Kinetics and Mechanism of Mercuriation of Aromatic Compounds by Mercury Trifluoroacetate in Trifluoroacetic Acid

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The mercuriation of a series of aromatic derivatives by mercury(II) trifluoroacetate in trifluoroacetic acid has been studied using titrimetric and spectrophotometric methods. The latter method has revealed the presence of a rapidly formed π-complex intermediate and values of the thermodynamic parameters of its formation have been computed. Only small kinetic isotope effects were found for the complex-forming step in contrast to the large values obtained for the slow step. The effect of added salts was investigated and the mechanism of the reaction discussed in detail in the light of these results. Mercuriation by a readily synthesised mixed acetate, $Hg(OCOCF_3)(OCOCH_3)$, is also reported as well as some preliminary studies of triptycene derivatives.

AROMATIC mercuriation has become increasingly important as a synthetic method due to the general ease of reaction and the facile cleavage of the product mercurial. As such, it has been the subject of several detailed kinetic studies.[1] Earlier work was devoted to a study of the reaction in solvent acetic acid using strong acids, such as perchloric acid, as catalysts.[2] However, the reactions were complicated by side reactions with the solvent[3] and were rather slow. Both these difficulties were circumvented by Brown[4] using mercury(II) trifluoroacetate as the electrophile in solvent trifluoroacetic acid. Rates were *ca.* 10^5 times faster than in acetic acid and the data were accurately described in terms of simple second-order kinetics. Brown also demonstrated that mercuriation conformed almost exactly with the selectivity relationship.[5]

It is generally agreed that electrophilic aromatic substitution reactions can be regarded as comprising a number of discrete steps [reaction (1; Ex = electrophile)] of which, in principle, any one may be rate

$$\mathrm{ArH} + \mathrm{Ex} \rightleftharpoons (\pi\ \text{complex})_1 \rightleftharpoons (\sigma\ \text{complex}) \rightleftharpoons (\pi\ \text{complex})_2 \longrightarrow \text{product} \qquad (1)$$

determining. If the breakdown of the σ complex is the slow step, then a kinetic isotope effect should be observed. For most electrophilic aromatic substitution processes an isotope effect close to unity is observed, but for mercuriation large isotope effects [$k_H/k_D = 6.0 \pm 0.1$ at 25° for benzene–$Hg(OAc)_2$] have been observed,[6] indicating that conversion of the σ intermediate into products is rate determining. The ρ value for mercuriation in CF_3CO_2H (−5.68)[4] was significantly higher than that found in glacial acetic acid[3] suggesting that, in spite of the enhanced rates in the former, mercuriation is a more selective reaction in the more polar solvent. One important general feature of the reaction is that it is reversible.

No attempt has been made to identify the nature of the intermediates for monosubstituted benzenes, although recently evidence has been presented which suggests that for polyalkylated derivatives rapidly equilibrating benzenium ions are formed.[7] In strongly acidic media (FSO_3H–SO_2) rapidly exchanging σ and π complexes have been postulated.[8] This paper presents kinetic evidence for the nature of one of the intermediates in mercuriation in trifluoroacetic acid.

RESULTS AND DISCUSSION

The progress of mercuriation reactions has usually been monitored using titrimetric methods. This, particularly in CF_3CO_2H, is not only a rather tedious procedure, but also expensive in terms of volumes of solvent used. Accordingly we first sought an alternative analytical method and examined the reactions directly by u.v. spectrophotometry. This method enables even quite fast reactions, such as those of toluene, to be measured accurately. Upon mixing equimolar solutions of benzene and mercury(II) trifluoroacetate (10^{-2}M), a rapid increase in absorption occurred in the region 280—320 nm, followed by a slow decrease ($\lambda_{max.}$ for this new absorption was close to the cut off of the solvent at 260 nm). Since starting materials and products showed little absorption in the above range, an intermediate complex had been formed. The situation was thus very similar kinetically to that observed for Diels–Alder reactions[9] and indeed is a rather common mechanistic scheme which can be generally represented as in equation (2) where C is a rapidly formed intermediate complex.

$$\mathrm{A} + \mathrm{B} \overset{K_1}{\rightleftharpoons} \mathrm{C} \xrightarrow{k_2} \text{products} \qquad (2)$$

It can easily be shown that if [B] >> [A] then equation (3) holds where k_1^{obs} is the observed pseudo-first-

$$k_1^{obs} = k_2K_1[\mathrm{B}]/(1 + K_1[\mathrm{B}]) \qquad (3)$$

order rate constant. Equation (3) can be rewritten as (4). Thus from a plot of $(k_1^{obs})^{-1}$ against $[\mathrm{B}]^{-1}$, k_2 and K_1

$$\frac{1}{k_1^{obs}} = \frac{1}{k_2K_1}\cdot\frac{1}{[\mathrm{B}]} + \frac{1}{k_2} \qquad (4)$$

can be evaluated. In practical terms this is possible only if K_1[B] is not very large or very small. Generally speaking, one can use either A or B in excess, but in this particular case excess of the mercuriating agent can lead to polymercuriation, and thus in this study the condition $[\mathrm{ArH}] \geqslant 10\ [\mathrm{HgX_2}]$ was maintained. The above formulation was justified in that k_1^{obs} increased with increasing [ArH] and the reciprocal plots showed good linearity with an average correlation coefficient of 0.986 (minimum of 9 data points per plot). Table 1 lists data for mercuriation of benzene at 50°. Further justification for the approach comes from the excellent agreement obtained between the overall titrimetric rate constant, $k_2^{\mathrm{obs}}(= k_2K_1)$ and the k_2K_1 term evaluated from the slopes of the above plots.

For benzene at 25°, $k_2^{\mathrm{obs}} = 0.026\,7$ *(0.028 5)[4] l mol^{-1} s^{-1}, whereas from u.v. data $k_2K_1 = 0.028\,2$ l mol^{-1} s^{-1}. Thus, this method allows not only an accurate method of evaluating the overall rate constant, but also enables one to dissect the rate constant into component parts k_2 (complex to products) and K_1 (formation constant of complex). For benzene at 25°, $k_2 = 3.5 \times 10^{-3}$ s^{-1} and $K = 8.2$ l mol^{-1}. From this data it is already apparent that the free energy of formation of the intermediate is close to zero. To confirm this the reaction was studied at various temperatures and activation and thermodynamic parameters (Table 3) calculated from the data appearing in Table 2. Given that $k_2^{\mathrm{obs}} = k_2K_1$ then equation (5) applies where ΔG_0 is the

$$\Delta G^{\ddagger}_{\mathrm{obs}} = \Delta G^{\ddagger}_2 + \Delta G_0 \qquad (5)$$

free energy of formation of the intermediate complex. Similar equalities obtain for the enthalpy and entropy terms. By the very nature of the reciprocal plots, the errors involved in calculating ΔH_0 and ΔS_0 are somewhat large particularly since $\Delta H^{\ddagger}_{\mathrm{obs}}$ and $\Delta H^{\ddagger}_2$ are very similar. However, the data obtained spectrophotometrically is in excellent agreement with that obtained titrimetrically (Table 4), the values of $\Delta H^{\ddagger}_{\mathrm{obs}}$ and $\Delta S^{\ddagger}_{\mathrm{obs}}$ being almost identical, again strong confirmation of the validity of the method.

TABLE 1

Variation of pseudo-first-order rate constants (k_1^{obs}) for the mercuriation of benzene by mercury(II) trifluoroacetate (5×10^{-3}M) in trifluoroacetic acid at 50°

10^2[benzene]/M	5.69	7.11	8.9	11.7	17.8	26.5	35.5
$10^3k_1^{\mathrm{obs}}$/s^{-1}	7.9	8.8	10.5	12.5	15.4	16.7	19.9
	7.3	8.6	9.5	11.6	13.6	16.4	19.1

$K_1k_2 = 0.185 \pm 0.007$ l mol^{-1} s^{-1}
$k_2 = 0.0262 \pm 0.0016$ s^{-1}
$K_1 = 7.1 \pm 0.7$ l mol^{-1}
Correlation coefficient = 0.991

TABLE 2

Values of relevant rate and formation constants for the mercuriation of benzene by mercury(II) trifluoroacetate in trifluoroacetic acid at various temperatures

T/°C	$10^2k_2k_1$/ l mol^{-1} s^{-1}	10^3k_2/ s^{-1}	K_1/ l mol^{-1}	Correlation coefficient	No. of data points
25.0	2.92 ± 0.08	3.53 ± 0.15	8.2 ± 0.5	0.995	9
25.0 [a]	0.51 ± 0.01	0.96 ± 0.05	5.4 ± 0.3	0.995	14
30.1	4.18 ± 0.40	4.67 ± 0.50	8.9 ± 1.9	0.971	10
35.1	7.82 ± 0.90	6.70 ± 0.80	11.6 ± 2.4	0.940	12
40.1	9.9 ± 0.61	10.8 ± 0.90	9.2 ± 1.3	0.979	11
45.0	12.7 ± 1.1	17.4 ± 2.3	7.3 ± 1.5	0.969	11
50.0	18.5 ± 0.7	26.2 ± 1.6	7.1 ± 0.7	0.991	14

[a] Values for C_6D_6 in 98 atom %D trifluoroacetic acid.

It is instructive to compare the data obtained for benzene and toluene. First the values of ΔG_0 are identical within experimental limits. Secondly the ΔS_0 terms have small negative values. This strongly indicates that the observed intermediate in the u.v. is a π rather than a σ complex, as the latter would involve substantial entropy loss and a correspondingly more negative ΔG_0 for toluene compared with benzene. Since the overall entropy loss is high ($\Delta S^{\ddagger}_{\mathrm{obs}}$ values −20.3 and −31.8 for benzene and toluene respectively), this is largely confined to the two principal remaining steps π-to-σ and σ-to-products. Table 5 lists the observed isotope effects. Again good agreement is found between the titrimetric and spectrophotometric methods ($k_{\mathrm{H}}/k_{\mathrm{D}}$ values of 6.4 and 5.6 respectively for the overall process). The dissection of the isotope effects into those on k_2 and K_1 reveals that as expected most of the effect is apparent in the k_2 values. The high values for k_2K_1 reflect rate-determining proton transfer, *i.e.* the breakdown of σ-complex to products. The value of $k_2^{\mathrm{H}}/k_2^{\mathrm{D}}$ is significantly higher for toluene † than for benzene. The σ intermediate should be more stable for toluene than for benzene (*ca.* 4 kcal mol^{-1} if the relative σ complex stability in ref. 10 is used) and hence the σ complex ⟶ product step is likely to be less exothermic. By the Hammond postulate the transition state will be ' later '

TABLE 3

Activation and thermodynamic parameters (ΔH/kcal mol^{-1}, ΔS/cal K^{-1} mol^{-1}) for the mercuriation of benzene and toluene

Compound	$\Delta H^{\ddagger}_{\mathrm{obs}}$	$\Delta H^{\ddagger}_2$	ΔH_0	$\Delta S^{\ddagger}_{\mathrm{obs}}$	$\Delta S^{\ddagger}_2$	ΔS_0
Benzene	13.5	15.2	−1.7	−20.3	−19.1	−1.2
	±0.9	±0.9		±3.0	±2.9	
Benzene [a]	13.3			−21.1		
	±0.7			±2.2		
Toluene	8.4	10.5	−2.1	−31.8	−28.0	−3.8
	±0.6	±0.4		±1.9	±1.4	

[a] Data obtained by titration.

TABLE 4

Observed second-order rate constants (k_2^{obs}) for the mercuriation of benzene by $Hg(OCOCF_3)_2$ in CF_3CO_2H at various temperatures (data obtained from titrimetric method)

T/°C	25.0	30.0	35.0	40.0
$10^2k_2^{\mathrm{obs}}$/l mol^{-1} s^{-1}	2.67	3.70	5.73	8.20

TABLE 5

Kinetic isotope effects for the mercuriation of benzene and toluene by mercury(II) trifluoroacetate in trifluoroacetic acid at 25°

	Isotope effect on		
Compound	k_2K_1	k_2	K_1
Benzene	5.6	3.7	1.5
Benzene [a]	6.4		
Toluene	7.0	7.5	0.93

[a] From titrimetric data.

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* Titrimetric value obtained in this work.

† We have recently observed a marked decrease in these values for toluene at higher temperatures (*ca.* 40°) and are currently investigating this phenomenon.

for toluene and involve greater proton transfer to the base ($CF_3CO_2^-$).

This effect is however somewhat compensated by the reduced stability (*ca.* 1.2 kcal mol^{-1}) of the toluene products compared to benzene (see Table 7). The importance of considering both factors (in this instance σ complex and product stability) when applying the Hammond postulate has been pointed out by Farcasiu.[11] The dominant effect nevertheless is that of σ complex stability. This seems to be supported by the greater entropy loss for toluene compared with benzene.

TABLE 6

Values of k_2^{obs}/l mol^{-1} s^{-1}, k_2/s^{-1}, and K_1/l mol^{-1} for the mercuriation of various aromatic derivatives in CF_2CO_2H at 25° together with relative stabilities of π and σ complexes (K_π, K_σ relative to benzene)

						K_π		
Compound	$10^2k_2^{obs}$	10^3k_2	K_1	K_1(rel)	*a*	*b*	*c*	K_σ [d]
Chlorobenzene	0.083	1.0	0.8	0.098				
Fluorobenzene	0.61	5.9	1.0	0.122				
Benzene	2.92	3.53	8.2	1.0	1.0	1.0	1.0	1.0
Benzene [e]	0.43							
Toluene	51	52	10	1.2	1.07	1.06	1.85	790
o-Xylene	281	70	40	4.9	1.29	1.81	3.5	7 900
o-Xylene [e]	6.6							
Triptycene [e]	17							
9-Methoxytriptycene [e] 9,10-Dimethoxytriptycene [e]				No reaction				

For [a] Ag$^+$, [b] I_2, and [c] TCNE complexes, see L. J. Andrews and R. M. Keefer, ' Molecular Complexes in Organic Chemistry, Holden-Day, San Francisco, 1964. [d] For HF–BF_3 complexes see ref. 10. [e] Solvent CF_3CO_2H–CCl_4 (10 : 1 v/v); titrimetric method.'

Effect of Substituents and Structure.—The relevant values of the rate and equilibrium constants appear in Table 6. The substituent effects on K_1 have already been discussed in part. The K_1 values correspond much more closely to those expected for a π rather than a σ complex, indeed the values are in reasonable agreement with those for the corresponding tetracyanoethylene (TCNE) complexes which involve very little transfer of charge.[12] As expected, the effects on k_2 are more marked although the substrate selectivity is quite low compared with other electrophilic substitutions. Using the product analyses determined by Brown,[4] the partial rate factors for the *para*- and *meta*-positions can be calculated for the k_2 step. The resulting Hammett plot shows a much better correlation with σ^+ than σ and the ρ value (−5.8) is almost identical with that observed by Brown for the overall reaction (−5.68). Recently, however, Olah and his co-workers [13] have redetermined the overall rates and isomer distributions for a number of monosubstituted benzenes from competitive experiments with benzene, analysing the products at very short reaction times. This work has revealed rather serious discrepancies between the two studies, Olah reporting higher *o*/*p* and lower *m*/*p* ratios than Brown. However the concentrations used by Olah were ten times higher in aromatic (0.5M). It would be illuminating to investigate the isomer distribution as a function of concentration. Generally speaking our values of the overall rates of monosubstituted benzenes relative to benzene agree well with those of Olah (in parentheses) and are somewhat at variance with Brown's results. If Olah's isomer ratios are used to calculate the partial rate factors a ρ value of −6.4 is obtained from σ^+ correlations. Both results are in keeping with small charge transfer in the π complex followed by a modest charge development in the transition state between the σ complex and products. One interesting feature is that for the fluorine substituent, k_2 is somewhat larger than that for benzene. Electron withdrawal by the fluorine atom is thus more than balanced by the strong resonance effect.

X	F	Cl	Me
Relative rate	0.21 (0.24)	0.028 (0.030)	17.5 (18)

Part of our original plan was to study systematically the mercuriation of triptycene and its derivatives. However, solubility problems necessitated the use of a co-solvent, CCl_4, and restricted the kinetic study to reactions at equimolar concentrations. U.v. scans showed the reaction to be qualitatively similar to those described above, *i.e.* rapid intermediate formation (at 345 nm) followed by slow decay. We were able to follow the reaction by the titrimetric procedure, and obtained for triptycene itself a rate 40 times that of benzene. This value is less than that obtained for nitration, a reaction known to show low substrate selectivity, but high positional selectivity.[14] The value of k_2^{obs} for triptycene is only slightly less than three times that for *o*-xylene, a factor which corresponds to the statistical rate increase due to the presence of three rings in the former. Interestingly, both 9-methoxy- and 9,10-dimethoxy-derivatives failed to react under our conditions. Presumably the oxygen atoms are protonated and hence the substituent acts as a powerful electron-withdrawing group which deactivates the rings to electrophilic substitution.

Product Analyses.—These appear in Table 7 and show that yields of the product mercurials decrease substantially on alkylation. This is probably the result of a combination of steric effects caused by Hg–alkyl group interactions and polar effects, the electropositive character of the mercury atom increasing the electron density in the aromatic ring with resulting destabilisation by the alkyl substituents.

Effect of Added Salts.—Table 8 shows the effect on the observed pseudo-first-order rate constant ([benzene] = 0.148M, $[HgX_2] = 4.93 \times 10^{-3}$M) of added salts and change of the added mercury(II) salt. Added CF_3CO_2Na has very little effect on k_1^{obs}. If attack were by the trifluoroacetatomercury(II) ion formed in the equilibrium

$$Hg(OCOCF_3)_2 \rightleftharpoons \overset{+}{H}gOCOCF_3 + \overset{-}{O}COCF_3 \quad (6)$$

TABLE 7

Yields of products and overall reaction equilibrium constants K_c for mercuriation reactions as determined by g.l.c. analysis

Compound	Reaction (%)	K_c
Benzene	91	11 500
p-Xylene	85	3 900
Toluene	77	1 600
o-Xylene	73	800
m-Xylene	64	500
Mesitylene	52	300
Benzene *	7	

* Values for reverse reaction using $PhHgOCOCF_3$.

TABLE 8

Effect of added salt on the rate of mercuriation of benzene (0.148M) with $Hg(OCOCF_3)_2$ (4.93×10^{-3}M) in CF_3CO_2H at 25°

Mercury salt supplied as	Salt added	10^3[salt]/M	$10^3k_2^{obs}/s^{-1}$
$Hg(OCOCF_3)_2$			2.67
$Hg(OCOCF_3)_2$	CF_3CO_2Na	1.0	2.67
$Hg(OCOCF_3)_2$	CF_3CO_2Na	3.0	2.62
$Hg(OCOCF_3)_2$	CF_3CO_2Na	5.0	2.62
$Hg(OCOCF_3)_2$	CF_3CO_2Na	7.0	2.64
$Hg(OCOCF_3)_2$	CF_3SO_3Na	7.0	3.30
$Hg(OCOCF_3)_2$	CF_3SO_3Na	5.0	3.56
$Hg(OCOCF_3)_2$	$LiClO_4$	7.0	4.05
$Hg(OAc)_2$			2.54
$Hg(OAc)_2$	CF_3SO_3Na	50.0	4.07

then added trifluoroacetate would suppress the ionisation and reaction rates would be lowered. However, Brown has shown that unionised electrophiles can act as efficient electrophilic reagents in his study of uncatalysed mercuriation of benzene with mercury(II) acetate.[15] The only other steps affected by the addition of the common ion should be those involving the forward and reverse reactions of the σ intermediate, apart from a general salt effect which at these concentrations (10^{-3}—10^{-2}M) is likely to be very small anyway.† The σ intermediate stage of mercuriation can be written as in reaction (7)

$$ArH + HgX_2 \xrightleftharpoons{K_1K_2} \overset{+}{\sigma} + \overset{-}{X} \xrightarrow{k_3} \text{products} \quad (7)$$

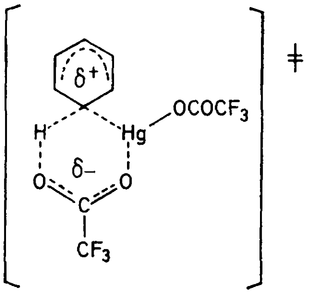
where K_2 is the equilibrium constant between π and σ intermediates. If it is assumed that $[CF_3CO^-{}_2]_{added} > [\overset{+}{\sigma}]$ then it can be easily shown that equation (8) holds.

$$[\overset{+}{\sigma}] = \frac{K_1K_2[ArH][HgX_2]}{[X^-] + K_1K_2[ArH]} \quad (8)$$

The overall rate of reaction v is given by equation (9). If $K_1K_2[ArH] >> [X^-]$, then the rate should increase with increasing $[X^-]$ whereas if $K_1K_2[ArH] << [X^-]$ then the rate should be independent of $[X^-]$. The latter situation obtains in our case. For this condition to occur, $[X^-]$ should be at least ten times $K_1K_2[ArH]$.

$$v = k_3[\overset{+}{\sigma}][X^-] = \frac{k_3K_1K_2[ArH][HgX_2][X^-]}{[X^-] + K_1K_2[ArH]} \quad (9)$$

The value of K_1 for benzene has been shown to be *ca.* 8 l mol^{-1}, and using the values of [ArH] and $[X^-]$ quoted above, K_2 should be $<10^{-3}$, *i.e.* the σ complex for the mercuriation of benzene is not very stable with a free energy of formation of $\geqslant +3$ kcal mol^{-1}. Indeed one questions whether in fact a discrete σ intermediate need necessarily be formed in the case of mercuriation. One could for instance formulate the mechanism involving synchronous bond fission and bond formation *via* the transition state (1) as suggested by Winstein and Traylor[16] in a study of the reverse reaction, protodemercuriation of diphenylmercury. This is consistent with the ρ value for mercuriation by mercury(II) trifluoroacetate, implying a modest development of positive charge in the rate-determining transition state. We have found no spectroscopic evidence for the existence of σ complexes in this system. Reutov *et al.*[7] have reported u.v. maxima at 261 and 303.5 nm for solutions of hexamethylbenzene and $Hg(OCOCF_3)_2$ in CF_3CO_2H.



(1)

These values are considerably lower than those reported for the hexamethylbenzenonium ion[17] (287 and 397 nm), though it is still unclear what effect would occur by substituting the hydrogen by the $HgOCOCF_3$ group. One interesting corollary of postulating attack by unionised $Hg(OCOCF_3)_2$ to give a σ complex is that the liberated anion would not be stereochemically in a position to accept the proton to give products. Quantum mechanical calculations have shown that the orientation of the $CF_3CO_2^-$ group in (2) is particularly favourable.[18]

The collapse of the π complex to the above σ complex would result in the $CF_3CO_2^-$ group being on the opposite side of the benzenium ion to the departing proton, which in this case would presumably be transferred to a solvent molecule followed by a proton-switch mechanism to finally protonate the anion. Whether the electrophilic mercury is supplied as $Hg(OCOCF_3)_2$ or the corresponding acetate makes very little difference to the observed rates (Table 8). Only one of the acetate groups is

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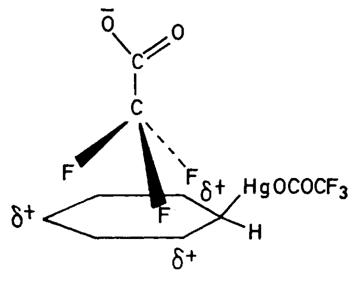
† In addition, complexation by the trifluoroacetate ion, *viz.* $Hg(OCOCF_3)_2 + \overset{-}{O}COCF_3 \rightleftharpoons [Hg(OCOCF_3)_3]^-$, is very unlikely in view of the extremely low nucleophilicity and poor ligand properties of the trifluoroacetate ion.

replaced by trifluoroacetate even on heating in an excess of CF_3CO_2H. The mixed acetate can be isolated in good

$$Hg(OCOCH_3)_2 + CF_3CO_2H \longrightarrow Hg(OCOCF_3)(OCOCH_3) + CH_3CO_2H \quad (10)$$

yields from CF_3CO_2H solutions as a crystalline solid, m.p. 199—200°. It therefore appears that the mixed acetate has almost the same electrophilicity as $Hg(OCOCF_3)_2$ and incidentally is a much cheaper reagent.



(2)

Added $LiClO_4$ and CF_3SO_3Na cause small rate increases, but it is not easy to interpret these effects because salt effects and anion exchange with the electrophile are difficult to separate.

EXPERIMENTAL

Preparation and Purification of Materials.—Trifluoroacetic acid was heated with a small quantity of P_2O_5 and fractionated. The deuteriated acid was prepared by the slow addition of D_2O (99.7 %D) to cool, well stirred trifluoroacetic anhydride in slight excess followed by fractionation to give trifluoroacetic acid with a deuterium content of 99.2 ± 0.4 %D. Spectroscopic grade CCl_4 was used without further purification. All liquid aromatic substrates were fractionated prior to use. Triptycene, 9-methoxytriptycene, and 9,10-dimethoxytriptycene were synthesised from the corresponding anthracenes by the method of Friedman and Logullo.[19]

Phenylmercury(II) trifluoroacetate, m.p. 107—109°, was prepared in 74% yield by reaction of phenylmercury(II) chloride with silver trifluoroacetate in acetonitrile. Mercury(II) trifluoroacetate was prepared by refluxing a mixture of yellow mercury(II) oxide (10 g, 0.05 mol) in CF_3CO_2H (10 ml, 0.147 mol) containing *ca.* 5% $(CF_3CO)_2O$ for 3 h. The crystalline product appeared on cooling, m.p. 165—167°.

Preparation of $Hg(OCOCF_3)(OCOCH_3)$.—Mercury(II) acetate (2.0 g, 6.3 mmol) was heated to boiling in CF_3CO_2H (10 ml). Most of the solvent was removed by rotary evaporation and the residue was triturated with CCl_4 at 0°. The crystals formed were filtered off and washed with a little cold $CHCl_3$ to give solid (1.8 g, 77%), m.p. 199—200° (Found: C, 12.6; H, 0.50. Calc. for $C_4H_3F_3HgO_4$: C, 12.9; H, 0.8), δ([$^2H_6$]acetone) 1.82 (s).

Kinetic Techniques.—(a) *Titrimetric methods.* Portions of reaction mixtures were withdrawn at suitable times, quenched in water, and titrated at 5° with thiocyanate using iron(III) ammonium sulphate as indicator. The first faint appearance of a red colour was taken as the end point. The reactions were generally conducted at equimolar concentrations and the observed second-order rate constant, k_2^{obs}, calculated from equation (11) where a is the initial concentration of both substrate and electrophile and T_0 and T_t are the titres obtained at time 0 and t, respectively. The form of the above equation is governed by the fact that the inorganic mercury compound reacts with *two* equivalents of thiocyanate and the product mercurial reacts with *one* equivalent.[20] Average standard deviations for this method were ±7%.

$$k_2^{obs} = \frac{2}{at}\left(\frac{T_0 - T_t}{2T_t - T_0}\right) \quad (11)$$

(b) *Spectroscopic method.* A solution of mercury(II) trifluoroacetate in trifluoroacetic acid (3 ml, 5×10^{-3}M) was pipetted into a 1 cm silica cell and placed in a thermostatted compartment of a Unicam SP 1750 spectrophotometer equipped with digital read-out facility and linear recorder. The reference cell contained a solution of the relevant aromatic compound in CF_3CO_2H at the same concentration as that used in the reaction. After 20 min thermal equilibration, the appropriate volume of substrate was injected by means of a Hamilton syringe and the chart trace started. The following analytical wavelengths were used: benzene, 280, [$^2H_6$]benzene 300, toluene 315, and *o*-xylene 345 nm. The reactions were performed using varying substrate excesses, always maintaining pseudo-first-order conditions, $[ArH] > 10\ [Hg(OCOCF_3)_2]$. For slow reaction (*e.g.* [$^2H_6$]benzene) the Guggenheim method of calculating pseudo-first-order rate constants was used. Average standard deviations of k_1^{obs} were ±1%. Values of K_1 and k_2 were obtained from the slopes and intercepts of equation (4). The relevant constants were obtained using an interactive data analysis programme for regression analysis (K.I. Macdonald, Dept. of Government, University of Essex). Activation parameters were also computed using this facility. Corrections were made for changes in density (d) of the solvent [21] using equation (12) where t is the reaction temperature.

$$d = 1.537\,5 - 0.002\,346t \quad (12)$$

Extinction Coefficients.—For the reaction of benzene with $Hg(OCOCF_3)_2$ at equimolar concentrations (0.02M) at 25°, the absorbance of the mercury salt alone was 0.31 at the analytical wavelength of 280 nm. This rose immediately on adding the benzene to a value of 2.26. Using the computed value of K_1 of 8.2 l mol^{-1}, the concentration of complex at $t = 0$ is 2.53×10^{-3}M which gives an extinction coefficient (ε) of 786 [*cf.* 15.5 for $Hg(OCOCF_3)_2$ alone]. Measurements at the $\lambda_{max.}$ for the complex (262 nm) must be viewed with some caution since this is very close to the absorption maximum of the solvent itself. Values of $\varepsilon_{max.}$ for the complex and mercury(II) salt were 3 740 and 61, respectively.

Product Analysis.—Equal volumes of 0.28M solution of substrate and $Hg(OCOCF_3)_2$ were mixed and allowed to stand for 24 h at 25.0 ± 0.1°. Portions (0.5 ml) were quenched in a mixture of AnalaR CCl_4 (2.0 ml) and saturated sodium chloride (1.0 ml). The lower CCl_4 layer was separated and dried with a little $MgSO_4$, then analysed for the aromatic using a Perkin-Elmer F17 chromatograph with a polar column (15% Carbowax on Chromosorb W, 2 m × $\frac{1}{8}$ in, N_2 flow rate 30 ml min^{-1}, column temperature 60°, injection temperature 225°). The concentration of aromatic was calculated by reference to chromatographs of standard solutions. Percentage yields were accurate to ±1%.

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[1] (*a*) For a summary of data prior to 1967 see C. H. Bamford and C. F. H. Tipper, 'Comprehensive Chemical Kinetics,' Elsevier, Amsterdam, vol. 13, p. 186 and references therein; (*b*) W. Kitching, *Organometallic Chem. Rev.*, 1968, **3**, 35.

[2] H. C. Brown and C. W. McGary, jun., *J. Amer. Chem. Soc.*, 1955, **77**, 2300, 2306, 2310.

[3] H. C. Brown and G. Goldman, *J. Amer. Chem. Soc.*, 1962, **84**, 1650.

[4] H. C. Brown and R. A. Wirkkala, *J. Amer. Chem. Soc.*, 1966, **88**, 1447, 1453, 1456.

[5] L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35.

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

[7] V. I. Sokolov, V. V. Bashilov, and O. A. Reutov, *Doklady Akad. Nauk S.S.S.R.*, 1971, **197**, 101.

[8] G. A. Olah, S. H. Yu, and D. G. Parker, *J. Org. Chem.*, 1976, **41**, 1983.

[9] L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, 1955, **77**, 6284.

[10] E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, 1958, **54**, 66, 187.

[11] D. Farcasiu, *J. Chem. Educ.*, 1975, **52**, 76.

[12] For a discussion of the role of π complexes in aromatic substitutions, see G. A. Olah, *Accounts Chem., Res*, 1971, **4**, 240.

[13] G. A. Olah, I. Hashimoto, and H. C. Lin, *Proc. Nat. Acad. Sci. U.S.A.*, 1977, **74**, 4121.

[14] J. H. Rees, *J.C.S. Perkin II*, 1975, 945.

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

[16] S. Winstein and T. G. Traylor, *J. Amer. Chem. Soc.*, 1955, **77**, 3747.

[17] W. von E. Doering and M. Saunders, *Tetrahedron*, 1958, **4**, 178.

[18] J. J. Dannenberg, *Angew. Chem. Internat. Edn.*, 1975, **14**, 641.

[19] L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, 1963, **85**, 1549.

[20] B. F. Hegarty and W. Kitching, *J. Org. Chem.*, 1976, **41**, 2247.

[21] J. J. Jasper and H. L. Wedlick, *J. Chem. Eng. Data*, 1964, **9**, 446.