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Substitution at Saturated Carbon. Part XI.¹ Substitution of Tetraethyltin by Mercury(II) Salts in Acetonitrile

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The substitution of tetraethyltin by mercury(II) chloride in acetonitrile, reaction (1 ; X = CI), follows second-order kinetics (first-order in each reactant) and is subject to positive kinetic salt effects and to positive co-solvent effects Et₄Sn + HgX₂ → EtHgX + Et₃SnX (1)

of added water. It is concluded that reaction (1; X = CI) proceeds by mechanism $S_{E}2$ (open). The analogous substitution (1 ; X = I) is also subject to positive kinetic salt effects in solvent acetonitrile, and mechanism $S_{E}2$ (open) is again suggested. Activation parameters for reaction (1; X = Cl or I) are reported; values of ΔS^{\ddagger} , on the molar scale, are -28 and -31 cal deg⁻¹ mol⁻¹ respectively. Relative rate coefficients for reaction (1) in acetonitrile are 4.5 (X = OAc), 1.0 (X = Cl), and 1.8 (X = I) whereas in methanol they are 250 (X = OAc), 1.0 (X = Cl), and 0.8 (X = 1).

WE have recently investigated ^{1,2} the kinetics of reaction (1; X = Cl) using as solvents water-methanol and t-butyl alcohol-methanol mixtures covering a dielectric constant range 48·2—12·5; reaction (1; X = I or OAc) was also studied kinetically, but in less detail. It

seemed of interest to study the effect of dipolar aprotic solvents on reaction (1; X = Cl, I, or OAc). It is THIT V I Et CnY THE I TIN

$$Et_4Sn + HgX_2 \longrightarrow EtHgX + Et_3SnX$$
 (1)

known³ that rate coefficients for $S_N 2$ reactions of the Menschutkin type are considerably increased in value ² M. H. Abraham and G. F. Johnston, J. Chem. Soc. (A), 1970, 188.
³ M. H. Abraham, J. Chem. Soc. (B), 1971, 299.

¹ Part X, M. H. Abraham and F. Behbahany, J. Chem. Soc. (A), preceding paper.

when hydroxylic solvents are replaced by dipolar aprotic solvents; both the Menschutkin reaction and reaction (1) are examples of reactions involving only neutral molecules as reactants. Acetonitrile ($\epsilon^{25} = 36.0$) was chosen as a suitable example of a dipolar aprotic solvent of about the same dielectric constant, ε , as methanol $(\varepsilon^{25} = 32.6).$

TABLE 1

Effect of various impurities on the rate coefficient for substitution of tetraethyltin by mercury(II) chloride at 25°. Initial concentrations: tetraethyltin, $9 \times$ 10^{-3} M; mercury(II) chloride 6×10^{-3} M

Solvent	$\frac{k_2}{1 \text{ mol}^{-1} \text{ min}^{-1}}$
Pure acetonitrile «	1.12
Crude acetonitrile b	0.85
Crude acetonitrile, dried with CaH ₂	0.81
0.112M-Water in pure acetonitrile	1.14
Pure acetonitrile, under air ","	1.15
Pure acetonitrile, under nitrogen a.c	1.16

^a Quinol present in concentration 6×10^{-5} M. ^b Initial value of k_2 given, since k_2 decreased with time. • These two runs were carried out concurrently, using the same batch of purified acetonitrile.

Substitution of Tetraethyltin by Mercury(II) Chloride.-Qualitative product analyses by t.l.c. showed only the presence of the products ethylmercury(II) chloride and triethyltin chloride. Two semi-quantitative isolations of ethylmercury(II) chloride gave yields of 83 and 85%, and seven gravimetric product analyses of ethylmercury(II) chloride [as the water-insoluble ethylmercury(11) iodide] gave yields between 84 and 93%, all yields being based on the stoicheiometry of reaction (1; X = Cl). Since all product analyses were carried out on reactions run under kinetic conditions, we conclude that (1; X = Cl) does indeed describe the stoicheiometry of the reaction under kinetic study.

Kinetics of reaction (1; X = Cl) were followed by our usual 1,2 procedure of quenching (ratio 1:100) aliquot portions of the reaction mixture in a methanol-water mixture containing potassium iodide. Unchanged mercury(II) chloride is quantitatively converted into HgI_3^- and the concentration of the latter is found by u.v. absorbance measurements. Because of the presence of acetonitrile (1%) in the quenched solution, it was necessary to construct new calibrations relating observed absorbance of the quenched solution to the (formal) concentration of mercury(II) chloride. Using 50 simulated reaction mixtures corresponding to between 0 and 100% reaction, new calibrations were prepared at wavelengths 302.5 and 315 nm. These calibrations are extremely close to the original ones obtained 2 in the absence of acetonitrile.

Initially it was extremely difficult to obtain reproducible kinetic data for reaction (1; X = Cl). We traced the origin of these kinetic disturbances to the solvent, and found that only by rigorous purification of the solvent was it possible to obtain reproducible values of the rate coefficient. Difficulty has been reported previously ^{4,5} in using acetonitrile as solvent for kinetic studies involving organometallic substrates. The only impurities in the acetonitrile that we could identify were benzene and water, but neither of these compounds when added to a purified sample of acetonitrile resulted in anomalous kinetic data. The presence of air (or oxygen) was shown not to affect the kinetics, because two concurrent runs, one carried out under nitrogen and the other under air, gave the same value of the rate coefficient. Table 1 gives results of a number of runs carried out under various conditions; it should be noted that use of an impure sample of solvent always gave low values of the rate coefficient, and that in these cases usually poor kinetic plots were obtained. We found that addition of quinol tended to increase reproducibility, without altering the average value of the rate coefficient; runs carried out using highly purified acetonitrile were therefore run in the presence of quinol $(6 \times 10^{-5} M)$. Some runs were carried out in presence of 6×10^{-4} Mquinol and yielded the same value of the rate coefficient.

Kinetic runs carried out using pure solvent were treated by application of the usual second-order rate equation; ca. 15 points were taken in any run, and the runs followed to ca. 70% reaction. Good straight lines were obtained, and rate coefficients calculated from data at 302.5 and at 315 nm were identical. Table 2 shows

TABLE 2

Second-order rate coefficients for the substitution of tetraethyltin by mercury(II) chloride in acetonitrile at 25°

Initial concer	tration 10 ² M	
$[Et_4Sn]$	[HgCl ₂]	$k_2/l \text{ mol}^{-1} \min^{-1}$
0.904	0.605	1.12
2.410	0.602	1.04
4.815	0.603	1.06
7.227	0.602	1.04
9.630	0.604	1.15
6.775	0.152	1.07
6.780	0.302	1.23
6.770	1·506 ª	1.21
6.777	3.015 •	1.22

 Absorbance measurements on quenched samples made using 0.1-cm cells.

values of the second-order rate coefficient for various initial concentrations of reactants. Although the reproducibility is not good (this was an early set of runs) the rate coefficient remains reasonably constant over the range of initial concentrations studied [10-fold variation in tetraethyltin, and 20-fold variation in mercury(II) chloride]. Reaction (1; X = Cl) is thus first-order in tetraethyltin, first-order in mercury(II) chloride, and second-order overall. After these preliminary experiments, we set up 21 identical kinetic experiments at 25°. Taking 15 points per run, each analysed at 302.5 and at 315 nm this represents 630 analytical points; the average value of the rate coefficient at 25° was 1.120 l mol⁻¹ min⁻¹ with a standard deviation of 0.033 l mol⁻¹ min⁻¹. The second-order rate coefficient

⁴ M. Gielen and J. Nasielski, J. Organometallic Chem., 1967, 7, 273. ⁵ R. M. G. Roberts, J. Organometallic Chem., 1968, **12**, 97.

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for reaction (1; X = Cl) obtained ² using methanol as solvent was 0.200 l mol⁻¹ min⁻¹ at 25°, so that replacement of methanol by acetonitrile has given rise to but a small rate enhancement. In Table 3 are values of the rate coefficient for reaction (1; X = Cl) at 25, 40, and 60°; corrections for solvent expansion have been applied in the calculation of rate coefficients at the higher temperatures.

TABLE 3

Second-order rate coefficients for the substitution of tetraethyltin by mercury(II) chloride and iodide in acetonitrile.^a Initial concentrations: tetraethyltin 9×10^{-3} M; mercury(II) halide 6×10^{-3} M

Temp./°C	Number of kinetic runs	k2/l mol-1 min-1
(a) With mercury(II) chloride	
25	21	1.120 ± 0.033 s
40	5	2.75 ± 0.02 °
60	19	9·24 \pm 0·24 »
(b) With mercury(II	i) iodide	
25	4	2.04 ± 0.02 c
40	2	4.92 ± 0.03 °
60	2	13.6 ± 0.4 \circ
~ · ·		

 o Quinol present in concentration $6\times 10^{-5}M.$ o Standard deviation. o Estimated standard deviation.

In order to deduce more about the mechanism of reaction (1; X = Cl), we investigated the effect of addition of lithium perchlorate, tetra-n-butylammonium perchlorate, and water to the acetonitrile solvent. Because of the aforesaid difficulties with solvent, each of these runs was set up side-by-side with a check kinetic run using the same batch of pure acetonitrile as solvent. Table 4 gives the values of k/k_0 , where k and

TABLE 4

Effect of added salts and of added water on the rate coefficient for substitution of tetraethyltin by mercury(II) chloride and iodide in acetonitrile^{*a*} at 25°. Initial concentrations: tetraethyltin 9×10^{-3} M; mercury(II) halide 6×10^{-3} M

Additive	(м)	k/k_0	Additive	(M)	k/k_0
(a) With me	ercury(11)	chloride	(a) With m	ercury(11)	chloride
LiClO₄,	0.20	1.23	H₂O,	0.271	1.05
LiClO ₄ ,	0.60	1.63	H_2O ,	0.541	1.09
$Bu_4^n NClO_4$,	0.50	1.19	H ₂ O,	0.814	1.16
Bun ₄ NClO ₄ ,	0.40	1.29	H ₂ O,	1.092	1.19
Bun NClO4,	0.60	1.33	H ₀ O,	1.641	1.25
Bun NClO4,	0.80	1.41	$H_{2}O$,	$2 \cdot 204$	1.28
н,0,	0.030	1.04	H ₂ O,	2.770	1.37
H.O.	0.060	1.02	-		
H.O.	0.112	1.02	(b) With me	ercury(II)	iodide
н,о,	0.167	1.04	Bun ₄ NClO ₄ ,	0.20	1.14 0
H.O.	0.219	1.07	KI.	0.006	0
			KI,	0.012	0

 $^{\rm e}$ Quinol present in concentration $6\times 10^{-5} \rm M.$ $^{\rm b}$ Initial value (see text).

 k_0 are the second-order rate coefficients in the presence and the absence of additive respectively. Addition of either perchlorate results in an increase in the value of the second-order rate coefficient. Values of k/k_0 for addition of salt to a concentration of 0.2M using solvent

⁶ L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, J. Chem. Soc., 1940, 979.

acetonitrile may be compared to similar figures for solvent methanol and methanol-water of mole fraction methanol 0.91:

The salt effects in solvent acetonitrile may be treated in terms of equation (2),^{1,6} where I is the ionic strength, N is the Avogadro number, e the electronic charge, ε the solvent dielectric constant, and k' the Boltzman constant. In the derivation of equation (2), the transi-

$$\left[\frac{\log (k/k_0)}{I}\right]_{I \to 0} = \frac{4\pi N e^4}{2303(\epsilon k'T)^2} \cdot Z^2 d \qquad (2)$$

tion state is assumed to behave as though it were a point dipole carrying charges +Z and -Z separated at a distance d/Å. Our calculated values of Z^2d are 0.652 (for tetra-n-butylammonium perchlorate) and 0.674 (for lithium perchlorate). If d is taken (as before) 1,2as the mercury-tin distance of ca. 3.1 Å, the corresponding values of Z are 0.46 and 0.47 units of charge respectively. Although these values are appreciably lower than those we have calculated 1 from salt effects on reaction (1; X = Cl) in methanol and methanol-water (0.84 and 0.75 respectively), they are still high enough for us to suggest that reaction (1; X = Cl) in solvent acetonitrile proceeds by mechanism $S_{\rm E}2$ (open) through a transition state such as (I; X = Cl) in which there is considerable separation of charge. We think that transition state (II; X = Cl), corresponding to mechanism $S_{\rm E}2$ (cyclic), is unlikely to be obtained with acetonitrile as the solvent.



Addition of water to the acetonitrile solvent also leads to an increase in the rate coefficient (see Table 4), again as expected if relatively non-polar reactants proceed to a polar transition state such as (I; X = Cl). The accelerating effect of water is less than in the corresponding ² addition of water to methanol solvent, addition of 2% v/v water to acetonitrile and to methanol increasing the value of the rate coefficient by factors of 1.20 and 1.37 respectively. Roberts,⁵ however, found that in cleavage of allyltriethylgermanium by mercury(II) bromide, traces of water had a profound retarding effect, and that addition of 2% v/v water to the solvent acetonitrile resulted in a decrease in value of the rate coefficient by a factor of 50. Roberts ⁵ has also shown that reaction (3) proceeded very rapidly in acetonitrile at

$AllylSnEt_3 + HgCl_2 \longrightarrow AllylHgCl + Et_3SnCl$ (3)

25°; from his data the second-order rate coefficient for (3) must be at least 3×10^4 l mol⁻¹ min⁻¹ so that [after

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correction for the statistical factor in reaction (1; X = Cl an allyl group must be cleaved from tin ca. 10⁵ times more rapidly than is an ethyl group, with mercury(II) chloride as electrophile and acetonitrile as solvent.

Substitution of Tetraethyltin by Mercury(II) Salts.— The kinetics of reaction (1; X = I) are complicated ⁷ by the subsequent rapid equilibrium (4), and in order to obtain values of the rate coefficient for reaction (1; X = I) it is necessary to know (roughly) the value of

$$Et_{3}SnI + HgI_{2} = Et_{3}Sn^{+} + HgI_{3}^{-} \qquad (4)$$

the equilibrium constant for reaction (4) under the kinetic conditions, $K_{\rm r}$. We evaluated $K_{\rm r}$ from the kinetic data on a trial-and-error basis (cf. ref. 1) by use of a modified version of Spalding's computer programme,⁸ as 8.0. If this is combined with the value 9 of 9×10^{5} 1 mol⁻¹ for the third stepwise formation constant for HgI₃⁻ in acetonitrile at 25°, a value of 9×10^{-6} l⁻¹ mol may be deduced for the equilibrium constant for reaction (5) in acetonitrile at 25° . Values of the second-order rate coefficient for reaction (1; X = I) are in Table 3. The effect of added tetra-n-butylammonium perchlorate

$$Et_{a}SnI \Longrightarrow Et_{a}Sn^{+} + I^{-}$$
 (5)

on the rate coefficient for reaction (1; X = I) was also studied, but we found that in the presence of this salt the value of the rate coefficient in any given kinetic run decreased as the run progressed. The value of k/k_0 given in Table 4 was therefore calculated from measurements of initial rates of reaction. When higher concentrations of the perchlorate were used, we could not even obtain rate coefficients from initial rates. We feel that addition of tetra-n-butylammonium perchlorate results in a genuine positive kinetic salt effect, but that superimposed on this effect is an apparent rate retardation possibly due to some decomposition. This was not further investigated, however, since the main purpose had been accomplished, *i.e.* that reaction (1;X = I) had been shown to be subject to a positive salt effect, and hence that the mechanism could be established as $S_{\rm E}2$ (open).

Activation parameters for reaction (1; X = Cl and I) are in Table 5, together with corresponding values for solvent methanol. The variations in ΔH^{\ddagger} and ΔS^{\ddagger} have not been analysed in detail, since it is not known how much these variations are influenced by initial-state effects. However, the four values of ΔS^{\ddagger} are all of the same order of magnitude $(-26\cdot4 \pm 4\cdot6)$ and are thus compatible with the assignment of mechanism $S_{\rm E}2$ (open) for all four reactions (although we stress that the mechanism cannot be deduced from these values of ΔS^{\ddagger}).

Finally, we have compared rate coefficients for * Mechanism $S_{\mathbf{E}}2$ (cyclic) corresponds to mechanism $S_{\mathbf{E}}i$ in

Ingold's terminology. 7 M. H. Abraham and T. R. Spalding, J. Chem. Soc. (A), 1968,

2530. ⁸ T. R. Spalding, Ph.D. Thesis, University of London, 1967. reaction (1; X = Cl, I, and OAc) by running a series of experiments in acetonitrile containing 8.3×10^{-4} Macetic acid: the presence of the acid was necessary to suppress slight solvolysis of mercury(II) acetate. Values

TABLE 5

Activation parameters a for the substitution of tetraethyltin by mercury(II) halides in acetonitrile and in methanol, at 298 K

Solvent	HgX_2	ΔG [‡]	ΔH	ΔS^{\ddagger}
Acetonitrile	$HgCl_2$	19,812 ^δ	11,300	- 28.5
Acetonitrile	HgI_2	19,456	10,200	- 31.0
Methanol	$HgCl_2$	20,832	14,350	- 21.8
Methanol 4	HgI_2	20,995	13,000	-26.7

• ΔG^{\ddagger} (± 6) and ΔH^{\ddagger} (± 200) in cal mol⁻¹, ΔS^{\ddagger} (± 0.7) in cal deg⁻¹ mol⁻¹, all on the molar scale. • ± 17 . • Ref. 2. • Calculated from $k_2^{25} = 0.152$ l mol⁻¹ min⁻¹ and $k_2^{40} = 0.457$ 1 mol⁻¹ min⁻¹.

for the rate coefficient for reaction (1; X = Cl and I) are, within experimental error, unaffected by the presence of acetic acid. Table 6 gives both the secondorder rate coefficients and relative rate coefficients for substitution of tetraethyltin by mercury(II) species in solvents methanol and acetonitrile. As far as the absolute rate coefficients are concerned, transfer from

TABLE	6
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Second-order rate coefficients for the substitution of tetraethyltin by mercury(II) salts in acetonitrile a at 25°. Initial concentrations: tetraethyltin 9×10^{-3} M; mercury(11) salt 6 \times 10⁻³M

	Solvent acetonitrile		Solvent methanol »	
Mercuric salt	$k_2/l \text{ mol}^{-1}$ min ⁻¹	rel. k_2	$k_2/l \mod^{-1} \min^{-1}$	rel. k_2
$Hg(OAc)_2$ $HgCl_2$	$5.02 \\ 1.12$	4·48 1	$51.0 \\ 0.200$	255 1
Hgl ₂ Hgl ₃ -	$2 \cdot 06$	1.84	0.152 0	0·76 0

" In presence of 8.33×10^{-4} M-acetic acid and 6×10^{-5} M-Each set of runs carried out in duplicate. • Ref. 1. auinol.

methanol to acetonitrile results in rate enhancements for reaction (1; X = Cl and I), by factors 6 and 13 respectively, but in a rate decrease for reaction (1; X = OAc) by a factor of 10. The relative rates lead to the reactivity sequence (6) in methanol and to the partially inverted sequence (7) in acetonitrile.

$$Hg(OAc)_{2} \gg HgCl_{2} > HgI_{2} > HgI_{3}^{-} = 0 \quad (6)$$

$$\operatorname{Hg(OAc)}_{2} > \operatorname{HgI}_{2} > \operatorname{HgU}_{2} > \operatorname{HgI}_{3}^{-} = 0 \quad (7)$$

$$\mathrm{Hg(NO_3)_2} > \mathrm{Hg(OAc)_2} > \mathrm{Hg(Hal)_2} > \mathrm{Hg(Hal)_3^{-}} (8)$$

It has been suggested ^{5,10} that reactivity sequences such as (6) and (8), for electrophilic attack on a given substrate in a given solvent, may be taken as characteristic of reactions proceeding by mechanism $S_{\rm E}2$ -(open), whereas if reaction proceeded by mechanism $S_{\rm E}2$ (cyclic)* then the reactivity sequence (9) would be

⁹ G. Ellendt and K. Cruse, Z. phys. Chem. (Leipzig), 1952,

^{201, 130.} ¹⁰ H. B. Charman, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 1959, 2530; R. M. G. Roberts, J. Organometallic Chem., 1968, 12, 89; R. M. G. Roberts, J. Organometallic Chem., 1969, 18, 307; B. J. Gregory and C. K. Ingold, J. Chem. Soc. (B), 1969. 276.

obtained. Although subject to criticism,^{2,11} this argument has been used several times 5,10 in the assignment

$$Hg(Hal)_{2} > Hg(OAc)_{2} > Hg(NO_{3})_{2}$$
(9)

of mechanism. We have now shown that the substitutions of tetraethyltin by mercury(II) chloride and mercury(II) iodide in solvents methanol and acetonitrile are all subject to positive kinetic salt effects, and hence we have assigned mechanism $S_{\rm E}2$ (open) to all four substitutions. Yet in methanol the order of reactivity is ${\rm HgCl}_2 > {\rm HgI}_2$, and in acetonitrile it is ${\rm HgI}_2 > {\rm HgCl}_2$. It seems clear that sequences of reactivity amongst the mercury(II) halides are of little mechanistic diagnostic value; it remains to be seen whether sequences such as (8) and (9) can be used as reliable criteria of mechanisms $S_{\rm E}2$ (open) and $S_{\rm E}2$ (cyclic) respectively.

EXPERIMENTAL

Preparation of Materials.—Acetonitrile (from Cambrian Chemicals Ltd.) was purified as follows 12: acetonitrile (1800 ml) was refluxed with benzoyl chloride (20 ml) and then distilled at a rate of 5-10 ml/min into water (20 ml). The distillate was then stirred and heated under reflux with anhydrous sodium carbonate (40 g) for 2 h, the solid material was filtered off, and the acetonitrile was distilled (with stirring) from fresh anhydrous sodium carbonate (20 g) and potassium permanganate (30 g). The distillate was carefully acidified with concentrated sulphuric acid and the acetonitrile was decanted from the white precipitate of ammonium sulphate and finally dried by refluxing over calcium hydride until evolution of hydrogen ceased (usually ca. 2 h). The dried acetonitrile was then fractionally distilled through a 60-cm column equipped with heating-tape and packed with 1/16-in stainless-steel Dixon rings. The column was operated at a boilup rate of 500 g/h with a reflux : take-off ratio of 50, thus allowing the collection of 10 g distillate/h. Under these conditions, the estimated plate value is 100. A forecut (usually ca. 100 ml) of distillate was rejected and pure acetonitrile of b.p. 81.8°/760 mmHg, ρ^{25} 0.7766, and η_D^{20} 1.3435 was collected (lit.,¹² b.p. 82.0°/763 mmHg, ρ^{25} 0.7768, and η_D^{20} 1.3439). A Karl Fischer titration showed that the water content of the purified acetonitrile was 0.03% w/w.

Methanol and mercury(II) chloride were purified as described ² before. Tetraethyltin and mercury(II) iodide were purified as described ⁷ by Abraham and Spalding; the tetraethyltin had b.p. $68 \cdot 5^{\circ}/12$ mmHg and $\eta_{\rm p}^{25}$ 1·4686 (lit., ⁷ b.p. 70—71°/17 mmHg and $\eta_{\rm p}^{25}$ 1·4687). Mercury(II) acetate was AnalaR grade. Lithium perchlorate was purified, and solutions of the salt were standardised, as described ¹³ previously, and tetra-n-butylammonium perchlorate was prepared and dried.²

Product Analyses.—Solutions, 9×10^{-3} M in tetraethyltin and 6×10^{-3} M in mercury(II) chloride, were thermostatted at 40° for 3 h and treated as follows: (i) examination of the reaction mixture by t.l.c. showed the presence of ethylmercury(II) chloride and (after concentration) triethyltin chloride; (ii) the reaction mixture was evaporated to small bulk and treated with ether to leave ethylmercury(II)

¹² J. F. O'Donnell, J. T. Ayres, and C. F. Mann, Analyt. Chem. 1965, **37**, 1161.

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chloride as a white solid of m.p. and mixed m.p. 188° (lit.,² 191--192°) in yields of 83·3 and 85·2% (two separate experiments) based on the stoicheiometry of equation (1; X = Cl); (*iii*) the reaction mixture was poured onto an aqueous solution of potassium iodide containing 2 mol of potassium iodide per mol of mercury(II) chloride. A white suspension of ethylmercury(II) iodide formed at once and coagulated on addition of ice. The coagulated precipitate was filtered off, with some difficulty, through a weighed sintered glass crucible, washed with cold water, and dried to constant weight. The weight of precipitate [as ethylmercury(II) iodide] corresponded to 84, 86, 83, 88, 86, 92, and 93% (seven separate experiments) of the initial mercuric chloride.

Kinetic Measurements.—Spectrophotometric measurements were made with an SP 500 spectrophotometer as described ¹⁴ previously. Kinetic runs were followed by withdrawing aliquot portions of the reaction mixture (0·2 ml) and quenching them by addition to $2\cdot5 \times 10^{-3}$ Mpotassium iodide in a methanol-water mixture of mol fraction methanol 0·91 (20 ml). This procedure results in quantitative conversion of mercury(II) chloride to HgI₃⁻, the latter being determined through its absorbance at either 302·5 or 315 nm. A series of 50 simulated reaction mixtures was prepared with acetonitrile as solvent and quenched by the usual mixture. The formal concentration of unchanged mercury(II) chloride in the quenched samples was found to be given by the equations

$$\begin{array}{l} D(302\cdot 5 \text{ nm}) = 1\cdot 189017 \times 10^4 \ [\text{HgCl}_2] + 0\cdot 0280 \\ D(315 \text{ nm}) = 1\cdot 010963 \times 10^4 \ [\text{HgCl}_2] + 0\cdot 0235 \end{array}$$

where D is the observed absorbance with 1-cm cells, and the formal concentrations are in mol l^{-1} ; the constants in the above equations were calculated by the method of least squares, using all 50 points. The equations were shown also to be valid when the mercuric salt was mercury(II) acetate or mercury(II) iodide.

Dilutions of the reaction mixture aliquot portions were determined by weight, and converted into volume dilutions by use of the density of the potassium iodide solution at 25° ($\rho = 0.7965$) and the density of the reaction mixture at 25° . The latter was calculated from the densities of the separate solutions of the reactants:

$\rho^{25} = 0.24381 [\text{HgCl}_2] + 0.7783$	$([HgCl_2] \leq 0.12M)$
$\rho^{25} = 0.08782 [\text{Et}_4 \text{Sn}] + 0.7776$	$([Et_4Sn] \leq 0.18M)$
$\rho^{25} = 0.00477[H_2O] + 0.7754$	$([H,O] \leq 2 \cdot 2M)$

For kinetic runs in the presence of lithium perchlorate or tetra-n-butylammonium perchlorate, the density of each reaction mixture was separately determined as described before.²

Corrections for thermal expansion of the solvent were made in the case of runs at 40 and at 60°; the required solvent densities were determined separately as: $\rho^{25} = 0.7766$, $\rho^{40} = 0.7611$, and $\rho^{60} = 0.7404$, in g cm⁻³.

The temperatures at which kinetic runs were set up, 25, 40, and 60°, were constant to at least 0.01 °C as measured against N.P.L. calibrated thermometers.

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¹¹ F. R. Jensen and B. Rickborn, 'Electrophilic Substitution of Organomercurials,' McGraw-Hill, New York, 1968, pp. 159– 160.

¹³ M. H. Abraham and T. R. Spalding, J. Chem. Soc. (A), 1969, 784.

¹⁴ M. H. Abraham, G. F. Johnston, and T. R. Spalding, J. Inorg. Nuclear Chem., 1968, **30**, 2167.