic processes.

TABLE 2

Comparison of the reactivity of phenyl with alkyl groups [a]

Substrate	Electrophile	Solvent	k(Ph)/k(Me)	k(Ph)/k(Et)	Refs.
R-$SnMe_3$	$HgCl_2$	Methanol	560,[b] 350 [c]		4, 6
R-$SnEt_3$	$HgCl_2$	Methanol		1.24×10^5	4, This work
R-$SnEt_3$	HgI_2	Methanol		3.77×10^4	*d*, This work
R-HgEt	HgI_2	Dioxan		7.25×10^3	*e*
R-$SnMe_3$	I_2	Methanol	203	1.41×10^3	*f*
R-Co(dmgH)$_2$	Hg^{2+}	Water	7.4	3.3×10^3	*g*
R-CO(dmgH)$_2$	Tl^{3+}	Water	1.4		*g*
R-Fe(CO)$_2\pi$-C_5H_5	SO_2	Liquid SO_2	0.0007	0.0006	*h*
			0.0017		*i*

[a] Observed rate constants statistically corrected where necessary. [b] Using the value of 0.97 l mol^{-1} s^{-1} for k(Me_4Sn) from ref. 6. [c] Using the value of 1.55 l mol^{-1} s^{-1} for k(Me_4Sn) from ref. 4. [d] M. H. Abraham and F. Behbahany, *J. Chem. Soc.* (*A*), 1971, 1469. [e] R. E. Dessy, Y. K. Lee, and J.-Y. Kim, *J. Amer. Chem. Soc.*, 1961, **83**, 1163 assuming only the phenyl group is cleaved in PhHgEt. O. Buchman, M. Grosjean, and J. Nasielski, *Helv. Chim. Acta*, 1964, **47**, 1679; S. Boué, M. Gielen, and J. Nasielski, *J. Organometallic Chem.*, 1967, **9**, 443. [g] P. Abley, E. R. Dockal, and J. Halpern, *J. Amer. Chem. Soc.*, 1973, **95**, 3166. See also G. Tauzher, R. Dreos, G. Costa, and M. Green, *J. Amer. Chem. Soc.*, 1974, **81**, 107. [h] U. Kunze and J. D. Koola, *J. Organometallic Chem.*, 1974, **80**, 281. [i] S. E. Jacobson and A. Wojcicki, *J. Organometallic Chem.*, 1974, **72**, 113.

Addition of I^- to the medium in reaction (1; X = I) results in conversion of the electrophile to HgI_3^- and total inhibition of the substitution. Since the action of mercury(II) acetate on phenytriethyltin is too fast to follow, we infer that the order of increasing electrophilic power towards phenyltriethyltin in methanol is $HgI_3^- \ll HgI_2 < HgCl_2 < Hg(OAc)_2$. This sequence is exactly the same as that for reactions involving tetra-alkyltins in methanol. In contrast, addition of halide ion catalyses the aryl- and alkyl-exchange reaction (3; R = Ph and alkyl) in alcoholic solvents,[11,12] no doubt through conversion of the substrate RHgX into a species, $RHgX_2^-$, that is more susceptible to electrophilic attack.[13,14] Since the complexing ability of R_4Sn compounds is small, the corresponding species R_4SnX^- are not formed and

$$RHgX + \overset{*}{H}gX_2 \longrightarrow R\overset{*}{H}gX + HgX_2 \qquad (3)$$

the addition of halide ion merely converts HgX_2 into the less reactive electrophile HgX_3^-.

TABLE 3

Rate constants and activation parameters [a] for the substitution of phenyltriethyltin by mercury(II) halides

		k_2/l mol^{-1} s^{-1}				
Reactants	Solvent [b]	273 K	298 K	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
$PhSnEt_3$ + $HgCl_2$	MeOH	29.8	103.4	12.81	7.4 [c]	−18.2 [c]
	98% MeOH	34.2	130.8	12.66	8.1	−15.3
	96% MeOH	40.4				
	94% MeOH	70.1	147.8	12.58	4.2	−28.0
$PhSnEt_3$ + HgI_2	MeOH	4.12	23.9	13.68	9.2	−14.9 [c]
$PhSnMe_3$ + $HgCl_2$	MeOH		135.0	12.65 [d]	6.5	−21.0 [d]

[a] Activation parameters at 298 K calculated after conversion of rate constants (uncorrected for solvent expansion or contraction from 298 K) to units of mol fraction^{-1} s^{-1}; $\Delta G^\ddagger$ (± 0.02) and $\Delta H^\ddagger$ (± 0.3) in kcal mol^{-1}, and $\Delta S^\ddagger$ (± 0.9) in cal K^{-1} mol^{-1}. Quoted errors are standard deviations for a 3% error in the rate constants. [b] The percentage (v/v) of methanol in methanol–water mixtures is given. [c] Calculated from the full data in Table 1. [d] From ref. 6 after conversion to the mol fraction scale.

Influence of Added Water.—At both 273 and 298 K rate constants for reaction (1; X = Cl) are increased in value on addition of water to the methanolic solvent (Table 3), although to an appreciably less extent than in the

---

[9] M. H. Abraham, D. F. Dadjour, M. Gielen, and B. de Poorter, *J. Organometallic Chem.*, 1975, **84**, 317.

[10] M. H. Abraham and T. R. Spalding, *J. Chem. Soc.* (*A*), 1969, 399.

[11] I. P. Beletskaya, I. I. Zakharycheva, and O. A. Reutov, *Zhur. Org. Khim. U.S.S.R.*, 1969, **5**, 793.

[12] H. B. Charman, E. D. Hughes, C. K. Ingold, and H. C. Volger, *J. Chem. Soc.*, 1961, 1142.

[13] V. Lucchini and P. Wells, *J. Organometallic Chem.*, 1975, **92**, 283.

[14] M. H. Abraham, P. L. Grellier, and M. J. Hogarth, *J.C.S. Perkin II*, 1977, 221.

corresponding aliphatic substitution of tetraethyltin.[4] The transition state for reaction (1; X = Cl) would thus seem to be not very polar in nature. Activation parameters are also in Table 3; those for reaction (1; X = Cl) in methanol are not very different to those found by Reutov *et al.*[6] for substitution of phenyltrimethyltin, and in each case $\Delta S^\ddagger$ is *ca.* −20 cal K^{-1} mol^{-1} (mol fraction scale). It can be seen (Table 3) that values of $\Delta H^\ddagger$ for reaction (1; X = Cl and I) are generally quite low, and for reaction (1; X = Cl) in the most aqueous solvent $\Delta H^\ddagger$ has the extraordinary low value of 4.2 kcal mol^{-1}. This may be explained as follows. The reactants form a complex, in an equilibrium step, with a standard enthalpy change ΔH°. The complex then decomposes to the products in a kinetic step with an activation enthalpy $\Delta H^\ddagger_c$. We have then that $\Delta H^\ddagger_{obs} = \Delta H^\circ + \Delta H^\ddagger_c$, so that an exothermic complex formation (ΔH° negative) could lead to a small positive value for $\Delta H^\ddagger_{obs}$ even though $\Delta H^\ddagger_c$ might be a quite large positive quantity. Two possible complexes that lie on the reaction path in aromatic electrophilic substitution are the well-known π- and σ-complexes. It is rare for these σ-complexes to be in equilibrium with the reactants, and since it is known that mercury(II) halides can act as π-complex acceptors towards aromatic compounds,[15] we suggest that a π-complex between the reactants is present as a reaction intermediate. The substitution could then involve first a π-complex and then a traditional σ-complex. Since the transition state seems not be highly polar, it probably resembles the π-complex rather than the highly polar σ-complex.

Influence of Added Salts.—We have shown (above) that addition of an excess of I$^-$ completely inhibits reaction (1; X = I), by conversion of all HgI_2 into unreactive HgI_3^-. The third stepwise stability constant in the Hg^{2+}–I$^-$ system in methanol is very large,[16] $K_3 = 7.6 \times 10^4$, so that there is essentially stoicheiometric conversion of HgI_2 into HgI_3^-.* This is not so for the Hg^{2+}–Cl$^-$ system in methanol, where K_3 is now very small. No direct measurement of the latter stability constant has been reported, but for the chloride system in water[16] $K_3 = 9$ and in 60% aqueous ethanol[17] $K_3 = 3$. These very low values mean that on addition of Cl$^-$ very little $HgCl_2$ is converted into (unreactive) $HgCl_3^-$. We can, therefore, use the addition of Cl$^-$ as a probe for HgCl$^+$ as a kinetically significant entity, because addition of Cl$^-$ will drastically reduce the (in any case small) concentration of HgCl$^+$. The second stepwise stability constant for the Hg^{2+}–Cl$^-$ system in methanol is very large; in water[16] it is 3.0×10^6 and consideration of free-energy data on $HgCl_2$, Cl$^-$, and various cations[18] suggests that in methanol K_2 will be of the order of 10^{11}. Experiments on the effect of added sodium chloride are reported in Table 4, together with the approximate percentages of HgCl$^+$ and $HgCl_3^-$ present. The effect of Cl$^-$ is to reduce slightly the value of the rate constant. Since even the first addition of Cl$^-$ reduces the % HgCl$^+$ present by a factor of *ca.* 10^4, it is clear that HgCl$^+$ cannot be a kinetically significant entity.† This was found to be the case also for substitution of tetraethyltin in methanol.[4] The reduction in the rate constant due to addition of Cl$^-$ could be the result of partial conversion of $HgCl_2$ to $HgCl_3^-$, although K_3 would have to be larger than 3 to account for this quantitatively. Alternatively, it is possible that there is a negative ionic strength effect of sodium chloride superimposed on the above chemical effects. We therefore examined a number of salts (Table 5) and found that in all cases there was indeed a negative kinetic salt effect; the retardation caused by sodium chloride is in no way anomalous. All these experiments were carried out at 273 K but we confirmed with one salt ([NBu$_4$]ClO$_4$) that the same phenomena occurred also at 298 K. We also chose three salts for a more detailed examination (Table 6) and observed that in all three cases addition of small quantities of the salts produces a considerable negative salt effect, but that on further addition the value of k/k_0 starts to increase again. For one salt (LiClO$_4$) there is actually produced a positive salt effect $k/k_0 > 1$ at higher salt concentrations. The generally

TABLE 4

Effect of added sodium chloride on rate constants for substitution of phenyltriethyltin by mercury(II) chloride in methanol at 273 K[a]

Added NaCl/M	k_2/k_2°	%[$HgCl_3^-$][b]	%[HgCl$^+$][c]
0	1	0	5×10^{-2}
3.2×10^{-4}	0.96	0.1	3×10^{-6}
4.0×10^{-3}	0.90	1.2	
1.0×10^{-2}	0.79	2.9	
5.0×10^{-2}	0.57	14.0	

[a] Initial concentrations of $PhSnEt_3$ 8×10^{-5}M, $HgCl_2$ 4×10^{-5}M. [b] Assuming $K_3 = 3$ (see text). [c] Assuming $K_2 = 10^{11}$ (see text).

TABLE 5

Effect of added salts on rate constants for substitution of phenyltriethyltin by mercury(II) chloride in methanol at 273 K[a]

	k/k_0	
Salt/M	2×10^{-3}	1×10^{-2}
NaCl	0.92	0.79
NaClO$_4$	0.96	0.86
NaClO$_3$	0.91	0.82
NaNO$_3$	0.77	0.89
LiClO$_4$	0.82	0.81
[NEt$_4$]ClO$_4$	0.90	0.86
[NBu$_4$]ClO$_4$	0.86	0.92
[NBu$_4$]ClO$_4$ (298 K)	0.87	0.85
[NBu$_4$]ClO$_4$		0.83[b]

[a] Initial concentrations as in Table 4. [b] In 94% methanol.

---

* Values of the stepwise stability constants K_2 and K_3 are in M^{-1}.

† If a significant proportion of reaction did indeed proceed *via* HgCl$^+$, then we would also expect the observed second-order constant to decrease with increase in initial concentration of $HgCl_2$; this behaviour is not observed (Table 1).

[15] I. M. Vezzosi, G. Peyronel, and A. F. Zanoli, *Inorg. Chim. Acta*, 1974, **8**, 229.

[16] G. B. Deacon, *Rev. Pure Appl. Chem.*, 1963, **13**, 189.

[17] R. Anataramen, A. Balusubramanian, and K. Saramma, *Talanta*, 1973, **20**, 515.

[18] M. H. Abraham, *J.C.S. Faraday I*, 1973, 1375; B. G. Cox, G. R. Hedwig, A. J. Parker, and D. W. Watts, *Austral. J. Chem.*, 1974, **27**, 477.

negative salt effect is not confined to solvent methanol, but also applies to addition of $[NBu_4]ClO_4$ to 94% aqueous methanol (see Tables 5 and 6). Kinetic salt effects are notoriously difficult to interpret, but the general effects of the 'inert' added salts (*i.e.* those not containing halide ion) seem to indicate a transition state that is not very polar. Interestingly, addition of $KClO_4$ to the aromatic substitution (3; R = Ph, X = Br) in methanol has also little effect on the rate constant.[11]

TABLE 6

Variation of k/k_0 with added salt in the substitution of phenyltriethyltin with mercury(II) chloride in methanol at 273 K [a]

Added $[NBu_4ClO_4]$/M	k/k_0
0	1
5.0×10^{-4}	0.69
8.0×10^{-4}	0.73
1.0×10^{-3}	0.87
1.5×10^{-3}	0.88
2.0×10^{-3}	0.86
1.0×10^{-2}	0.92
1.3×10^{-1}	0.84
Added $[LiClO_4]$/M	k/k_0
0	1
2.0×10^{-3}	0.82
1.0×10^{-2}	0.81
2.5×10^{-1}	1.08
4.4×10^{-1}	1.15
Added $[NaNO_3]$/M	k/k_0
1.0×10^{-4}	0.82
3.0×10^{-4}	0.87
2.0×10^{-3}	0.77
1.0×10^{-2}	0.89
Added $[NBu_4ClO_4]$/M	k/k_0 [b]
1.0×10^{-2}	0.83
6.0×10^{-2}	0.96
9.2×10^{-2}	0.75

[a] Initial concentrations as in Table 4. [b] In 94% methanol.

General Analysis.—The aromatic substitution, reaction (1), follows simple second-order kinetics with only the covalent species HgX_2 (X = Cl and probably I) acting as the effective reagent. The effects of added water and inert salts to the solvent methanol suggests a transition state that is not very polar, whilst the low activation energies observed suggests the presence of an intermediate complex. A reaction sequence could involve a π-complex followed by a σ-complex, with the transition state nearer to the π-complex. Chipperfield, Hayter, and Webster [19] have analysed their data on the reaction of various metal–metal bonded compounds with mercury(II) halides in terms of an intermediate complex, equation (4). Using equations derived by Pyun [20] they

$$A + B \overset{K}{\rightleftharpoons} C \xrightarrow{k_1} \text{Product} \qquad (4)$$

show for the specific case in which (i) equilibrium conditions with respect to A, B, and C are assumed, (ii) the method of following the kinetics includes the concentration of C, and (iii) the initial concentration of A, a_0, is much larger than the initial concentration of B, b_0:

$$\frac{1}{k_2(\text{obs})} = \frac{1}{k_1K} + \frac{a_0}{k_1} \qquad (5)$$

We have used the analysis of Beringer and Gindler,[21] who derive an equation for the general equilibrium situation, equation (6), where a, b, and c are the concentrations of A, B, and C at time t.

$$\text{rate} = -\text{d}\frac{(a + c)}{\text{d}t} = -\text{d}\frac{(b + c)}{\text{d}t} = \frac{k_1K(a + c)\,(b + c)}{1 + K(a + b + c)} \qquad (6)$$

When K, and hence c, is small, approximations (7) and (8) may be deduced, of which (8) is probably better than (7). Of course when

$$\log_e k_2(\text{obs}) = \log_e (k_1K) - K(a_0 + b_0) \qquad (7)$$

$$\frac{1}{k_2(\text{obs})} = \frac{1}{k_1K} + \frac{(a_0 + b_0)}{k_1} \qquad (8)$$

$c \longrightarrow 0$, all three equations (6)—(8) collapse to the equilibrium/steady-state approximation that $k_2(\text{obs}) = k_1K$.

In the present work, reaction (1) was followed by quenching the medium with I^- to convert unchanged HgX_2 into HgI_3^- the latter being determined spectrophotometrically. If some intermediate π-complex is formed, addition of I^- should result in the breakdown of the complex also to HgI_3^-. Hence we include c with a (if A is HgX_2) and can then apply equation (8) which predicts that as $(a_0 + b_0)$ increases so $k_2(\text{obs})$ will decrease.* Inspection of the data in Table 1 shows that this is not so, and hence in the present work K cannot be significantly large. Either K and c are so small that the equilibrium/steady-state situation applies with $k_2(\text{obs}) = k_1K$ or the kinetics can be said to be compatible with a simple bimolecular elementary reaction; in view of the discussion above we suggest that the intermediate situation with $k_2(\text{obs}) = k_1K$ probably applies. Interestingly, in the related substitution of aryltriethyltins by mercury(II) acetate in tetrahydrofuran, relative rate constants have been interpreted in terms of a mechanism also involving a π-complex intermediate.[22]

EXPERIMENTAL

Phenyltriethytin was prepared by the action of phenylmagnesium bromide on triethyltin chloride. The product, after two distillations, had b.p. 74—77 °C/18 mmHg (Found: C, 50.6; H, 7.0. $C_{12}H_{20}Sn$ requires C, 50.9; H, 7.1%), and both the n.m.r. spectrum and g.l.c. analysis were consistent with phenyltriethyltin as the only observable species present. Methanol, the aqueous methanolic solvents, and the mercury(II) compounds were as before.[4] For the product analysis, a solution in methanol that was 0.05M in phenyltriethyltin and 0.05M in mercury(II) chloride was set aside at 25 °C for a few hours, then poured into water

---

* If reaction takes place *via* HgX^+ then $k_2(\text{obs})$ will decrease when a_0 (HgX_2) increases. An observed decrease in $k_2(\text{obs})$ with increase in a_0 could thus be due either to HgX^+ being significant or to the kinetic situation discussed here.

[19] J. R. Chipperfield, A. C. Hayter, and D. E. Webster, *J.C.S. Dalton*, 1977, 485.

[20] C. W. Pyun, *J. Chem. Educ.*, 1971, **48**, 194.

[21] F. M. Beringer and E. M. Gindler, *J. Amer. Chem. Soc.*, 1955, **77**, 3200.

[22] H. Hashimoto and Y. Morimoto, *J. Organometallic Chem.*, 1967, **8**, 271.

containing sodium chloride (0.1M), and the aqueous solution extracted with chloroform. The extracts were dried and on evaporation to small bulk yielded the crystalline phenylmercury(II) chloride admixed with the pale yellow liquid triethyltin chloride. Hexane was added to this mixture to dissolve the liquid, and the phenylmercury(II) chloride was filtered off through a sintered glass crucible, washed with hexane, and dried to constant weight. The uncrystallised product, isolated in 93% yield, had m.p. 251 °C (lit.,[23] 251, 251, 251, 252, 252, and 258) and an n.m.r. spectrum that was consistent with pure phenylmercury(II) chloride.

Kinetic measurements were carried out essentially as described before,[4] except that much lower concentrations of reactants were used. In addition, because of the high reaction rates encountered, aliquot portions (5 ml) were withdrawn from the kinetic solution by means of a special reaction vessel in which the solution was forced by pressure of nitrogen into a calibrated pipette and thence into the quench solution. The entire apparatus and calibrated pipette was thermostated (to ±0.05 °C) and with practice it proved possible to withdraw aliquot portions every 25 s.

We thank Dr. G. J. Buist for details of the special reaction vessel and the Iranian Ministry of Science and Higher Education for a scholarship (to M. R. S-H.).

[7/1615 *Received*, 12*th September*, 1977]

---

[23] L. G. Makarova and A. N. Nesmeyanov, in 'The Organic Compounds of Mercury,' North-Holland Press, Amsterdam, 1967, p. 232.