Aromatic Mercuration. The Reaction of Mercury(II) Acetate with *p*-Tolyltrimethylsilane and with Anisole

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Both mercuridesilylation of *p*-tolyltrimethylsilane and mercuration of anisole by mercury(II) acetate in glacial acetic acid involve both un-ionized mercury(II) acetate and positive acetatomercury(II) ions as electrophiles. The positive ion is at least 15 times more reactive than molecular mercury(II) acetate in the mercuridesilylation, and at least twice as reactive in the mercuration. Activation parameters for mercuration and mercuridesilylation are similar, and indicate a highly ordered activated complex. The rate of mercuridesilylation increases with increase in the water content of the solvent, and is also affected by the silane concentration and by other non-polar molecules, whereas the mercuration of anisole is unaffected by such factors. The equilibrium constant for the formation of the triacetatomercurate(II) anion has been obtained from the kinetic data and independently measured.

THE reaction of mercury(II) acetate with aromatic compounds is well known.[1] Both in the absence and in the presence of acids, mercury(II) acetate reacts as an electrophile and substitutes the aromatic compound [equation (1); X = H]. For the uncatalysed reaction little effort has been made to identify the active mercurating

$$RC_6H_4X + Hg(OAc)_2 \longrightarrow RC_6H_4{\cdot}HgOAc + XOAc \quad (1)$$

electrophile, whereas perchloric acid-catalysed aromatic mercuration has been extensively investigated.[2]

The reactions of organosilyl-substituted aromatic compounds with mercury(II) acetate [equation (1); X = $SiMe_3$] have been investigated by Benkeser [3,4] and by Eaborn and Webster.[5,6] In these studies the mercury-containing species responsible for the desilylation was not identified. Benkeser studied the overall second-order reaction under pseudo-first-order conditions with either the mercury(II) acetate or the silane in excess. When the observed first-order rate coefficients are divided by the excess of concentration of the second reagent, inconsistent second-order rate coefficients are obtained. The present study was undertaken to discover the mercurating species in aromatic mercuration and in mercuridesilylation, and to investigate the inconsistencies reported above.

RESULTS

A typical silane and aromatic compound were required for this study. *p*-Tolyltrimethylsilane and anisole were chosen as their reaction rates with mercury(II) acetate in glacial acetic acid could be conveniently measured by determining the amount of unchanged mercury(II) present in the mixture as a function of time. The reactant, mercury(II) acetate, will combine with 2 equiv. of thiocyanate; the product, an arylmercury(II) acetate will react with only 1 equiv. For the reaction of the silane, the product, in addition to the arylmercury(II) acetate, was shown by n.m.r. spectroscopy to be trimethylsilyl acetate; as the reaction proceeded a peak at τ 9·77 due to the trimethylsilyl group attached to the benzene ring disappeared, and was replaced by a peak at τ 9·74 due to trimethylsilyl acetate. The overall reactions are given in equation (1; X = H, R = MeO or X = $SiMe_3$, R = Me) and, under our conditions, with an excess of anisole or the silane, they were found to be first order both in the absence and in the presence of sodium acetate.

First-order rate coefficients for the reaction of mercury(II) acetate with *p*-tolyltrimethylsilane and with anisole in glacial acetic acid at 25°, in the absence and in the presence of sodium acetate, are given in Tables 1 and 2. As is shown later, the decrease in the reaction rates on addition of sodium acetate is due initially to neutralization of traces of H^+ present in the solvent, suppression of the ionization of mercury(II) acetate [equation (2)], and then to formation of the inactive triacetatomercurate(II) ion [equation (4)]. Activation parameters for the reactions were determined in the usual way (see Table 3).

TABLE 1

The reaction of *p*-tolyltrimethylsilane and mercury(II) acetate in glacial acetic acid with added sodium acetate at 25·0°

[Silane]/ mol l^{-1}	$[Hg(OAc)_2]$/ mol l^{-1}	[NaOAc]/ mol l^{-1}	$10^3k_1^{obs}$/ min^{-1}
0·4	0·04	0	3·41
0·4	0·04	0·001	2·62
0·4	0·04	0·01	2·26
0·4	0·04	0·1	1·72
0·4	0·04	0·2	1·34
0·8	0·04	0·01	3·30

TABLE 2

The reaction of anisole and mercury(II) acetate in glacial acetic acid with added sodium acetate at 25·0°

[Anisole]/ mol l^{-1}	$[Hg(OAc)_2]$/ mol l^{-1}	[NaOAc]/ mol l^{-1}	$10^3k_1^{obs}$/ min^{-1}
1·0	0·04	0	1·07
1·0	0·04	0·001	1·03
1·0	0·04	0·01	0·965
1·0	0·04	0·05	0·791
1·0	0·04	0·1	0·670
1·0	0·04	0·2	0·507

The mercuridesilylation was found to increase in rate when water was added to the solvent, and under these conditions the effect of sodium acetate was more marked than in the anhydrous solvent (Table 4).

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[1] See, for example, W. Kitching, *Organometallic Chem. Rev.*, 1968, **3**, 35.

[2] A. J. Kresge, M. Dubeck, and H. C. Brown, *J. Org. Chem.*, 1967, **32**, 745.

[3] R. A. Benkeser, D. I. Hoke, and R. A. Hickner, *J. Amer. Chem. Soc.*, 1958, **80**, 5294.

[4] R. A. Benkeser, T. V. Liston, and G. M. Stanton, *Tetrahedron Letters*, 1960, 1.

[5] F. B. Deans, C. Eaborn, and D. E. Webster, *J. Chem. Soc.*, 1959, 3031.

[6] D. E. Webster, Ph.D. Thesis, University of London, 1958

Benkeser[3] has studied dilatometrically the reactions of phenyltrimethylsilane and of *o*- and *p*-tolyltrimethylsilane with mercury(II) acetate, with the silane or the mercury(II) acetate in excess. We have repeated this work, using the titrimetric method for the reactions with excess of silane, and g.l.c. for the reactions with excess of mercury(II) acetate. Our results (Table 5) show an unexpected decrease in the second-order rate coefficients with increase in the silane concentration. To see if this was a specific or a general effect, four inert compounds were added to reaction mixtures. The compounds chosen, hexamethyldisiloxane, tetramethylsilane, benzene, and cyclohexane, were inert in the sense that they would not be expected to be involved in the reaction. All four compounds reduced the observed second-order rate coefficient (Table 6). Added cyclohexane also affects the reaction in the presence of sodium acetate (Table 7). Similar experiments with anisole (Table 8) show that for this reaction the second-order rate coefficients are not affected by the concentration of the excess of anisole or by added hexamethyldisiloxane.

TABLE 3

The reaction of mercury(II) acetate with *p*-tolyltrimethylsilane (0·4M) or anisole (1·0M) in glacial acetic acid with added sodium acetate (0·001M)

Substrate	t/°C	$10^3k_1^{obs}$/min^{-1}	$10^3k_2^{obs}$/l mol^{-1} min^{-1}	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal mol^{-1} K^{-1}
Silane	25·0	2·62	6·55		
	35·0	5·68	14·2		
	50·0	17·1	42·8	13·8	−30·4
Anisole	25·0	1·03	1·03		
	35·0	2·69	2·69		
	50·0	10·4	10·4	17·1	−22·9

TABLE 4

The reaction of *p*-tolyltrimethylsilane (0·4M) with mercury(II) acetate (0·04M) in 5% aqueous acetic acid (v/v) at 25·0° in the presence of sodium acetate

[NaOAc]/mol l^{-1}	$10^3k_1^{obs}$/min^{-1}	$10^3k_2^{obs}$/l mol^{-1} min^{-1}	k_1^{obs} (in 5% aqueous acetic acid) / k_1^{obs} (in glacial acetic acid) *
0	133	333	39
0·1	16·7	41·8	10
0·2	12·6	31·5	9

* From Table 1.

TABLE 5

The reaction of $RC_6H_4SiMe_3$ (R = H, *o*-Me, or *p*-Me) with mercury(II) acetate in glacial acetic acid at 25·0°

R	[Silane]/ mol l^{-1}	[Hg(OAc)$_2$]/ mol l^{-1}	$10^3k_1^{obs}$/ min^{-1}	$10k_2^{obs}$/ l mol^{-1} min^{-1}
H	0·4	0·04	0·422	1·06
H	0·8	0·04	0·571	0·72
o-Me	0·4	0·04	3·87	9·68
o-Me	0·55	0·057	4·32	7·85
p-Me	0·2	0·02	2·61	13·1
p-Me	0·4	0·02	3·41	8·53
p-Me	0·8	0·02	5·00	6·25
H	0·0092	0·18	0·67	3·70
o-Me	0·0092	0·18	5·23	29·0
p-Me	0·0092	0·18	5·00	27·7

TABLE 6

The reaction of *p*-tolyltrimethylsilane (0·4M) with mercury(II) acetate (0·04M) in glacial acetic acid at 25·0° with various inert compounds (L)

L	[L]/ mol l^{-1}	$10^3k_1^{obs}$/ min^{-1}	$10^3k_2^{obs}$/ l mol^{-1} min^{-1}
		3·41	8·53
Tetramethylsilane	0·45	2·23	5·58
Cyclohexane	0·40	2·42	6·05
Hexamethyldisiloxane	0·20	2·75	6·88
Benzene	0·40	2·73	6·83

The equilibrium constant for the formation of the triacetatomercurate(II) ion (K_{OAc}) [equation (4)] can be calculated from the kinetic data (see Discussion section). It was also determined independently by measuring the solubility of mercury(II) acetate in glacial acetic acid at 25°; the concentration required to give a saturated solution was 0·195M. The solubility of mercury(II) acetate in glacial acetic acid containing 0·41M-sodium acetate was similarly determined as 0·383M. The increase in solubility is due to the formation of the triacetatomercurate(II) anion [equation (4)]. The equilibrium constant K_{OAc} is thus (0·383 − 0·195)/0·195 {0·41 − (0·383 − 0·195)}, which is 4·3 l mol^{-1}.

TABLE 7

The reaction of *p*-tolyltrimethylsilane with mercury(II) acetate (0·04M) in glacial acetic acid at 25·0° with added sodium acetate (0·01M) and cyclohexane

[Silane]/ mol l^{-1}	[Cyclohexane]/ mol l^{-1}	$10^3k_1^{obs}$/ min^{-1}	$10^3k_2^{obs}$/ l mol^{-1} min^{-1}
0·4	0	2·26	5·65
0·4	0·4	1·79	4·48
0·8	0	3·30	4·12
0·8	0·4	2·57	3·21

TABLE 8

The reaction of anisole with mercury(II) acetate in glacial acetic acid at 25·0°

[Anisole]/ mol l^{-1}	[Hg(OAc)$_2$]/ mol l^{-1}	$10^3k_1^{obs}$/ min^{-1}	$10^3k_2^{obs}$/ l mol^{-1} min^{-1}
0·48	0·05	0·492	1·03
0·50	0·05	0·520	1·04
1·0	0·05	1·07	1·07
2·0	0·05	1·90	0·95
2·0 *	0·04	1·80	0·90

* 0·2M-Hexamethyldisiloxane also present.

DISCUSSION

Mercury(II) acetate in glacial acetic acid will exist as un-ionized molecules in equilibrium with the acetatomercury(II) ion. In this solvent, which has a low dielectric constant, the ionization is complicated by ion-pair formation [equation (2)]. Any, or all, of these

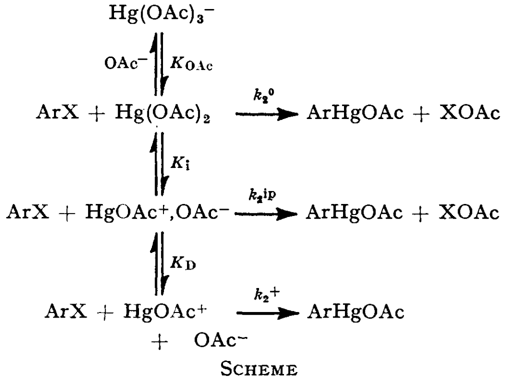
$$\mathrm{Hg(OAc)_2} \overset{K_\mathrm{i}}{\rightleftharpoons} \mathrm{HgOAc^+,OAc^-} \overset{K_\mathrm{D}}{\rightleftharpoons} \mathrm{HgOAc^+ + OAc^-} \quad (2)$$

species could be the electrophile. Traces of a stronger acid present in the acetic acid will also produce acetatomercury(II) ions according to equation (3).

$$\mathrm{Hg(OAc)_2 + H^+} \overset{K_\mathrm{A}}{\rightleftharpoons} \mathrm{HgOAc^+ + HOAc} \quad (3)$$

The acetatomercury(II) ion would be expected to be the more reactive, and the mercury(II) acetate the less reactive species. If acetate ions are present then the triacetatomercurate(II) ion would also be formed [equation (4)]; similar complexes with mercury(II) halides are well known.[7] As this is a negatively charged ion it would not be a mercurating agent. If acetate ions are introduced into the reaction mixture, by adding sodium acetate, then the concentration of acetatomercury(II) ions will be reduced and the concentration of triacetatomercurate(II) ions will be increased; the rate of the reaction will be expected to decrease. This is shown in Tables 1 and 2. With the silane as the reactant there is a sharp decrease in the reaction rate on the addition of $<10^{-2}$M-sodium acetate, owing to the removal of the reactive acetatomercury(II) ion. Addition of more sodium acetate continues to reduce the rate of the reaction as the reactive mercury(II) acetate is complexed to the unreactive triacetatomercurate(II) ion. For the reaction with anisole the initial decrease in rate is much less, indicating that for this reaction the acetatomercury(II) ion and the molecular mercury(II) acetate are closer in reactivity. Additional added acetate continues to complex the mercury(II) acetate and reduce the reaction rate.

$$\mathrm{Hg(OAc)_2 + OAc^-} \overset{K_\mathrm{OAc}}{\rightleftharpoons} \mathrm{Hg(OAc)_3^-} \quad (4)$$

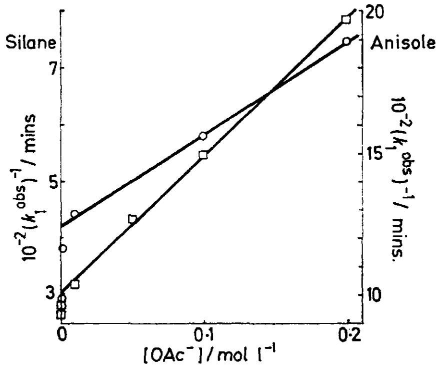


SCHEME

A reaction scheme that takes into account all the possible equilibria and reactions is shown (Scheme). It can be readily shown that the rate of appearance of the arylmercury acetate is given by equation (5), where p =

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \left(k_2{}^0 + k_2{}^{\mathrm{ip}} \,.\, K_\mathrm{i} + \frac{k_2{}^+ \,.\, K_\mathrm{i} \,.\, K_\mathrm{D}}{[\mathrm{OAc^-}]}\right) \frac{(a-p)(Ar_0-p)}{\left(1 + K_\mathrm{i} + \dfrac{K_\mathrm{i}K_\mathrm{D}}{[\mathrm{OAc^-}]} + K_\mathrm{OAc}[\mathrm{OAc^-}]\right)} \quad (5)$$

concentration of ArHgOAc, a = initial concentration of mercury(II) acetate, Ar_0 = initial concentration of ArX, $K_\mathrm{D} = [\mathrm{HgOAc^+}][\mathrm{OAc^-}]/[\mathrm{HgOAc^+,OAc^-}]$, $K_\mathrm{i} = [\mathrm{HgOAc^+,OAc^-}]/[\mathrm{Hg(OAc)_2}]$, $K_\mathrm{OAc} = [\mathrm{Hg(OAc)_3^-}]/[\mathrm{Hg(OAc)_2}][\mathrm{OAc^-}]$, and $k_2{}^0$, $k_2{}^{\mathrm{ip}}$, and $k_2{}^+$ are the rate coefficients for the reactions of the aromatic compound with mercury(II) acetate, the acetatomercury(II)-acetate ion pair, and the acetatomercury(II) ion, respectively.



$1/k_1{}^{\mathrm{obs}}$ against the concentration of acetate ion for the reaction of mercury(II) acetate with p-tolyltrimethylsilane (○, 0·4M), or with anisole (□, 1M) in glacial acetic acid at 25°

The reaction Scheme may be simplified for the case with sodium acetate present, as the concentration of acetatomercury(II) ions will be small, and, when $Ar_0 \gg a$, equation (5) simplifies to equation (6), where $k_2{}^{\phi} = k_2{}^0 + k_2{}^{\mathrm{ip}} \,.\, K_\mathrm{i}$.

$$\mathrm{d}p/\mathrm{d}t = \{k_2{}^{\phi}(a-p)Ar_0\}/(1 + K_\mathrm{i} + K_\mathrm{OAc}[\mathrm{OAc^-}]) \quad (6)$$

The observed first-order rate coefficients are given by equation (7). Hence $k_1{}^{\mathrm{obs}}$ is as given in equation (8), since K_i, the equilibrium constant for ion-pair formation, will be small.[2] Equation (8) contains the concentration of acetate ions. As first-order behaviour is observed throughout a reaction the acetate ion concentration must remain constant. If equation (8) is correct, a plot of $1/k_1{}^{\mathrm{obs}}$ against acetate ion concentration should be a

$$\frac{\mathrm{d}p}{\mathrm{d}t} = k_1{}^{\mathrm{obs}}(a-p) \quad (7)$$

$$k_1{}^{\mathrm{obs}} = (k_2{}^{\phi} \,.\, Ar_0)/(1 + K_\mathrm{OAc}[\mathrm{OAc^-}]) \quad (8)$$

straight line with slope $K_\mathrm{OAc}/k_2{}^{\phi}Ar_0$ and intercept $1/k_2{}^{\phi}Ar_0$. With p-tolyltrimethylsilane as the reactant this is so for the higher acetate ion concentrations where these equations apply (Figure). The rate coefficient with 10^{-3}M-added sodium acetate is higher than expected from the Figure, owing to traces of formic acid (see

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[7] A. B. Garrett, *J. Amer. Chem. Soc.*, 1939, **61**, 2744.

later) still present in the solution. From this graph values of k_2^{ϕ} and K_{OAc} are obtained. As the actual concentrations of acetate ion in solution differ slightly from the added concentrations, k_2^{ϕ} and K_{OAc} were used to calculate the actual concentrations of acetate ion. These corrected values can be used to give new values of k_2^{ϕ} and K_{OAc}. Successive iterations lead to constant values for *p*-tolyltrimethylsilane of $k_2^{\phi} = 5{\cdot}85 \times 10^{-3}$ l mol^{-1} min^{-1} and $K_{OAc} = 4{\cdot}06$ l mol^{-1}. A similar plot for anisole as the reactant gives $k_2^{\phi} = 0{\cdot}987 \times 10^{-3}$ l mol^{-1} min^{-1} and $K_{OAc} = 5{\cdot}3$ l mol^{-1}. This equilibrium constant, for the formation of the triacetatomercurate(II) ion, was measured independently as 4·3 l mol^{-1}. This is comfortingly near to the values obtained from the kinetic experiments.

The relative reactivities of the un-ionized mercury(II) acetate, the acetatomercury(II) ion and the acetatomercury(II)–acetate ion pair can be calculated from these results. The equilibrium constant for the overall dissociation of mercury(II) acetate into ions (*i.e.* K_iK_D) has been measured as 10^{-12} mol l^{-1} by a potentiometric method.[8] Hence at a mercury(II) acetate concentration of 0·04M the concentration of the ions is given by equation (9). Hence from equation (9) $[HgOAc^+] = 2 \times 10^{-7}$M.* If the solution contains 10^{-3}M-sodium acetate then, from equation (9), $[HgOAc^+] = 4 \times 10^{-11}$M, *i.e.* there is a five thousand-fold decrease in the concentration of the acetatomercury(II) ion and mercury(II) acetate should be the only electrophile.

$$[HgOAc^+][OAc^-] = 4 \times 10^{-14}\ \text{mol}^2\ \text{l}^{-2} \qquad (9)$$

However, we find (Figure) that the addition of 0·001M-sodium acetate does not reduce the rate constant to the predicted k_2^{ϕ} value, *i.e.* some acetatomercury(II) ions are still present in the solution. These are formed by the presence in the glacial acetic acid of a trace of a stronger acid, probably formic acid † which has a pK_a value one unit lower than acetic acid (in water) and should be almost completely ionized. The H$^+$ so formed will react with the mercury(II) acetate according to equation (3) to form the acetatomercury(II) ions. Addition of 0·01M-sodium acetate completely neutralizes the H$^+$ and k_2^{obs} is equal to k_2^{ϕ} as predicted.

Kresge *et al.*[2] have evaluated the ion-pair formation constant (K_i) as 2×10^{-8} l mol^{-1}, and have concluded that the ion pair is not a significant electrophile for aromatic mercuration in the absence of acid. Certainly its concentration is much less than the concentration of the free ion. At a concentration of mercury(II) acetate of 0·04M the ratio $HgOAc^+ : HgOAc^+,OAc^- = (2 \times 10^{-7}) : (8 \times 10^{-10}) = 250 : 1$. Kresge *et al.* did not consider the possibility of the ion pairs dissociating to give the acetatomercury(II) ion, but this clearly occurs as addition of a little sodium acetate markedly reduces the rate both for the reaction of the silane and for the anisole; the concentration of ion pairs should be independent of the acetate ion concentration. Kresge's limited conclusion is however correct; the ion pairs are not a significant electrophile, and can be ignored.

In the absence of sodium acetate when $Ar_0 \gg a$ and ignoring the ion pair, equation (5) reduces to $\mathrm{d}p/\mathrm{d}t = (k_2^0[Hg(OAc)_2] + k_2^+[HgOAc^+])Ar_0$. Substitution of $[HgOAc^+]$ from equation (3) in this equation, and combining with equation (7) gives equation (10), which applies in the presence of added acid. If the concentration of the acid impurity is F then $[H^+] + [HgOAc^+] = F$. Combining this with the equilibrium constant for equation (3) gives $[H^+] = F/(1 + K_A[Hg(OAc)_2])$.

$$k_1^{obs} = (k_2^0 + k_2^+K_A[H^+])Ar_0 \qquad (10)$$

From equation (10) $k_1^{obs} = \{k_2^0 + (k_2^+K_AF)/(1 + K_A[Hg(OAc)_2])\}Ar_0$. Hence equation (11) is obtained.

$$\begin{aligned} &k_1^{obs}\ (\text{in absence of NaOAc}) - k_1^{obs}\ (\text{with } 0{\cdot}001\text{M-NaOAc}) \\ &\quad = (k_2^+K_A)(\{F/(1 + K_A[Hg(OAc)_2])\} - \\ &\qquad\qquad (F - 0{\cdot}001)/\{1 + K_A[Hg(OAc)_2]\})Ar_0 \\ &\quad = \{k_2^+ . K_A . (0{\cdot}001)Ar_0\}/\{1 + K_A[Hg(OAc)_2]\} \qquad (11) \end{aligned}$$

Now, for the silane, $[Hg(OAc)_2] = 0{\cdot}04$M, $Ar_0 = 0{\cdot}4$M, $K_A = K_iK_D/K_s = 278$ mol l^{-1}, and for the silane k_1^{obs} (in the absence of NaOAc) $= 3{\cdot}41 \times 10^{-3}$ min^{-1} and k_1^{obs} (with 0·001M-NaOAc) $= 2{\cdot}62 \times 10^{-3}$ min^{-1}. From equation (11) $k_2^+ = 86{\cdot}1 \times 10^{-3}$ l mol^{-1} min^{-1}, and hence $k_2^+/k_2^0 = (86{\cdot}1 \times 10^{-3})/(5{\cdot}85 \times 10^{-3}) = 15$.‡ An identical calculation for anisole gives $k_2^+/k_2^0 = 2$,‡ *i.e.* for the silane the relative reactivity of the acetatomercury(II) ion to un-ionized mercury(II) acetate is 8 times that for anisole.

It is not clear why this is so. Phenyltrimethylsilanes have a greater availability of electrons at the reaction site than do simple aromatic compounds. This greater nucleophilic power is a consequence of the polar carbon–silicon bond, and the more reactive the nucleophile, the less it discriminates between two electrophiles. For example, chloro- and bromo-desilylations are of approximately equal rate whereas chlorination of aromatics is 10^4 times faster than bromination.[10] Hence it would be expected the mercury(II) acetate and acetatomercury(II) ions would be closer in reactivity for the mercuri-

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* The autoprotolysis constant for acetic acid has been measured by Kolthoff[9] as $3{\cdot}6 \times 10^{-15}$ mol^2 l^{-2}. This is sufficiently small to be ignored.

† AnalaR acetic acid contains approximately 0·02% (w/w) formic acid. This is sufficient to cause the effect reported here. To provide further evidence that formic acid is responsible we have carried out mercuridesilylations with added 98% formic acid. Whereas the addition of 0·001M-sodium acetate reduces the observed first-order rate coefficient by 23%, addition of 0·002M-formic acid increases this rate coefficient by the same amount.

‡ The relative reactivities are at least the values given. These values have been calculated using literature values for K_i, K_D, and K_s. K_s is particularly dependent on the purity of the solvent and is likely to have a higher value than that used here. This would give a lower concentration of acetatomercury(II) ion in the solution and hence it would have a higher reactivity. The comparison of relative reactivities (k_2^+/k_2^0) for the silane and anisole is unaffected.

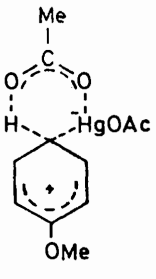
[8] O. W. Kolling, *Inorg. Chem.*, 1962, **1**, 561.

[9] S. Bruckenstein, in 'Treatise on Analytical Chemistry,' eds. I. M. Kolthoff and A. J. Elving, Wiley, New York, 1959, vol. 1, part I, p. 499 *et seq.*

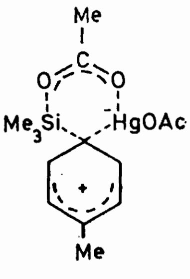
[10] C. Eaborn and D. E. Webster, *J. Chem. Soc.*, 1960, 179.

desilylation than for the mercuration, but the opposite is found. Another related factor to be considered was first pointed out by Benkeser,[4] namely that mercuridesilylation is of low selectivity [11] and in terms of the Hammond postulate [12] the activated complex for mercuridesilylation will resemble the reactants in that very little breaking of the carbon–silicon bond has occurred.† It must be that under these circumstances the reactivity difference is enhanced.

The activation parameters for the reactions in the presence of added acetate are given in Table 3. They are similar for the two compounds, indicating a similarity of mechanism. The negative activation entropies could indicate a cyclic activated complex. It has been suggested by Kresge [14] that there is a cyclic activated complex for mercuration by the acetatomercury(II) ion, and our results would support such a complex for uncatalysed mercuration of both anisole and *p*-tolyltrimethylsilane,[11] (1) and (2).



(1)



(2)

For the perchloric acid-catalysed mercuration of benzene the reaction is retarded when water is added to the glacial acetic acid solvent; [2] this is because the water is competing with the mercury(II) acetate for the perchloric acid. The effect of water on the mercuridesilylation is to increase markedly the rate, as is shown in Table 4; in the absence of added acetate the rate increases 39 fold, in the presence of added acetate it increases *ca.* 10 fold. This indicates that water has two major effects: it encourages the dissociation of the mercury(II) acetate and so increases the relative concentration of acetatomercury(II) ions, and it increases the rate of the reaction of mercury(II) acetate by increasing the polarity of the medium. An approximate value for this rate coefficient k_2^0 [$= k_2^\phi$ of equation (6) if the acetatomercury(II)–acetate ion pairs are ignored] can be obtained from a plot of $1/k_1^{\text{obs}}$ against acetate ion concentration as was done for the reaction in glacial acetic acid. A value of $60{\cdot}6 \times 10^{-3}$ l mol^{-1} min^{-1} is obtained for k_2^0; this is 10 times that for the reaction in glacial acetic acid.

Benkeser [3] has reported the reaction of phenyl- and *o*- and *p*-tolyl-trimethylsilanes with mercury(II) acetate in glacial acetic acid. If his first-order rate coefficients are divided by the concentration of the reagent in excess then inconsistent second-order rate coefficients are obtained (Table 9), the rate coefficients with excess of mercury(II) acetate being about four times those with excess of silane. We repeated these measurements under similar conditions and confirmed Benkeser's results (Table 5). We also found that our second-order rate coefficients were approximately half those obtained by Benkeser, presumably because of small differences in the water and formic acid content of our solvent and his. Furthermore, we find that the second-order rate coefficient varies with the concentration of the silane; as the silane concentration is increased the second-order rate coefficient decreases. It is not apparent why this should be so, and to see if it was a specific effect of the reactant silane, or a more general effect, the desilylation of *p*-tolyltrimethylsilane was studied with various neutral compounds present (Table 6). Tetramethylsilane and hexamethyldisiloxane were chosen as examples of organosilicon compounds which should not be involved in the reaction, benzene was selected as the reactant, silane, is a benzene derivative, and cyclohexane is a molecule that would not be expected to be involved in the reaction in any way. All four compounds significantly reduced the reaction rate. Perhaps the most obvious explanation of these results is that these added compounds affect the ionization of mercury(II) acetate and reduce the concentration of the acetatomercury(II) ions, but this is not so as shown in Table 7 where the effect of cyclohexane on the reaction in the absence of acetatomercury(II) ions, *i.e.* in the presence of 0·01M-sodium acetate, is given. There is a 20% decrease in the second-order rate coefficient in the presence of 0·4M-cyclohexane. In view of these results we have briefly looked at the mercuration of anisole with different concentrations of anisole in excess (Table 8). We obtained consistent second-order rate coefficients as is expected for

TABLE 9

The reaction of $RC_6H_4SiMe_3$ with mercury(II) acetate in glacial acetic acid at 25·0° *

R	[Silane]/ mol l^{-1}	[Hg(OAc)$_2$]/ mol l^{-1}	10^3k_1/ min^{-1}	10^3k_2/ l mol^{-1} min^{-1}
H	0·400	0·0400	0·616	1·54
o-Me	0·400	0·0400	6·95	17·4
p-Me	0·400	0·0400	6·60	16·5
H	0·017	0·1788	1·10	6·15
o-Me	0·017	0·1788	11·9	66·6
p-Me	0·017	0·1788	12·7	71·0

* From R. A. Benkeser, D. I. Hoke, and R. A. Hickner, *J. Amer. Chem. Soc.*, 1958, **80**, 5294.

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† Benkeser [4] suggested an interesting test of whether or not this is so. If very little positive character is developed in the aromatic ring in the activated complex there will be very little demand upon the electron-releasing properties of the ring substituents and relative rates of mercuridesilylation should correlate more satisfactorily with Hammett's σ constants [13] than with Brown's σ^+ constants.[13] Data exist to make this test.[6] The correlation coefficient of 14 substituents for log k with σ^+ is $-0{\cdot}94$ and with σ it is $-0{\cdot}97$.

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[11] See L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, 35 for details.

[12] G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

[13] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420; H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[14] A. J. Kresge and J. F. Brennan, *J. Org. Chem.*, 1967, **32**, 752.

a simple bimolecular reaction and in agreement with that reported by Brown and Dubeck.[15] The reaction was also unaffected by the presence of hexamethyldisiloxane. These results confirm the conclusion above, that for the mercuridesilylation the excess of silane or of added compounds does not suppress the formation of the acetatomercury(II) ions, as these compounds are reactants when anisole is the substrate. The only explanation of our results for the mercuridesilylation is that this reaction is particularly sensitive to the polarity of the solvent, and the addition of the less polar organic compounds to the acetic acid reduces the polarity of the medium and hence reduces the reaction rate.

EXPERIMENTAL

The silanes were prepared from the appropriate aromatic chloro-compound and trimethylchlorosilane by a Wurtz reaction; they were purified by fractional distillation. Anisole, commercial grade, was also purified by fractional distillation. All compounds were shown to be $\geqslant 99\cdot9\%$ pure by g.l.c.

AnalaR grade mercury(II) acetate, sodium acetate, and acetic acid were used without further purification.

Reaction mixtures were analysed by titration with silver nitrate for reactions with excess of organic compound, and by g.l.c. for reactions with excess of mercury(II) acetate. In the titrimetric method samples of the reacting mixture were added to an excess of potassium thiocyanate solution, and the excess of thiocyanate was determined by back titration with silver nitrate with ferric alum as indicator. In the g.l.c. method a non-reacting compound (nitrobenzene) was added as internal marker. In both cases first-order plots of log $(a - p)$ against time were straight lines, and duplicate runs gave values of k_1^{obs} to within 2%.

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[15] H. C. Brown and M. Dubeck, *J. Amer. Chem., Soc.*, 1960, **82**, 1939.