Substitution at Saturated Carbon. Part XVII.[1] Substitution of Tetraethyltin by Mercury(II) Carboxylates in Methanol

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Observed second-order rate constants for the S_E2 substitution of tetraethyltin by mercury(II) carboxylates, $Hg(OCOR)_2$, in methanol increase along the series R = Bu^t < Et < Me < Ph < $ClCH_2CH_2$ < $MeOCH_2$ < $ClCH_2$. From the observed rate constants and the corresponding Hg^{2+}–RCO_2^- stability constants, actual rate constants have been calculated for attack of various mercury(II) species on tetraethyltin; it is shown that under the kinetic conditions *ca.* 60% reaction takes place through the species $Hg(OCOR)_2$. Rate constants for attack of $Hg(OCOR)_3^-$, $Hg(OCOR)_2$, and $HgOCOR^+$ are in the order 0 : 1 : 10^2, and for substitution by both $Hg(OCOR)_2$ and $HgOCOR^+$ the calculated rate constants yield the above reactivity sequence in R (R = Bu^t < Me < $MeOCH_2$). It is suggested that substitution of tetraethyltin by the species $Hg(OCOR)_2$ in methanol takes place by the S_E2(open) mechanism, and not through a cyclic transition state.

MERCURY(II) ACETATE occupies a peculiar position as an electrophile in kinetic and mechanistic studies of bimolecular substitutions at saturated carbon (S_E2 reactions). Ingold and his co-workers[2] have suggested that the electrophilic reactivity sequence (1) is characteristic of reactions proceeding through open transition

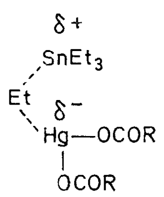
$$HgHal_3^- < HgHal_2 < Hg(OAc)_2 < Hg(NO_3)_2 \quad (1)$$

states, and this sequence has subsequently been used to assign mechanism S_E2(open) to several reactions of mercury(II) acetate.[2-5] Jensen and Rickborn,[6] and others,[7-9] have questioned the usefulness of sequences such as (1) in the assignment of open or cyclic mechanisms, but very few studies have been carried out either to verify Ingold's suggestion by independent methods or to determine the exact mechanism of S_E2 reactions with mercury(II) acetate as the electrophile.

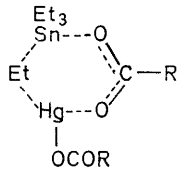
Substitution of di-s-butylmercury by mercury(II) acetate in ethanol proceeds[2] with retention of configuration at the site of substitution, and this seems to be the general stereochemical rule for metal-for-metal exchanges (see ref. 1). It is not easy to distinguish between the two main consequent mechanisms, S_E2(open)Ret and S_E2(cyclic), although for mercury(II) acetate reactions attempts have been made through kinetic salt effects.[3,10] For reaction of a mercury(II) salt, HgX_2, with a neutral substrate, mechanism S_E2(open) should give rise to positive kinetic salt effects and mechanism S_E2(cyclic) to small or zero salt effects. However, addition of a salt M^+Y^- (where Y^- can also be the common ion X^-) can result in a number of severe complications. (i) If the mercury(II) species dissociates in solution to HgX^+ and X^-, addition of M^+Y^- should increase the proportion of HgX^+ through an ionic strength effect. Were the electrolyte added to contain the common ion X^-, then the proportion of HgX^+ would be reduced. (ii) Anion exchange between HgX_2 and Y^- could result in formation of the species HgXY; this effect would be inconsequential for addition of M^+X^-. (iii) Complexes of type HgX_2Y^- and HgX_3^- may be formed. Since the various species HgX^+, HgX_2, HgXY, HgX_2Y^-, and HgX_3^- will in general react with the substrate at different rates, any alteration in their proportion present caused by addition of the electrolyte will affect the observed rate constant.

Solvent effects on rate constants for the reaction between tetraethyltin and HgX_2 (X = Cl, I, and OAc) have been studied[10] and a dissection into initial-state and transition-state effects has been carried out.[11] Such studies can only help to distinguish between the open and cyclic mechanisms if the reaction mechanism is constant over the solvent range used, and if the active electrophile does not alter.

In the present work we have studied the S_E2 reaction (2), using a variety of mercury(II) carboxylates in solvent methanol. If the open transition state (I) is in force,



(I)



(II)

$$Et_4Sn + Hg(OCOR)_2 \longrightarrow EtHgOCOR + Et_3SnOCOR \quad (2)$$

electron-attracting substituents in R should aid reaction, but if the cyclic transition state (II) obtained, there should be but little substituent effect.

A number of mercury(II) carboxylates were therefore prepared and rate constants for reaction (2) obtained

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TABLE 1

Second-order rate constants for the substitution of tetraethyltin by mercury(II) carboxylates in methanol at 30°; initial concentration $4{\cdot}8 \times 10^{-4}$M in Et_4Sn and $2{\cdot}5 \times 10^{-4}$M in $(RCO_2)_2Hg$

R	Bu^t	Et	Me	Ph	$ClCH_2CH_2$	$MeOCH_2$	$ClCH_2$
k_2/l mol^{-1} min^{-1}	26·7 [a]	52·2	71·5 [a]	85·5	89·3	233	329
Relative k_2	0·37	0·73	1	1·20	1·25	3·26	4·60
$10^2[RCO_2H]$/M [b]	1·57	1·60	1·79	1·64	2·12	2·55	2·60

[a] These values are not quite consistent with those, obtained in different sets of kinetic runs, given in Tables 3 and 4. [b] Added to suppress solvolysis.

TABLE 2

Relative rate constants and equilibrium constants [a] for reaction of carboxylic acid derivatives

No.	Process	Solvent	R	Bu^t	Et	Me	Ph	$ClCH_2CH_2$	H	$MeOCH_2$	$ClCH_2$	Cl_2CH	Cl_3C	Ref
1	$Ph_2Hg + RCO_2H$	Dioxan				1	4·7		4·2			310	3000	12
2	$Bu_4{}^nSn + (RCO_2)_2Hg$	Methanol		0·3	0·6	1	1·5	1·6			4·9			13
3	$Et_4Sn + (RCO_2)_2Hg$	Methanol		0·4	0·7	1	1·2	1·3		3·3	4·6			This work
4	$Et_3B + RCO_2H$	Diglyme		1·7	1·0	1	0·9				0·11	$1{\cdot}2 \times 10^{-2}$	Small	14
5	$MeHg^+ + RCO_2^-$	Water		2·1	1·6	1		(0·47)	0·31	(0·26)	0·10	$1{\cdot}0 \times 10^{-2}$		15
6	$SnCl_4 + RCO_2H$	o-$C_6H_4Cl_2$		5·6	2·1	1		0·09			0·01			16
7	$Pr_3{}^nSn^+ + RCO_2^-$	Water		(1·8)	(1·3)	1		(0·17)	0·10	(0·07)	0·01	$5{\cdot}8 \times 10^{-4}$		17
8	$H^+ + RCO_2^-$	Water		1·9	1·3	1		0·17	0·10	0·06	0·01	$4{\cdot}0 \times 10^{-4}$		18

[a] Values in parentheses obtained from linear plots of log K against pK_a of the corresponding acid in water.

using our standard kinetic procedures.[1] In order to prevent solvolysis of the mercury(II) carboxylates, small quantities of the corresponding carboxylic acid were added to the reactant solutions. Figure 1 shows the effect of such additions on the rate constants for reaction (2); in each case the value of the rate constant rises to a maximum as solvolysis is suppressed and then slowly decreases. In Table **1** are given the maximum 'plateau' values of the second-order rate constants. These values increase steadily with increase in the K_a values for the corresponding carboxylic acids (although values of log k_2 are not linearly related to the pK_a values). Hence, by the argument outlined above, we suggest transition state (I) for the various substitutions, equation (2). It is true that the use of sequence (1) has been criticised on the grounds that the reaction mechanism could change if the electrophile was altered, but we feel that the various electrophiles $Hg(OCOR)_2$ are similar enough to assume a constant mechanism along the series.

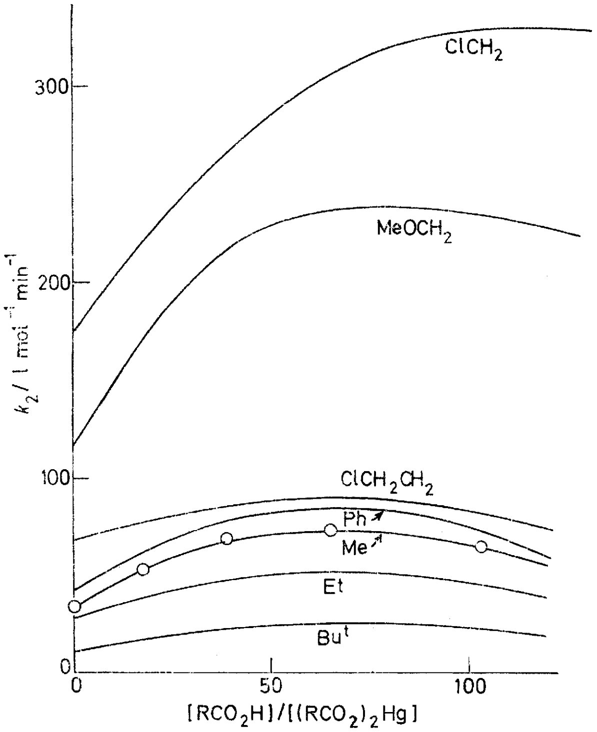
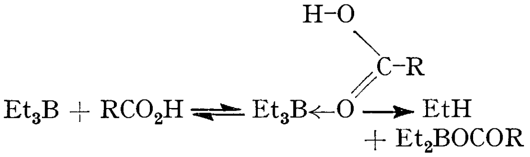


FIGURE 1 Variation in rate constant for reaction (2) with the ratio $[RCO_2H]/[Hg(OCOR)_2]$; curves labelled in terms of the alkyl group, R

In Table 2, the present rate data are compared with those for various rate [12-14] and equilibrium [15-18] processes involving carboxylates and carboxylic acids. Whenever the carboxylates or carboxylic acids act as nucleophiles (cases 4—8) the sequence of rate constants or equilibrium constants is always the reverse of that shown in reaction (2). The prime example of such a nucleophilic process is the acidolysis of triethylboron [14] where the carboxylic acid first co-ordinates to the boron atom [equation (3)]. Conversely, in the aromatic



$$Et_3B + RCO_2H \rightleftharpoons Et_3B{\leftarrow}O{=}C(R){-}O{-}H \longrightarrow EtH + Et_2BOCOR \quad (3)$$

substitution (case 1) an open transition state with predominant electrophilic attack of the acid is probable,

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since the large Hg–C–H angle in the transition state makes formation of a cyclic six-centred transition state sterically rather difficult. Finally, the close correlation between relative rate constants for reaction (2) and for the related reaction of tetra-n-butyltin [13] suggests that effects of the various groups R are, as we imply, polar in nature. Were steric effects important, it is unlikely that the same sequence of relative rates would be obtained in the two cases.

TABLE 3

Second-order rate constants for the substitution of tetraethyltin by mercury(II) acetate in methanol [a] at 30°

Initial concentration		
$10^4[Et_4Sn]$/M	$10^4[Hg(OAc)_2]$/M	k_2/l mol^{-1} min^{-1}
3·96	2·99	73·1
4·95	2·99	75·9
5·93	2·99	72·4
6·92	2·99	72·6
7·91	2·99	76·0
8·90	2·99	73·4
9·89	2·39	79·9
9·89	2·99	74·9
9·89	3·59	70·2
9·89	4·19	69·3
9·89	5·08	64·9
9·89	5·98	63·6

[a] All runs carried out in presence of 1·79 × 10^{-2}M-$MeCO_2H$.

During the above work, we observed that rate constants for reaction (2; R = Me) varied with initial concentration of mercury(II) acetate even though excellent second-order kinetics were observed in each kinetic run; details of the variation are in Table 3. We have found in the present work that mercury(II) acetate, like mercury(II) chloride, is monomeric in methanol, but we suspected that the rate variation could be due to the presence of a small amount of a highly reactive electrophile $HgOCOMe^+$. If this were so, then the observed rate constant should be reduced in value on addition of an electrolyte containing the common ion $MeCO_2^-$; details of such experiments are in Table 4, and bear out our expectation. The above rate retardation is unlikely to be due to a normal negative kinetic salt effect, since added sodium acetate has no effect on the rate constant for the related reaction between tetraethyltin and mercury(II) chloride (Table 4). [This latter result does not conflict with our previous observation of positive kinetic salt effects in the Et_4Sn–$HgCl_2$ reaction because the concentrations of added electrolyte in the present work (1·0—4·0 × 10^{-3}M) were very much less than those used[10] previously (0·01—0·30M)]. Similar experiments involving change in initial concentration of $Hg(OCOBu^t)_2$ and $Hg(OCOCH_2OMe)_2$ were also carried out. Results are in Table 5 and parallel closely those for the mercury(II) acetate reactions.

TABLE 4

Effect of added sodium acetate on rate constants for reaction of tetraethyltin with mercury(II) acetate and chloride in methanol at 30°

Added 10^4[NaOAc]/M	k_2/k_2^0
(a) With mercury(II) acetate [a]	
0	1
1·18	1·01
1·89	0·95
2·36	0·91
3·54	0·89
4·72	0·86
(b) With mercury(II) chloride [b]	
0	1
10·0	0·98
20·0	1·01
30·0	1·01
40·0	0·99

[a] Initial concentrations, Et_4Sn 8·8 × 10^{-4}M, $Hg(OAc)_2$ 2·36 × 10^{-4}M, and HOAc 1·25 × 10^{-3}M. [b] Initial concentrations, Et_4Sn 100·4 × 10^{-4}M and $HgCl_2$ 50·5 × 10^{-4}M.

TABLE 5

Variation of rate constant with initial concentration of mercury(II) carboxylate in the substitution of tetraethyltin in methanol at 30°

Initial $10^4[(RCO_2)_2Hg]$/M	k_2/l mol^{-1} min^{-1}
(a) With $(Bu^tCO_2)_2Hg$ [a]	
1·82	32·8
2·42	29·8
3·03	29·8
3·63	28·5
4·84	25·7
6·05	24·9
(b) with $(MeOCH_2CO_2)_2Hg$ [b]	
1·79	292
2·39	263
2·99	225
3·59	211
4·49	194
5·38	202

[a] Initial concentration of Et_4Sn was 10·02 × 10^{-4}M, and all runs carried out in the presence of 1·57 × 10^{-2}M-Bu^tCO_2H. [b] Initial concentration of Et_4Sn was 10·05 × 10^{-4}M, and all runs carried out in the presence of 2·55 × 10^{-2}M-$MeOCH_2CO_2H$.

The retardation caused by added sodium acetate (see Table 4a) contrasts with the effects of added acetic acid (Figure 1) where an initial rate acceleration is followed by a ‘ plateau ’ and finally by a rate retardation. The steady retardation caused by added sodium acetate (in the presence of acetic acid) arises, we suggest, through a reduction in the concentration of the highly active species $HgOAc^+$ by a normal common-ion effect. In the complete absence of acetic acid, mercury(II) acetate undergoes partial solvolysis to yield inactive (and possibly associated and/or colloidal) species such as mercury(II) oxide. Addition of small quantities of acetic acid converts these products back to mercury(II) acetate and hence the observed values of k_2 increase to their plateau values when solvolysis has completely been suppressed. The subsequent retardation on further addition of acetic acid could be due to a combination of a small solvent effect and a partial suppression of the species $HgOAc^+$ by the acetate ion that arises from the very slight dissociation of acetic acid in methanol.

In order to investigate these effects more fully, the stepwise stability constants for the Hg^{2+}–X^- systems are required. Two studies have been reported on the Hg^{2+}–OAc^- system in water, but the results are mutually quite inconsistent (values of K in l mol^{-1} for the Hg^{2+}–OAc$^-$ system in water):

K_1	K_2	K_3	K_4	Ref.
$3{\cdot}6 \times 10^5$	$5{\cdot}5 \times 10^3$	$9{\cdot}6 \times 10^3$	$6{\cdot}1 \times 10^3$	19
$6{\cdot}0 \times 10^4$	6·7	2·5		20

Neither set of results is in accord with recent [21] Raman and i.r. measurements which suggest that in water mercury(II) acetate exists largely as a covalent entity and is not significantly complexed by OAc$^-$. Kreshkov and Balyatinskaya [20] have also obtained values for the Hg^{2+}–OAc$^-$ system in methanol, at 20° and 2M ionic strength:

K_1	K_2	K_3	Ref.
1×10^7	4×10^2	25	20

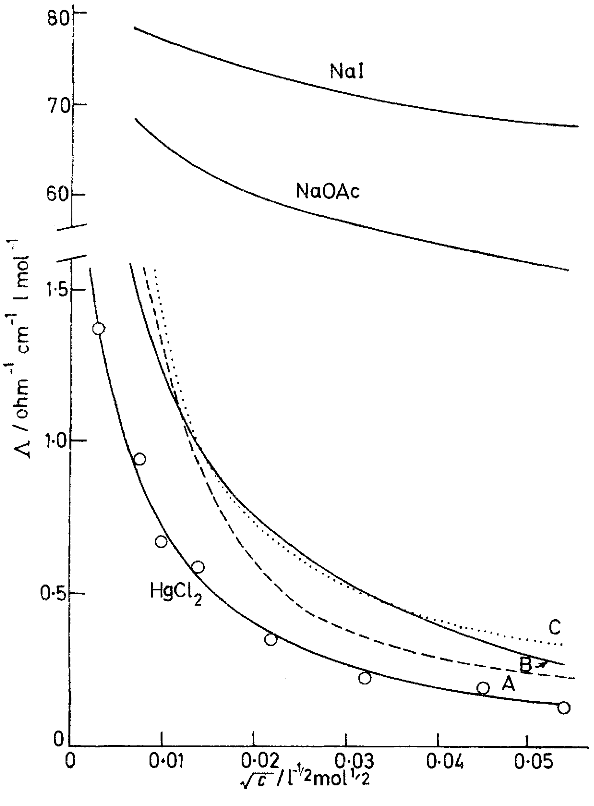

FIGURE 2 Molar conductances of HgCl$_2$ and Hg(OCOR)$_2$ in methanol at 30°: curve A ---- for R = Bu^t; curve B —— for R = Me; and curve C ···· for R = MeOCH$_2$. Also given are conductances for NaI and NaOAc (note the large change in vertical scale for these compounds)

TABLE 6

Values of the stepwise stability constants (l mol^{-1}) for mercury(II)–anion complexes in methanol at 30°

Anion	K_2	K_3
Cl$^-$	$3{\cdot}3 \times 10^8$	Small [a]
Bu^{t}CO$_2^-$	$3{\cdot}5 \times 10^7$	$1{\cdot}2 \times 10^2$ [b]
MeCO$_2^-$	$2{\cdot}1 \times 10^7$	1×10^2
MeOCH$_2$CO$_2^-$	$1{\cdot}8 \times 10^7$	$0{\cdot}8 \times 10^2$ [b]

[a] Deduced from kinetic results in ref. 7. [b] Assumed values (see text).

However, their value of K_2 seems extraordinarily small (as does also their value of K_2 for the same system in water) [20] and in an attempt to resolve this problem we measured the conductivities of several mercury(II) salts in methanol at 30°; as usual, the solvent contained a small quantity of the corresponding carboxylic acid to suppress solvolysis. Results are shown in Figure 2, together with molar conductivities of typical 1 : 1 electrolytes. All four mercury(II) salts behave as extremely weak electrolytes so that K_2 must clearly be very large. Since K_1 must certainly be much larger even than K_2, the salts may be treated as weak 1 : 1 electrolytes and, using the method of Shedlovsky,[22] we thus calculated approximate values for the stability constants, K_2 (Table 6). The value of K_2 for the Hg^{2+}–Cl$^-$ system in methanol ($3{\cdot}3 \times 10^8$) is a realistic one, being *ca.* 100 times the value of K_2 in water ($3{\cdot}0 \times 10^6$),[23] so that our procedure seems to yield reasonable values. However, our value of K_2 ($2{\cdot}1 \times 10^7$) for the Hg^{2+}–OAc$^-$ system in methanol at 30° and effectively zero ionic strength is totally different from that at 20° and 2M ionic strength obtained [20] before (4×10^2). We also attempted to determine a value for K_3 for the Hg^{2+}–OAc$^-$ system in methanol through solubility measurements of mercury(II) acetate in the presence of sodium acetate. Values of the molar solubility at 30° were found to be (in presence of $1{\cdot}79 \times 10^{-2}$M-acetic acid):

[Added sodium acetate]/M	0	0·10	0·30	0·50
Hg(OAc)$_2$ solubility/M	0·40	0·53	0·82	0·90

There is almost quantitative uptake of mercury(II) acetate with added sodium acetate; under these conditions a value for K_3 cannot be calculated although we estimate that K_3 must be *ca.* 1×10^2 l mol^{-1}.

Using the values of K_2 and K_3 in Table 6, we then dissected the observed second-order rate constants, k_2, into contributions from HgOCOR$^+$ (k_a), Hg(OCOR)$_2$ (k_b), and Hg(OCOR)$_3^-$ (k_c) from the data on the variation of k_2 with initial concentration of mercury(II) carboxylate. First we calculated the initial concentrations of the various mercury(II) species, taking into account the dissociation of the carboxylic acid present, and then determined the various contributions by solution of sets of simultaneous equations. An example of the results obtained is in Table 7, for the case of the mercury(II) acetate reaction. Results for the pivalate were more consistent, and results for the methoxyacetate rather less consistent, than those in Table 7. However, in all three cases with R = Bu^t, Me, and CH$_2$OMe we find that $k_c = 0$ so that the ions Hg(OCOR)$_3^-$ are ineffective as electrophiles towards tetraethyltin (as is also the ion HgI$_3^-$ in methanol). Values of k_a, k_b, and k_c are in Table 8, with those for R = Me and CH$_2$OMe rounded off. We calculate that under the kinetic conditions *ca.*

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60% reaction proceeds through the neutral species $Hg(OCOR)_2$; since, however, the proportion of the very reactive species $HgOCOR^+$ decreases with increase in the mercury(II) carboxylate concentration, use of much higher initial concentrations of mercury(II) carboxylate would result in a considerably higher percentage reaction through the neutral species. We also carried out a similar calculation using the variation of k_2 with added sodium acetate (Table 4); results were not very consistent but we find for the mercury(II) acetate reaction that k_a is very large, $k_b \simeq 46$ l mol^{-1} min^{-1}, and we confirm that $k_c = 0$; these results are thus in agreement with those given in Table 8.

TABLE 7

Calculation of k_a, k_b, and k_c for the tetraethyltin–mercury(II) acetate reaction in methanol at 30° from the variation of k_2 with $[Hg(OAc)_2]$ [a]

$10^6[Hg(OAc)_2]$/M [b]	$10^6[HgOAc^+]$/M [b]	$10^6[Hg(OAc)_2]$/M [b]	$10^6[Hg(OAc)_3^-]$/M [b]	k_a	k_b	k_{2calc} [c]	k_{2obs}
239·0	2·842	236·064	0·094	3270	41·6	76·9	79·9
299·0	3·322	295·552	0·126	3300	38·7	74·3	74·9
359·0	3·681	355·154	0·165	3290	36·9	71·6	70·2
419·0	3·979	414·813	0·208	3280	38·6	69·1	69·3
508·0	4·461	503·267	0·272	3270	36·6	66·8	64·9
598·0	4·848	592·804	0·348	3240	37·7	64·6	63·6
				3275 [d]	38·4 [d]		

[a] Rate constants in l mol^{-1}. [b] In column 1 are values of the stoicheiometric initial concentration of mercury(II) acetate used, and in columns 2—4 are the calculated actual initial concentrations of the three species. [c] Calculated from the average values of k_a and k_b (k_c was found to be zero throughout). [d] Average values.

TABLE 8

Approximate values of k_a, k_b, and k_c (l mol^{-1} min^{-1}) for attack of mercury(II) species on tetraethyltin in methanol at 30°

R	Bu^t	Me	$MeOCH_2$
k_a, RCO_2Hg^+	$1·4 \times 10^3$	$3·3 \times 10^3$	$1·5 \times 10^4$
k_b, $(RCO_2)_2Hg$	17	40	140
k_c, $(RCO_2)_3Hg^-$	0	0	0
Relative k_a	0·42	1	4·5
Relative k_b	0·42	1	3·5
Relative [a] k_2	0·37	1	3·26

[a] From the observed values of k_2 (Table 1).

We therefore find that the order of electrophilic strength towards tetraethyltin in methanol is (i) $Hg(OCOR)_3^- < Hg(OCOR)_2 < HgOCOR^+$ in the ratio $0 : 1 : 10^2$ for each of the three cases with $R = Bu^t$, Me, and CH_2OMe, (ii) $HgOCOBu^{t+} < HgOCOMe^+ < HgOCOCH_2Me^+$ in the ratio $0·42 : 1 : 4·5$, and (iii) $Hg(OCOBu^t)_2 < Hg(OCOMe)_2 < Hg(OCOCH_2OMe)_2$ in the ratio $0·42 : 1 : 3·5$. It is a little surprising that the sequence in $HgOCOR^+$ is quantitatively the same as that in $Hg(OCOR)_2$. A compression of the sequence in the case of $HgOCOR^+$ would be expected first because there is only one substituent in the cation but two in the neutral species and secondly because of the greater reactivity of the cations. More pertinent, however, is the observation that the sequence in values of k_b is quantitatively the same as the sequence in the observed k_2 values in Table 1, so that the relative k_2 values there presented may indeed be taken as those for the neutral species $Hg(OCOR)_2$, as we have done. All these results are in accord with the hypothesis that both $HgOCOR^+$ and $Hg(OCOR)_2$ react with tetraethyltin in methanol by mechanism S_E2(open).

There are only few comparisons that may be made with other work.* Webster and his co-workers [25] have shown that for the aromatic demetallation of $MeC_6H_4SiMe_3$ by mercury(II) acetate in acetic acid $k_a/k_b \geqslant 15$, so that again $HgOCOMe^+$ is appreciably more electrophilic than $Hg(OCOMe)_2$. On the other hand, for the substitution of tetraethyl-lead by Cu^IOCOMe in acetic acid, the active species is Cu^IOCOMe itself [26] and not the cationic species Cu^+. In solvents more polar than methanol, it is to be expected that the percentage reaction through the species $HgOCOMe^+$ will increase; Schrauzer and his co-workers [27] have suggested (without giving experimental details) that for the substitution of alkylcobaloximes in water, the attacking electrophile is indeed $HgOCOMe^+$.

For the substitution of tetraethyltin by mercury(II) species in methanol the order of electrophilic reactivity is as follows (this work and refs. 7 and 10): HgI_3^-, $Hg(OAc)_3^- \ll HgI_2 < HgCl_2 < Hg(OAc)_2 < HgOAc^+$. Since it has now been established that the reactions of all the above species (with the exception of HgX_3^-) take place by mechanism S_E2(open), it follows that the suggestion of Ingold [2] is verified for this particular set of substitutions. It is known, however, that the halide sequence $HgI_2 < HgCl_2$ is not obeyed for S_E2(open) reactions in acetonitrile [8] and it remains to be seen whether a limited series such as $HgX_3^- < HgHal_2 < Hg(OAc)_2$ can be considered characteristic of the open mechanism in solvents other than methanol. As we

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* Larock and Brown [24] observed the following qualitative series of reactivity towards tricyclopentylboron in tetrahydrofuran [R in $Hg(OCOR)_2$]: Me $<$ Pr^n $<$ Ph $<$ CF_3, but it is not known to what extent this reflects the solubility of the mercury(II) carboxylates in tetrahydrofuran rather than the actual electrophilic property of the carboxylates.

[24] R. C. Larock and H. C. Brown, *J. Organometallic Chem.*, 1971, **26**, 35.

[25] J. R. Chipperfield, G. D. France, and D. E. Webster, *J.C.S. Perkin II*, 1972, 405.

[26] N. A. Clinton and J. K. Kochi, *J. Organometallic Chem.*, 1972, **42**, 229.

[27] G. N. Schrauzer, J. H. Weber, T. M. Beckham, and R. K. Y. Ho, *Tetrahedron Letters*, 1971, 275.

have shown, though, the observed rate constant for substitution by a particular mercury(II) salt may not correspond to the actual rate constant for substitution by the neutral species [*e.g.* HgX_2 or $Hg(OAc)_2$] and this complication will have to be taken into account.

EXPERIMENTAL

Methanol and tetraethyltin were purified as before.[7] Mercury(II) monochloroacetate was prepared by the method of Bateman and Conrad.[28] The other mercury(II) carboxylates were prepared by refluxing a solution of the carboxylic acid in methanol with mercury(II) oxide. The hot mixture was filtered, and on cooling the clear filtrate, the mercury(II) carboxylate crystallised out. All the mercury(II) carboxylates were recrystallised from dry ethyl acetate containing a trace of the corresponding carboxylic acid. The purity of the recrystallised products was ascertained by spectrophotometric determination[29] of mercury(II). Details of the carboxylates prepared are in Table 9. We also attempted to prepare the mercury(II) salts of dichloroacetic acid and trichloroacetic acid but because of extensive decomposition of the reaction mixtures we were unable to isolate the required products (*cf.* also ref. 28).

Kinetic measurements were carried out by the procedure described before[1] for the tetraethyltin–mercury(II) acetate reaction in methanol. Good second-order plots were obtained for the reactions of tetraethyltin with all the mercury(II) carboxylates used. It was found that mercury(II) benzoate absorbed slightly at the wavelengths (301·5 and 315 nm) used for the analysis of kinetic reaction mixtures, and in this case spectrophotometric measurements were made with the appropriate concentration of mercury(II) benzoate in the reference cell.

TABLE 9

Mercury(II) carboxylates prepared in this work

Carboxylate	M.p. (°C) [a]	Purity (%) [b]
Pivalate	215	99·23
Propionate	105 [c]	99·98
Acetate	167 [d]	99·98
Benzoate	163 [e]	98·02
β-Chloropropionate	120	99·81
Methoxyacetate	119	99·96
Chloroacetate	143 [f]	99·14

[a] On a Kofler block. [b] Spectrophotometrically (see text). [c] Lit., m.p. 108—110°, K. P. Butin, I. P. Beletskaya, P. N. Belik, A. N. Ryabtsev, and O. A. Reutov, *J. Organometallic Chem.*, 1969, **20**, 11. [d] Found: C, 15·4; H, 1·9. Calc. for $C_4H_6H_gO_4$: C, 15·1; H, 1·9%. The m.p. using the normal method was 170—172°. [e] Lit., m.p. 160° (footnote *c*) and 161—162°.[24] [f] Lit., m.p. 142° (footnote *c*).

Molecular weights of mercury(II) acetate and chloride in methanol at 40° were determined by an isopiestic method using benzil as the reference solute. The two compounds were found to be monomeric. Conductances of the mercury(II) salts in methanol at 30° were determined over the concentration range 1×10^{-5}—3×10^{-3}M; Shedlovsky plots were linear with some scatter and the derived values of $K_A(K_2)$ are in Table 6. Although these stability constants are approximate only, we feel that they are of the correct order of magnitude, and the sequence of K_2 values with respect to R (Table 6) is that expected from a consideration of the data in Table 2.

We thank the British Council and the Iranian Ministry of Science and Higher Education for support (to D. F. D.), and the S.R.C. for aid from a grant. We are grateful to Mr. C. J. Holloway for a prior investigation into methods of preparation of mercury(II) carboxylates.

[3/1629 *Received, 2nd August*, 1973]

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