Kinetics and Mechanism of the Reaction of 9-Arylfluoren-9-yl Cations with Polymethylbenzenes in Trifluoroacetic Acid Solution

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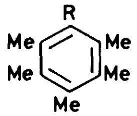
9-Arylfluoren-9-yl cations, ArFl$^+$, generated from the alcohol in CF_3CO_2H solution, are reduced to ArFlH by the polymethylated aromatic hydrocarbons (Ar^1CH_3) hexamethylbenzene, pentamethylbenzene, 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-tetramethylbenzene, 1,3,5-trimethylbenzene, and 9,10-dimethylanthracene. Simple hydride-ion transfer, $ArFl^+ + Ar^1CH_3 \longrightarrow ArFlH + Ar^1CH_2{}^+$, is thermodynamically unfavourable, but analysis indicates that $Ar^1CH_2{}^+$ reacts further, to give stable products. Rates of disappearance of ArFl$^+$ ($=k_2[ArFl^+][Ar^1CH_3]$) measured spectrophotometrically show wide variation depending on the nature of Ar and Ar^1, and kinetic isotope effects in the range 2.8—4.2 at 30 °C resulting from experiments using perdeuteriohexamethylbenzene. The rate variation with changing Ar^1CH_3 correlates best with the ability of Ar^1CH_3 to form charge-transfer complexes with fluoranil or to undergo one-electron oxidation. It is concluded that in the transition state for hydride transfer, electron transfer may have progressed further than nuclear motion of the migrating hydrogen. The possibility of intermediate formation of the pair $ArFl^\cdot$–$Ar^1CH_3{}^{+\cdot}$ is also considered. 4-Substituents in the phenyl group of PhFl$^+$ have a remarkably constant effect on reaction rates with a range of Ar^1CH_3 of varying reactivity.

This investigation has its origin in two earlier studies of the behaviour of carbocations in trifluoroacetic acid solution. The first was an examination of structural effects on intermolecular hydride transfer from tri- and di-arylalkanes to 9-arylfluoren-9-yl cations (ArFl$^+$), which indicated that a combination of electronic and steric factors controlled the relative reactivities of the hydride donors.[1] The other investigation was of the mechanism of photo-oxidation of triarylmethanes sensitised by triphenylmethyl, xanthydryl, and 5*H*-dibenzo[*a*,*d*]cycloheptenyl cations,[2] in which it was inferred that an excited triplet state of the sensitiser cation initially abstracted an electron from the hydrocarbon yielding the corresponding radical cation which then proceeded to products.

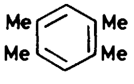
In the course of that work it was established that 9-phenylfluoren-9-yl cation did not act as a sensitiser and at the time we surmised that in this case the triplet carbocation might have too low an energy to permit electron abstraction from triphenylmethane. Since the parent cyclopentadienyl cation is known to be a ground-state triplet species,[3] the possibility that the triplet states of 9-arylfluoren-9-yl cations might be thermally accessible also suggested itself. An important piece of evidence for the electron-transfer mechanism proposed for the carbocation-sensitised photo-oxidation of triarylmethanes was our observation of e.s.r. signals attributable to triphenylmethyl radicals and hexamethylbenzene radical cations when solid solutions of triphenylmethyl cation and hexamethylbenzene in trifluoroacetic acid were irradicated and allowed to warm up. Attempts to repeat this type of experiment using 9-phenylfluoren-9-yl cation and hexamethylbenzene led to a *thermal* reaction in which the carbenium ion was rapidly consumed. Kinetic and mechanistic studies on this reaction are the subject of the present report.

Results

Reaction Systems and Products.—Reactions were carried out in trifluoroacetic acid, usually containing a few percent of a co-solvent, e.g. acetic acid or benzene, to facilitate solution. Such solvent mixtures are known to convert the 9-arylfluoren-9-ols used in this investigation into the corresponding carbenium ion essentially completely. Addition of hexamethylbenzene (1) and other polymethylated aromatics in excess to such carbenium ion solutions at room temperature led to the immediate onset of reaction with fading of the colour of the reactant ion. With (1) reaction was complete within a few minutes, leaving a coloured reaction mixture with absorbance in the range 500—700 nm. Besides (1), the following polymethylated aromatic compounds were used: pentamethylbenzene (2), 1,2,4,5-tetramethylbenzene (durene) (3), 1,2,3,4-tetramethylbenzene (prehnitene) (4), 1,2,3,5-tetramethylbenzene (isodurene) (5), 1,3,5-trimethylbenzene (mesitylene) (6), and 9,10-dimethylanthracene (7). The 9-aryl groups in the fluorenyl cations were *p*-substituted phenyl and included 2,4,6-trimethylphenyl. All reaction systems showed similar behaviour albeit with widely different reaction rates.



(1) R = Me
(2) R = H



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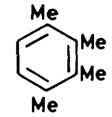

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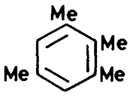

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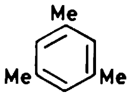

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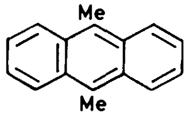

(7)

Chromatographic examination of reaction products showed them to be fairly complex mixtures. The principal identifiable product was always the 9-arylfluorene, *i.e.* formally the product of hydride transfer to the 9-arylfluoren-9-yl cation. In preparative-scale experiments (100 mg of the 9-arylfluoren-9-ol and a 50-fold excess of polymethylated benzene) isolated yields of 9-arylfluorene exceeded 80% of the theoretical with hexamethylbenzene and 70% with durene. In the more dilute solutions used in kinetic experiments (typically 3 × 10^{-5}M-carbocation) yields were much lower. G.c.–mass spectrometric examination of the by-products showed the presence of small amounts of pentamethylbenzene and a tetramethylbenzene in reactions in which (1) was used, while reactions involving (3) yielded a little pentamethylbenzene and heptamethyldiphenylmethane (*m*/*z* 266, 251, 147, and 133), presumably the 2,2′,3,4′,5,5′,6-isomer. It would seem, therefore, that carbocations generated from the polymethylated aromatic compound react with the aromatic compounds

Table 1. Wavelength of maximum residual absorbance after reaction of ArFl$^+$ with Ar^{1}CH$_3$

Ar	Ar^{1}CH$_3$	$\lambda_{max.}$/nm
C_6H_5	(1)	625
4-ClC_6H_4	(1)	625
C_6H_5	(3)	570
C_6H_5	(6)	555

Table 2. Rate constants ($k_{obs.}$/l mol^{-1} s^{-1}) for the reaction of ArFl$^+$ with Ar^{1}CH$_3$ in trifluoroacetic acid at 30 °C

	$k_{obs.}$[a]						
Ar	(1)	(2)	(3)	(4)	(5)	(6)	(7)
C_6H_5	26.6(7)[b]	3.11(8)	0.587(7)	2.52(1)	0.398(7)	0.067 9(50)	1 120(40)
4-MeC_6H_4	2.40(2)	0.204(6)	0.046 3(11)			0.006 95(11)	85.6(9)
4-$MeOC_6H_4$	0.026 7(9)	0.003 71(4)	0.000 504(14)			0.000 072 3(22)	
4-PhC_6H_4	2.71(3)						
2-MeC_6H_4	42.8(3)						
2,4,6-$Me_3C_6H_2$	0.036 4(16)						

[a] Numbers in parentheses are standard deviations expressed in terms of the last significant figure. [b] In the presence of a ten-fold excess of 9-phenylfluorene the value is 27.2 l mol^{-1} s^{-1}.

Table 3. Second-order rate constants (k_2^D) for reaction of ArFl$^+$ with perdeuteriohexamethylbenzene at 30 °C

Ar	k_2^D/l mol^{-1} s^{-1}	k_2^H/k^D
C_6H_5	8.05 ± 0.12	3.30 ± 0.10
2-$CH_3C_6H_4$	15.5 ± 0.6	2.76 ± 0.11
4-$CH_3C_6H_4$	0.598 ± 0.012	4.01 ± 0.09
4-$CH_3OC_6H_4$	0.0064 ± 0.0001	4.20 ± 0.17

present, including, for example, 9-phenylfluorene in the late stages of reaction.

The colours of the reaction mixtures at the end of the reaction period throw further light on these secondary reactions. It was observed (Table 1) that the wavelength of maximum absorption of such solutions was independent of the 9-arylfluorenyl cation, but varied with the nature of the polymethyl aromatic compound. Moreover, the appearance of the final colouration began only after all or nearly all the colour of the reactant cation had disappeared. Although diarylmethanes generated in secondary reactions could in principle act as hydride donors towards ArFl$^+$ and so produce the diarylmethyl cations responsible for the final colours, it is clear that such a process does not contribute significantly to the rate of disappearance of the 9-arylfluoren-9-yl cations investigated here.

Reaction Kinetics.—All experiments were conducted at 30 °C. In almost all cases initial carbenium-ion concentrations were *ca.* 3×10^{-5}M and the polymethylbenzene (Ar^{1}CH$_3$) was in at least ten-fold excess. Under these conditions reaction mixtures were homogeneous throughout and on completion of the reaction showed negligible absorbance at the wavelength of maximum absorption of ArFl$^+$. Reactions were, therefore, followed spectrophotometrically by the disappearance of the absorption of ArFl$^+$ and this obeyed a first-order kinetic law over two or more half-lives. For some of the slower reactions, however, first-order rate coefficients were determined from initial rate measurements. Variation of the excess of polymethylbenzene established (1) as the kinetic law.

$$-d[ArFl^+]/dt = k_{obs.}[ArFl^+][Ar^1CH_3] \quad (1)$$

Because of its rapidity, the reaction between PhFl$^+$ and 9,10-dimethylanthracene (7) was carried out with equal initial concentrations of the reactants and adhered to a simple second-order kinetic law.

Values of the second order velocity constants $k_{obs.}$ for the polymethylated aromatics (1)—(7) are in Table 2. They show a wide variation with structural change in both ArFl$^+$ and Ar^{1}CH$_3$. In reactions with (1), changing the 9-aryl substituent from *o*-tolyl to mesityl changes $k_{obs.}$ by a factor of 1600, the two rather hindered cations giving the highest and lowest values. Generally, however, $k_{obs.}$ increases as pK_{R^+} becomes more negative. Changing Ar^{1}CH$_3$ from mesitylene to 9,10-dimethylanthracene increases $k_{obs.}$ by a factor of over 16 000, while within the series of polymethylbenzenes $k_{obs.}$ generally increases with the number of methyl groups.

Kinetic measurements were also made on the reaction between perdeuteriohexamethylbenzene and four different ArFl$^+$. The results in Table 3 show substantial primary kinetic isotope effects in the range 2.8—4.2 at 30 °C, the magnitude varying with the substituent in Ar. The values are rather similar to those measured in hydride-transfer reactions between triphenylmethane and 4,4′-dimethoxydiphenylmethane and ArFl$^+$ under similar conditions.

It was established that irradiation of reaction mixtures with visible light neither accelerated nor retarded the reaction.

Discussion

Reaction Mechanism.—Thermodynamic considerations rule out the possibility that the reaction of ArFl$^+$ with hexamethylbenzene and related polymethylbenzenes consists simply of a hydride-ion transfer. Values of pK_{R^+} for the reactant carbocations are in the range -6.63 (Ar = 2,4,6-$Me_3C_6H_2$) to -10.69 (Ar = Ph),[1] whereas the product carbenium ion from hexamethylbenzene, the pentamethylbenzyl cation, has pK_{R^+} *ca.* -17.* Other polymethylbenzyl cations probably have rather similar values, making the wide variation in k_2 difficult to explain. These reactions are thus quite different from the reactions of ArFl$^+$ with good hydride donors like triphenylmethane upon which we have previously reported;[1] ΔpK_{R^+} for those reactions is substantially positive indicating a thermodynamically favourable process. Nor does it seem likely that an unfavourable hydride-transfer pre-equilibrium of ArFl$^+$ and Ar^{1}CH$_3$ precedes a rate-limiting reaction of the product carbenium ion. 9-Arylfluorene would be formed in the pre-equilibrium and we have established that its presence in excess in reaction mixtures has a negligibly small effect on the

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* For 2,4,6-trimethylbenzyl cation, pK_{R^+} is reported to be -17.3.[4] The tertiary carbenium ion, heptamethylbenzyl cation, has pK_{R^+} -12.4, little affected by removal of the 3- and 5-methyl groups.

Table 4. Linear free energy correlations for variations in Ar^1CH_3

	Ar^1CH_3	10^3K_6 [a]	K_7 [b] kg mol^{-1}	$E_{\frac{1}{2}}$ [c]/V
	(7)			0.65
	(1)	89.0	15.4	1.16
	(2)	8.70	7.9	1.28
	(3)	0.12	4.9	1.29
	(5)	6.50	4.5	1.43
	(4)	0.17	4.5	1.40 [d]
	(6)	2.80	2.2	1.58
$C_6H_5Fl^+$	Slope (r) [e]	0.349 (0.428)	2.973 (0.946) [g]	−4.436 (0.957)
	log $k_2°$ (n) [f]	−0.056(6)	−2.105(6)	6.081(7)
$4\text{-}CH_3C_6H_4Fl^+$	slope (r) [e]	0.621 (0.948)	2.989 (0.994)	−4.513 (0.966)
	log $k_2°$ (n) [f]	−1.325(4)	−3.281(4)	5.006(5)
$4\text{-}CH_3OC_6H_4Fl^+$	slope (r) [e]	0.643 (0.977)	3.093 (0.995)	−5.687 (0.917)
	log $k_2°$ (n) [f]	−3.249(4)	−5.271(4)	4.689(4)

[a] Values relative to that for *p*-xylene = 1.0.[11] [b] In CCl_4 at 33.5 °C.[12] [c] V *versus* Ag–Ag$^+$.[13] [d] This work; using s.c.e. and corrected to Ag–Ag$^+$. [e] Correlation coefficient. [f] Size of data set. [g] Omitting the result for (4), slope 3.118, r 0.997, log $k_2°$ −2.328.

$$ArFl^+ + Ar^1CH_3 \rightleftharpoons ArFl\cdot + Ar^1CH_3^{+} \quad (2)$$

$$ArFl + Ar^1CH_3^{+} \longrightarrow ArFlH + Ar^1CH_2^{+} \quad (3)$$

$$\left.\begin{array}{l} Ar^1CH_2^{+} + ArCH_3 \longrightarrow \\ Ar^1CH_2^{+} + ArFlH \longrightarrow \end{array}\right\} \text{By-products} \quad (4)$$

rate of the reaction between 9-phenylfluoren-9-yl cation and hexamethylbenzene (see Table 2). Thus, if ArFlH and $Ar^1CH_2^+$ are the initial products of the observed reaction, they must rapidly react further to give more stable products (in order to satisfy the thermodynamic criterion for reaction) and by a process not involving reverse hydride transfer.

We discount electrophilic aromatic substitution as a major pathway in the quenching of $ArFl^+$ by Ar^1CH_3. Thus, (3) has two equivalent unsubstituted ring positions where (1) has none, yet both gave rather similar yields (*ca.* 80%) of 9-phenylfluorene with $PhFl^+$ in preparative experiments, but at rates differing by a factor of 45.

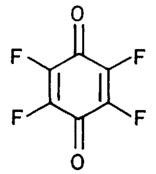
Finally, we examine the possibility of an electron-transfer mechanism for the reaction, as shown in reactions (2)—(4). One-electron reduction of carbenium ions has been recognised for many years [5] and has been the subject of extensive study by Okamoto and his co-workers.[6] In the present reactions, however, it seems unreasonable to suggest that electron transfer is the rate-limiting step because of the large kinetic isotope effect observed when perdeuteriohexamethylbenzene is used. Although theoretical considerations suggest that kinetic isotope effects should occur in electron-transfer reactions in polar media under certain conditions,[7] there have been no reports, as far as we are aware, of the experimental determination of substantial effects. Indeed, our earlier inference of electron transfer as the key step in carbenium-ion-sensitised photo-oxidation of triarylmethanes [2] was in part based on the absence of a kinetic hydrogen isotope effect. Foster [8] has reported hydrogen-isotope effects on charge-transfer equilibria, involving fluoranil and simple aromatic hydrocarbons like benzene and toluene, that are in the range K_H/K_D 0.9—1.0; earlier reports [9] of effects in the opposite direction in similar charge-transfer equilibria seem to be in error.[10] The magnitude of the effects in Table 3 thus seems to require cleavage of C–H bonds in the rate-limiting step of the reaction and this could only be accommodated in an electron-transfer mechanism if reaction (2) were a rapidly established pre-equilibrium, followed by a slow hydrogen-atom transfer. The observed value of $k_{obs.}$ would then be given by equation (5). Published redox properties of $PhFl^+$ and (1) do not provide support for

$$k_{obs.} = K_2k_3 \quad (5)$$

such an interpretation, however; in 10.2M-H_2SO_4, $PhFl^+$ has E_p^{red} −0.01 V *versus* Hg–Hg^{2+} (≡ +0.25 V *versus* s.c.e.)[11] and (1) in CH_3CN is reported [12] to have $E_{\frac{1}{2}}^{ox}$ 1.16 V *versus* Ag–Ag$^+$ (≡ 1.65 V *versus* s.c.e.). Taken at face value, these results would lead to a very low K_2, and k_3 would necessarily be very large and in excess of the value for a diffusion-controlled process. Of course, the combination of potentials measured under widely divergent conditions and on irreversible electrochemical processes cannot be expected to yield realistic values of K_2. Nevertheless the data do not encourage the view that single-electron transfer is a key step in the reduction of $FlAr^+$ by polymethyl aromatics.*

$$Ar^1CH_3 + HF/BF_3 \rightleftharpoons (HAr^1CH_3)^+ + BF_4^- \quad (6)$$

Ar^1CH_3 +



$\rightleftharpoons$ CT complex (7)

$$ArFl^+ + Ar^1CH_3 \rightleftharpoons (ArFl/Ar^1CH_3)^+ \quad (8)$$

$$(ArFl/Ar^1CH_3)^+ \longrightarrow ArFlH + Ar^1CH_2^{+} \quad (9)$$

Faced with this apparent impasse, we have sought to proceed indirectly by the use of linear free energy relations. With the aim of distinguishing single-electron-transfer mechanisms

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* *Note added in proof.* Using Marcus Theory, Professor K. Okamoto (personal communication) has estimated that the rate constant for electron transfer from (1) to $PhFl^+$ should be *ca.* 2 × 10^{-17} l mol^{-1} s^{-1}, to be compared with the observed rate constant of 26.6 l mol^{-1} s^{-1}. On the same basis, electron transfer from (7) to $PhFl^+$ is predicted to be much faster, but is still too slow to contribute significantly to the observed rate for these reactants.

Table 5. Linear free energy correlation for variation of substituents in ArFl$^+$ [a]

		Hammett (σ^+)			Dauben ($-\mathrm{p}K_{\mathrm{R}^+}$)		
Ar^{1}CH$_3$	n	ρ	$\log k_2^\circ$	r	ρ	$\log k_2^\circ$	r
(7)	2	3.60	3.05	(1.0)	0.90	-6.53	(1.0)
(1)	4	3.86	1.48	0.986	0.94	-8.57	0.998
(2)	3	3.75	0.48	0.998	0.91	-9.23	0.999
(3)	3	3.96	-0.18	0.999	0.96	-10.46	0.999
(6)	3	3.85	-1.09	0.997	0.93	-11.07	0.998

[a] Symbols: ρ = slope; $\log k_2^\circ$ = value at σ^+ or $\mathrm{p}K_{\mathrm{R}^+} = 0$; n = number of points, r = correlation coefficient.

from heterolytic processes, a linear regression analysis has been carried out on the dependence of the kinetic data on the following properties of the polymethylated aromatics: (1) equilibrium constants (K_6) for σ-complex formation at 20 °C according to reaction (6);[13] (2) association constant (K_7) for the charge-transfer complex formation with fluoranil;[14] (3) half-wave oxidation potentials for Ar^{1}CH$_3$ measured[12] at 25 °C at a platinum anode in $\mathrm{CH_3CN}$–0.1M-$\mathrm{Bu_4N^+ClO_4^-}$.

The data and the derived regression parameters are in Table 4. It can be seen that the smaller data sets for 4′-methyl- and 4′-methoxy-substituted PhFl$^+$ are fairly well correlated by all three parameters. However, for the largest set (PhFl$^+$ itself), the correlation of $k_{\mathrm{obs.}}$ with the basicity of Ar^{1}CH$_3$ is very poor confirming our view that the quenching of ArFl$^+$ by Ar^{1}CH$_3$ does not involve an electrophilic attack of the carbenium ion on the aromatic ring. The correlations with $\log K_7$ and $E_{\frac{1}{2}}^{\mathrm{ox}}$ are much better; there is some scatter of points but the trend of $k_{\mathrm{obs.}}$ increasing with increasing ease of one-electron oxidation of Ar^{1}CH$_3$ is clearly defined. The correlation between $k_{\mathrm{obs.}}$, and $\log K_7$, can be improved still further if the data point for the reaction between PhFl$^+$ and (4) is omitted from the regression. An obvious inference is that rapid charge-transfer complexation of ArFl$^+$ and Ar^{1}CH$_3$ (8) precedes a rate-determining step in which hydrogen transfer occurs (9). These two steps are then followed by reactions (4) which are rapid and ensure that all the ArFl$^+$ is consumed. On this basis, with K_8 small, $k_{\mathrm{obs.}} = K_8k_9$; no appreciable absorbance that can be assigned to the charge-transfer complex is observed. This interpretation is preferable to that expressed by reactions (2)—(4) since reaction mixtures showed no e.s.r. spectroscopic evidence for doublet intermediates, nor was CIDNP observable in PhFlH produced when saturated solutions of PhFl$^+$ and excess of (1) were mixed and transferred to the probe of an n.m.r. spectrometer. Moreover, unambiguously radical-derived products such as substituted bibenzyls have not been found. The possibility remains that the observed reaction involves no intermediates at all, but that, in the transition state for reaction, electron transfer has progressed further than nuclear motion of the transferred hydrogen. Rates of reaction would then correlate with properties of the donors related to their one-electron oxidation rather than the stabilities of the derived carbocations, but there would be sufficient weakening of the Ar^{1}CH$_2$–H bond that a substantial isotope effect would be observed.

Our mechanistic conclusion is that the overall hydride transfer proceeds through a transition state having considerable electron-transfer character and with loosening of the transferred hydrogen. There is no direct positive evidence for a discrete intermediate in the process, either a radical + ion radical pair, or a charge-transfer complex, but equally, these possibilities cannot be excluded. Indeed, a spectrum of mechanisms can be envisaged, which could be represented in a two-dimensional free energy diagram of the Jencks–More O'Ferrall type, with the stepwise process *via* ArFl$^\cdot$ and Ar^{1}CH$_3^{+\cdot}$ representing one extreme.

Carbenium-ion Reactivity and Selectivity.—The effect of variation of the 4′-substituent in ArFl$^+$ on k_2 for reactions with donors (1)—(3), (6), and (7) is also revealing. We have correlated $\log k_2$ with σ^+ for the substituent (Hammett correlation) and with $-\mathrm{p}K_{\mathrm{R}^+}$ for the carbenium ions[1] (modified Dauben correlation*); linear regression parameters are in Table 5. Although the data sets are small the slopes ρ are defined well enough to show that they are substantially different from values found for the exoergonic hydride transfer from 4,4′-dimethoxydiphenylmethane and other donors to the same carbocations. Hammett ρ values are larger in the present reaction and the Dauben slopes average 0.93, suggesting that the reactant carbenium ions have lost 93% of their positive charge in the transition state compared with 67—74% in the exoergonic cases. A later transition state would be expected in the present endoergonic reaction, but it should be remembered in the context of our earlier mechanistic discussion that neutralisation of the charge can be achieved by electron transfer as well as by hydride-ion transfer. It may also be noted that despite the variation in reactivity of ArFl$^+$ with Ar^{1}CH$_3$, as indicated by $\log k_2^\circ$, by over four powers of ten, the selectivity of the carbenium ions indicated by ρ remains remarkably constant and shows no discernible trend. Thus, a 4′-methyl substituent lowers the reactivity of PhFl$^+$ towards all five Ar^{1}CH$_3$ examined by roughly a factor of 10 while the retarding effect of a 4′-methoxy-group is a factor of *ca.* 1 000. In its modest way, this constancy of substituent effects represents the same sort of failure of the Reactivity Selectivity Principle as has been described by Ritchie[16] and discussed at length by him and others.[17]

The Dauben correlation of the kinetic results for the reaction of ArFl$^+$ with (1) permits the inclusion of carbenium ions with 2′-substituents where the transition state for a simple hydride transfer would be expected to be highly congested. We have previously found that in exoergonic hydride transfers to such hindered carbenium ions, rates are roughly one-tenth of the values expected on the basis of $\mathrm{p}K_{\mathrm{R}^+}$. In the present endoergonic cases the hindered carbocations react faster than expected, the enhancements being by factors of 1.8 (Ar = 2-methylphenyl) and 9 (Ar = 2,4,6-trimethylphenyl). These observations are consistent with our mechanistic proposal in

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* The original Dauben correlation[15] is of $\log k_2$ with $\Delta\mathrm{p}K_{\mathrm{R}^+}$ for the reaction. In the exoergonic reactions of ArFl$^+$, with 4,4′-dimethoxydiphenylmethane for example, where k_2 decreases as ArFl$^+$ becomes more stable slopes (ρ) are positive. In the present endoergonic reactions the same pattern of substituent effects would lead to negative slopes. Correlation with $-\mathrm{p}K_{\mathrm{R}^+}$ for ArFl$^+$ gives the same sign in both reaction series without modifying the absolute value of ρ.

which, depending on the donor and the thermodynamics of the overall hydride-ion transfer, the transition state has a greater or lesser degree of electron-transfer character. In congested situations, the approach of the hydrogen donor and acceptor so as to permit the nuclear transfer would be opposed by severe steric compressions, and the transition state might be expected therefore to show enhanced electron-transfer character. Consistently, the kinetic isotope effects for the reactions of the 4′-substituted carbenium ions with (1) parallel those for the hydride transfer from 4,4′-dimethoxydiphenylmethane but that for the 2′-methyl-substituted cation is much lower than expected.

Experimental

Materials.—The 9-arylfluoren-9-ols were the samples used in an earlier investigation.[1] The polymethyl aromatic compounds were all commercial samples, purified by recrystallisation (hexamethylbenzene, pentamethylbenzene, 9,10-dimethylanthracene) or fractional distillation, until their physical properties coincided with literature values. The purity of liquid samples was confirmed by g.l.c. analysis. All solvents were fractionated before use. Perdeuteriohexamethylbenzene was prepared by exchange of 1,2,3,4,5,5-hexamethyl-6-methylenecyclohexa-1,3-diene[18] prepared using the procedure of Hart and Waring;[19] recrystallised from ethanol, it had m.p. 163 °C and contained $> 95\%$ deuterium.

Kinetics.—The procedures used were as previously described using initial carbenium-ion concentrations in the range $(2—4) \times 10^{-5}$M and the polymethyl aromatic compound in at least ten-fold excess to ensure a first-order law. For reactions between 9-phenylfluoren-9-yl cation and 9,10-dimethylanthracene, however, the rapid reaction rate necessitated the use of very low concentrations of the latter and the initial carbocation concentration was 3.67×10^{-6}M.

Acknowledgements

S.E.R.C. support for P. N. C. and G. J. H. and stimulating discussions with Professors K. Okamoto and K. Takeuchi are gratefully acknowledged.

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Received 6th *April* 1983; *Paper* 3/539