Kinetic Hydrogen Isotope Effects in Intermolecular Hydride Transfer from Arylalkanes to 9-Arylfluoren-9-yl Cations

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Rates of hydride-ion transfer to a series of 9-phenylfluoren-9-yl cations, substituted in the phenyl group, from triphenylmethane and 4,4'-dimethoxydiphenylmethane have been measured at 30 °C in trifluoroacetic acid solution containing 6% v/v acetic acid. Deuterium kinetic isotope effects have been measured directly and show evidence of a broad maximum, the peak value occurring when the difference in pK_{R^+} values between the product and reactant carbenium ions is around zero. Application of Marcus theory suggests that the intrinsic barrier to hydride transfer in these systems is substantially larger than for hydride transfer from formate ion to a series of triphenylmethyl cations. A limited series of measurements has also been made of tritium kinetic isotope effects on hydride transfer from 4,4'-dimethoxydiphenylmethane to 9-arylfluoren-9-yl cations and these have been used to derive deuterium–tritium isotope effects. The relevance of the results to the question of the origin of isotope-effect maxima is briefly discussed.

THE elementary reaction (1) in which hydrogen is transferred intermolecularly as a proton, a hydrogen atom, or as a hydride ion between the atoms or groups represented by A and B shows in general a kinetic hydrogen isotope effect. The magnitude of the effect is known to vary according to the chemical nature of A and B and experimentally it is found in solution that the kinetic deuterium isotope effect passes through a maximum value when the free energy change in the reaction is approximately zero.[1,2] Thus for example, if values of the kinetic deuterium isotope effect for the proton transfer (1) under defined conditions are plotted against ΔpK_a ($= pK_a^{BH} - pK_a^{AH}$), the maximum value is reached when $\Delta pK_a \approx 0$. Analogous maxima have been reported for hydrogen atom transfer,[3] the thermodynamic parameter in this case being the difference in bond dissociation energies of B–H and A–H, and for hydride transfer reactions between formic acid and a series of triarylmethyl cations of known pK_{R^+}.[4]

$$AH + B \longrightarrow [A \ldots H \ldots B] \longrightarrow A + HB \quad (1)$$

The origin of the experimentally observed maxima is a matter of some debate. For some time the view was held, following Westheimer,[5] that the magnitude of kinetic hydrogen isotope effects reflected the symmetry of the binding of the transferred hydrogen to the groups A and B in the transition state, equal strengths of binding minimising the zero-point energy difference between the protio- and deuterio-forms of the transition state and hence maximising the effect of the zero-point energy difference in the reactants. An alternative view supported by theoretical calculations was advanced by Bell *et al.*[6] and suggested that the variation in the kinetic isotope effect arises from variation in the correction necessary to allow for quantum mechanical tunnelling, an important contributor to the rate of protium transfer, but negligible for deuterium and tritium. However, Saunders[7] has demonstrated in one case at least that the tunnelling correction could not account for the maximum observed in k_H/k_D in the *E*2 reaction of 2-phenylethyltrimethylammonium bromide as the composition of the H_2O + DMSO solvent was varied.

The aim of the present investigation was two-fold, namely, to shed light on the intermolecular transfer of hydride ion from arylalkanes to a carbenium centre, specifically that of a series of 9-arylfluoren-9-yl cations, and also to attempt to differentiate between Westheimer's and Bell's interpretation of the maxima observed in kinetic hydrogen isotope effects. To this latter end, we have applied a simple test. Values of k_H/k_D and k_H/k_T have been measured and combined to yield k_D/k_T (for which the tunnel correction is negligible) for a series of carbenium ions of known pK_{R^+}.

RESULTS

Reaction Systems.—In all cases the carbenium ions used were 9-arylfluoren-9-yl cations, their intrinsic interest being the weak antiaromatic character associated with the dibenzocyclopentadienyl cationic moiety. The hydride donors were all arylalkanes and most of the work was conducted using triphenylmethane and 4,4'-dimethoxydiphenylmethane. Trifluoroacetic acid was the solvent used in most experiments, usually containing 6% (v/v) of acetic acid to facilitate dissolution and mixing of the reactants. The acidity of trifluoroacetic acid is such as to convert all the 9-arylfluoren-9-ols essentially completely to the corresponding carbenium ion. However, solutions of 9-phenylfluoren-9-yl cation so generated slowly decomposed, the rate accelerating as the proportion of acetic acid was increased and showing a second order dependence on 9-phenylfluoren-9-yl cation. The product of this process was a mixture containing several components with very similar chromatographic behaviour having the elemental composition of bis-9-phenylfluoren-9-yl ethers. The decomposition could be stopped by addition of sulphuric acid to trifluoroacetic acid but this tended to lead to oxidation of triphenylmethane and 4,4'-dimethoxydiphenylmethane, the hydride donors, although this was not rapid enough to interfere with the kinetics of hydride transfer. The substituted 9-phenylfluoren-9-yl cations showed no decomposition.

On a preparative scale hydride transfer from triphenylmethane or 4,4'-dimethoxydiphenylmethane to 9-arylfluoren-9-yl cations is fast and quantitative. For the kinetic studies however, it was necessary to work at much lower concentrations, the carbenium ion concentration being typically 3×10^{-5}M and the hydride donor in greater than ten-fold excess. Under these conditions the faster reacting solutions usually showed good isosbestic points in their visible spectra indicating quantitative conversion into 9-arylfluorene and product carbenium ions. This was especially true of the reactions using 4,4′-dimethoxydiphenylmethane as donor; oxidative processes, including photochemical oxidation[8] sometimes led to yields of triphenylmethyl cation from the donor triphenylmethane being higher than the initial concentration of fluorenyl cation used. Slower hydride transfers were less well behaved in the later stages, however and the yield of 9-arylfluorene determined by n.m.r. using a suitable standard fell sometimes to as low as 80% Subsequent experiments suggested that the competing reaction was between 9-arylfluoren-9-yl cation and the product 9-arylfluorene, since it was found that the rate of disappearance of 9-phenylfluoren-9-yl cation in trifluoracetic acid was enhanced by the addition of 9-phenylfluorene and gave rise to a product having the following spectroscopic data, *m/z* 482, 241, and 165; δ 6.8—8.0 (25 H m), and 4.9 (1H, s). This corresponds to an aromatic ring alkylated 9-phenylfluorene, $C_{38}H_{26}$, and, significantly, using 9-deuterio-9-phenylfluorene in place of the light hydrocarbon had no effect on the rate of disappearance of 9-phenylfluoren-9-yl cation.

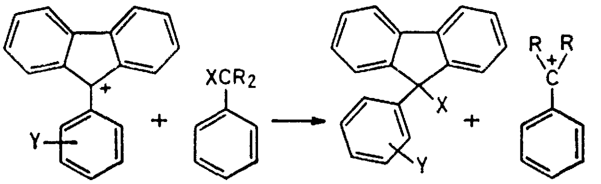
TABLE 1

Properties of carbenium ions in solution at 30 °C

Carbenium ion	Substituent(s)	$\lambda_{max.}$/nm [a]	$\epsilon_{max.}$/l mol^{-1} cm^{-1}	pK_{R^+} [b] This work	pK_{R^+} [b] Lit.	Ref.
9-Phenylfluorenyl		486	40 500	−10.69 ± 0.09	−10.8	11
	4′-Cl	502	33 900	−11.10 ± 0.12		
	4′-OMe	454	43 100	−7.48 ± 0.03	−7.64	11
		539	17.900			
	4′-Me	476	32 300	−9.44 ± 0.03	−9.43	11
		508	38 500			
	2′-Me	484	30 700	−10.68 ± 0.07		
	4′-Ph	445	9 100	−9.96 [c]		
		474	22 100			
		594	45 100			
	2′,6′-Me_2	463	11 300	−6.77 ± 0.10		
		492	29 000			
		568	5 900			
	2′,4′,6′-Me_3	460	10 100	−6.63 ± 0.5		
		486	25 600			
		613	9 900			
Triphenylmethyl		401	38 700	−6.54 ± 0.10	−6.44 [d]	12
		424	39 800			
	4′-OMe	397	19 700		−3.20 [d]	12
		474	63 600			
Diphenylmethyl	4,4′-$(OMe)_2$	501	137 000		−5.60 [d]	12

[a] In trifluoroacetic acid containing 6% v/v acetic acid. [b] In aqueous sulphuric acid. [c] Carbenium ion too unstable in aqueous sulphuric acid for experimental determination. pK_{R^+} determined by interpolation from a plot of pK_{R^+} for 4′-substituted 9-phenylfluorenyl cations against σ^+. [d] At 25 °C.

Thermodynamics.—For the reaction (2; X = OH), the free energy change is clearly simply proportional to the difference in pK_{R^+} between the reactant and product carbenium ions. For (2; X = H) the same should also be true assuming that no important steric influences change in replacing OH by H.



(2)

Values of pK_{R^+} were determined for all the 9-arylfluoren-9-ols used in the present investigation by standard spectrophotometric methods[9] over a range of aqueous sulphuric acid solutions of known H_R.[10,11] Results are given in Table 1 and compared with values from literature sources.

Kinetic Deuterium Isotope Effects.—These were all determined by direct spectrophotometric measurement of the rate of disappearance of the carbenium ion in the presence of a usually large excess of the donor either light or deuteriated. Second-order velocity constants for the hydride transfer were evaluated by least squares analysis of first-order rate coefficients determined over a two- to five-fold range of donor concentrations. Results from triphenylmethane as hydride donor are in Table 2, for 4,4′-dimethoxydiphenylmethane in Table 3, and for 9-(4-methoxyphenyl)fluorene in Table 4.

It should be noted that the isotope effect for 4,4′-dimethoxydiphenylmethane was determined using the diprotio- and dideuterio-compounds. Consequently the observed rate ratios contain not only the primary kinetic isotope effect but also a secondary α-deuterium isotope effect. This has to be eliminated if meaningful comparisons are to be made between the different donors. Our procedure involved the preparation of monodeuterio-4,4′-dimethoxydiphenylmethane and using it in conjunction with varying amounts of the dideuterio-compound as the hydride source, with subsequent n.m.r. analysis of the deuterium content of the product 9-arylfluorene. The symbolism is indicated in equations (3)—(5), where the superscript symbol outside the

$$Ar_2CH_2 + Ar'Fl^+ \xrightarrow{2(k_2H)^H} Ar_2CH^+ + Ar'FlH \quad (3)$$

$$Ar_2CD_2 + Ar'Fl^+ \xrightarrow{2(k_2D)^D} Ar_2CD^+ + Ar'FlD \quad (4)$$

$$Ar_2CHD + Ar'Fl^+ \begin{cases} \xrightarrow{(k_2H)^D} Ar_2CD^+ + Ar'FlH \\ \xrightarrow{(k_2D)^H} Ar_2CH^+ + Ar'FlD \end{cases} \quad (5)$$

parentheses indicates the non-transferred nucleus.

In an experiment using $Ar_2CHD + Ar_2CD_2$, the rates of

TABLE 2

Kinetics of hydride–deuteride transfer from triphenylmethane to 9-arylfluoren-9-yl cations in trifluoroacetic acid + 6% acetic acid at 30 °C

	Ph_3CH			Ph_3CD		
Substituent in 9-phenylfluoren-9-yl cation	n	r	$10^3k_2^H$/l mol^{-1} s^{-1}	n	r	$10^3k_2^D$/l mol^{-1} s^{-1}
	10	0.999	140 ± 2	8	0.996	41.2 ± 0.3
	5		(677 ± 48) [a]	5		(335 ± 17) [a]
4′-Me	10	0.990	22.8 ±0.6	8	0.999	6.12 ± 0.17
	2		(111) [a]			(67.4) [a]
4′-Ph	6	0.999	35.7 ± 1.2	10	0.994	7.41 ± 0.39
4′-OMe	8	0.988	1.14 ± 0.023	6	0.997	0.320 ± 0.004
4′-Cl	6	0.999	140 ± 4	8	0.992	44.3 ± 1.5

[a] 4-Methoxytriphenylmethane as donor.

TABLE 3

Kinetics of hydride–deuteride transfer from 4,4′-dimethoxydiphenylmethane to 9-arylfluoren-9-yl cations in trifluoroacetic acid + 6% acetic acid at 30 °C

	Ar_2CH_2			Ar_2CD_2		
Substituent in 9-phenylfluoren-9-yl cation	n	r	$10^3k_2^H$/l mol^{-1} s^{-1}	n	r	$10^3k_2^D$/l mol^{-1} s^{-1}
	6	0.997	59 800 ± 1 600	4	0.999	20 000 ± 350
4′-Me	10	0.999	9 950 ± 150	12	0.999	2 650 ± 60
4′-Ph	12	0.999	13 700 ± 200	8	0.999	3 640 ± 50
4′-OMe	6	0.999	255 ± 2	6	0.999	66.0 ± 0.1
2′-Me	6	0.999	7 110 ± 50	6	0.998	1 780 ± 40
2′,6′-Me_2	4	0.999	9.59 ± 0.07	4	0.999	2.17 ± 0.05
2′,4′,6′-Me_3	6	0.999	4.98 ± 0.04	4	0.999	1.13 ± 0.03

TABLE 4

Kinetics of hydride–deuteride transfer from 9-(4-methoxyphenyl)fluorene to 9-arylfluoren-9-yl cations in trifluoroacetic acid + 6% acetic acid at 30 °C

	AnFlH			AnFlD		
Substituent in 9-phenylfluoren-9-yl cation	n	r	k_2^H/l mol^{-1} s^{-1}	n	r	k_2^D/l mol^{-1} s^{-1}
	8	0.995	351 ± 11	4	0.998	83.6 ± 0.7
4′-Me	4	0.999	66.1 ± 1.4	4	0.999	18.3 ± 0.3
4′-Cl	4	0.999	1 140 ± 100	4	0.999	247 ± 7

production of protio- and deuterio-9-arylfluorene are given by (6) and (7) respectively. Using a large excess of donor over carbenium ion, the differential equation obtained by

$$\mathrm{d}[\mathrm{Ar'FlH}]/\mathrm{d}t = (k_2^{\mathrm{H}})^{\mathrm{D}}[\mathrm{Ar_2CHD}][\mathrm{Ar'Fl^+}] \qquad (6)$$

$$\mathrm{d}[\mathrm{Ar'FlD}]/\mathrm{d}t = \{2(k_2^{\mathrm{D}})^{\mathrm{D}}[\mathrm{Ar_2CD_2}] + (k_2^{\mathrm{D}})^{\mathrm{H}}[\mathrm{Ar_2CHD}]\}[\mathrm{Ar'Fl^+}] \qquad (7)$$

$$\frac{[\mathrm{Ar'FlD}]}{[\mathrm{Ar'FlH}]} = \frac{2(k_2^{\mathrm{D}})^{\mathrm{D}}[\mathrm{Ar_2CD_2}]}{(k_2^{\mathrm{H}})^{\mathrm{D}}[\mathrm{Ar_2CHD}]} + \frac{(k_2^{\mathrm{D}})^{\mathrm{H}}}{(k_2^{\mathrm{H}})^{\mathrm{D}}} \qquad (8)$$

dividing (6) by (7) may be integrated giving (8) which expresses the product ratio when reaction is complete. The results in Table 5 which refer to the 9-phenylfluorenyl cation permit an approximate value to be determined for $(k_2^H)^D/(k_2^D)^D$ of 3.24. The kinetically derived isotope effect, 3.69, is $(k_2^H)^H/(k_2^D)^D$ so that the secondary isotope effect, $(k_2^H)^H/(k_2^H)^D$, is obtained by division as 3.69/3.24 = 1.14. A less accurate estimate relating to deuteride transfer is obtained by dividing the slope and intercept giving $(k_2^D)^H/(k_2^D)^D$ = 3.24/2.97 = 1.09, but the agreement is as good as can be expected.

TABLE 5

Deuterium content of 9-phenylfluorene obtained by reaction of 9-phenylfluoren-9-yl cation (3×10^{-5}M) with mixtures of mono- and dideuterio-4,4′-dimethoxydiphenylmethane in trifluoroacetic acid + 6% acetic acid at 30 °C

$[An_2CD_2]/[An_2CHD]$	[PhFlD]/[PhFlH]
0.026	0.339
0.102	0.386
0.152	0.460

Since the secondary isotope effect is dependent upon the degree of hybridisation change in the transition state, the value appropriate to each carbenium ion–hydride donor pair should vary. The variation is, however, likely to be small and probably less than the uncertainty in our method of determination. Accordingly we have used the value 1.14 throughout. It may be noted that Streitwieser *et al.*[13] determined the α-deuterium isotope effect on the rate of solvolysis of diphenylmethyl chloride in 70% aqueous acetone at 25 °C. Their value of 1.12 is remarkably similar to the indirectly determined value above.

Tritium Isotope Effects.—These were obtained competitively by allowing the 9-arylfluoren-9-yl cation to react with a large (*ca.* 100-fold) excess of donor and isolating the product 9-arylfluorene using a dilution method to facilitate separation of the product from the excess of donor. In early experiments, reactions were allowed to proceed to completion, but this led to extremely large apparent isotope effects which could not be related to the corresponding deuterium isotope effects through the Swain–Schaad equation,[14] even approximately. It was established that the tritiated product was stable in trifluoracetic acid as were the tritiated donors, all of them being recovered with unchanged specific activities. Moreover, oxidation of the donors confirmed that essentially 100% of the tritium present was available for transfer.

The source of the problem appears to be the occurrence during the late stages of reaction of the attack by the reactant carbenium ion on the product hydrocarbon. As a result, even though the side reaction shows no kinetic isotope effect, tritiated product is converted into an alkylated form which is not then isolated in the dilution procedure. The difficulty was overcome therefore by quenching reaction mixtures after *ca.* 20% decomposition of the carbenium ion (accurately determined for the purposes of isotopic dilution). It was separately established that the isotope effect determined in this way was essentially invariant between 15 and 30% reaction, although the method leads to isotope effects subject to a substantial uncertainty (see Table 6).

TABLE 6

Tritium kinetic isotope effects in reaction of 4,4′-dimethoxydiphenylmethane with 9-arylfluoren-9-yl cations in trifluoroacetic acid + 6% acetic acid at 30 °C

Substituent in 9-phenylfluoren-9-yl cation	$\frac{(k_2{}^H)^H}{(k_2{}^T)^H}$ Observed	$\frac{(k_2{}^H)^H}{(k_2{}^T)^H}$ Calculated[a]
	4.29 ± 0.33[b]	4.02 ± 0.21
4′-Me	5.36 ± 0.41	5.58 ± 0.25
4′-OMe	5.58 ± 0.43	5.81 ± 0.08
2′-Me	6.14 ± 0.47	6.10 ± 0.23

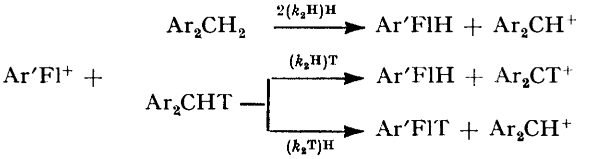
[a] From the observed values of $(k_2{}^H)^H/(k_2{}^D)^H$ using the Swain–Schaad relation. [b] Estimated 95% confidence limits.

The short reaction-time method was restricted to experiments using 4,4′-dimethoxydiphenylmethane as the donor. Again consideration has to be given to statistical and secondary isotope effects. The competitive method can be represented by equation (9) The production of labelled and unlabelled product is then given by (10). If we neglect the contribution to Ar′FlH arising from the reaction with

$$\frac{d[Ar'FlH]}{d[Ar'FlT]} = \frac{2(k_2{}^H)^H[Ar_2CH_2] + (k_2{}^H)^T[Ar_2CHT]}{(k_2{}^T)^H[Ar_2CHT]} \quad (10)$$

tritiated donor which will be small compared with that coming from reaction of the unlabelled donor, then for a large and constant excess of donor, (11) results, showing that the apparent isotope effect is twice the true primary isotope effect with no complication from secondary effects. The results are in Table 6.

$$\frac{[Ar_2CHT][Ar'FlH]}{[Ar_2CH_2][Ar'FlT]} = \frac{2(k_2{}^H)^H}{(k_2{}^T)^H} = \frac{\text{Specific activity of donor}}{\text{Specific activity of product}} \quad (11)$$



$$Ar'Fl^+ + \begin{cases} Ar_2CH_2 \xrightarrow{2(k_2H)H} Ar'FlH + Ar_2CH^+ \\ Ar_2CHT \begin{cases} \xrightarrow{(k_2H)T} Ar'FlH + Ar_2CT^+ \\ \xrightarrow[(k_2T)H]{} Ar'FlT + Ar_2CH^+ \end{cases} \end{cases} \quad (9)$$

DISCUSSION

It will be assumed throughout that the hydride transfers examined are elementary, bimolecular processes.[15] Although this assumption cannot be proved, all our kinetic evidence is consistent with it. Moreover, the mass balance is in general good and the side reactions observed appear to involve the hydride-transfer product. They are not consistent with partitioning of an intermediate on the hydride-transfer pathway. In particular there is no evidence that would suggest the participation of radical intermediates.

Substituent Effects on the Rate of Reaction.—The general pattern of results in Tables 2—4 is that electron-releasing 4′-substituents in the 9-arylfluorenyl cation retard the reaction while electron release by substituents in the hydride donor accelerate reaction. Rates correlate with σ^+ substituent constants, the parameters of linear regression being in Table 7(a) for the various reaction series, both protio- and deuterio-donors being included. Table 7(b) has corresponding regression parameters from so-called Dauben plots[16] of log *k versus* ΔpK_{R^+}, the difference in pK_{R^+} between the product and reactant carbenium ion. Again, in general, the rate of hydride transfer increases with increasing ΔpK_{R^+}, implying progression to earlier and more reactant-like transition states. In these correlations, *ortho*-substituents have been excluded. Points for reactions in which such substituents are present can readily be included in the Dauben plot for reactions using 4,4′-dimethoxydiphenylmethane as donor, and all three show negative deviations from the regression line indicating that the rate is slower by about an order of magnitude than would be expected on the basis of ΔpK_{R^+}. There appears to be no significant difference in the retardation between the reactant carbenium ion with a single *o*-methyl substituent and those with two.

The reactivity of the hydride donors on the other hand

TABLE 7

Linear regression parameters for Hammett and Dauben plots of kinetic data on hydride and deuteride transfer to substituted 9-phenylfluoren-9-yl cations

	H⁻ Transfer[a]				D⁻ Transfer[a]			
Donor	ρ_H	log $k_H{}^0$	*n*	*r*	ρ_D	log $k_D{}^0$	*n*	*r*
(a) Hammett plots								
Ph_3CH	2.44	−0.98	5	0.991	2.47	−1.55	5	0.989
$4\text{-}MeOC_6H_4FlH$	2.79	2.65	3	0.989	2.74	2.04	3	0.978
$(4\text{-}MeOC_6H_4)_2CH_2$	3.02	1.79	5	0.996	3.17	1.27	5	0.985
(b) Dauben plots								
Ph_3CH	0.67	−3.60	4	0.998	0.66	−4.17	4	0.993
$4\text{-}MeOC_6H_4FlH$	0.70	0.41	3	0.983	0.66	−0.07	3	0.978
$(4\text{-}MeOC_6H_4)_2CH_2$	0.74	−1.97	5	0.997	0.78	−2.67	5	0.997

[a] Symbols: ρ = slope, log k^0 = value at σ^+ or $\Delta\ pK_{R^+} = 0$, *n* = number of points, *r* = correlation coefficient.

TABLE 8

Kinetic deuterium-isotope effects (k_H/k_D) on hydride transfer to X-substituted 9-phenylfluorenyl cations

Donor	Ph_3CH		An_2CH_2[b]		FlAnH[b]	
X	k_H/k_D	ΔpK_{R^+}	k_H/k_D	ΔpK_{R^+}	k_H/k_D	ΔpK_{R^+}
H	3.40 ± 0.05 (2.02 ± 0.18)[a]	4.15 (7.49)[a]	2.99 ± 0.10	5.09	4.20 ± 0.14	3.21
4-Cl	3.16 ± 0.14	4.56			4.62 ± 0.43	3.62
4-Ph	4.82 ± 0.20	3.42	3.76 ± 0.08	4.36		
4-OMe	3.56 ± 0.09	0.94	3.86 ± 0.03	1.88		
4-Me	3.73 ± 0.14 (1.65)[a]	2.90 (6.24)[a]	3.76 ± 0.10	3.84	3.61 ± 0.10	1.96
2-Me			3.99 ± 0.09	5.08		
2,6-Me_2			4.42 ± 0.11	1.17		
2,3,4-Me_3			4.41 ± 0.12	1.03		

[a] Donor: 4-methoxytriphenylmethane. [b] An = 4-Methoxyphenyl.

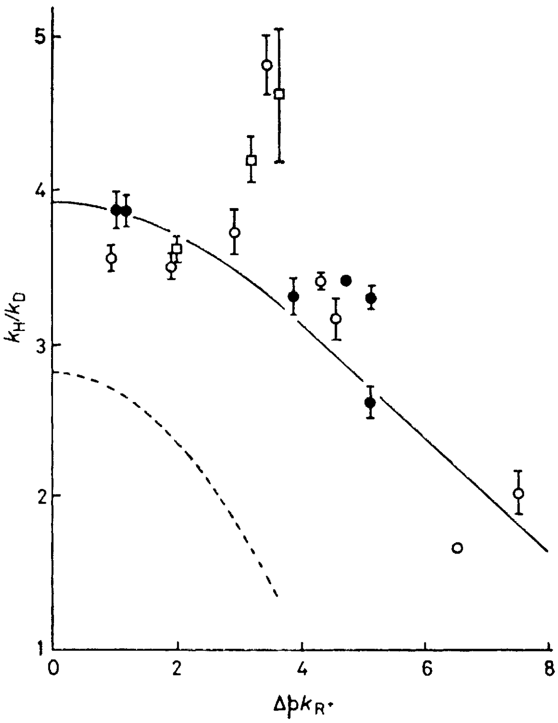
presents a more complex pattern. The sequence of decreasing reactivity is 4,4′-dimethoxydiphenylmethane > 4-methoxytriphenylmethane > 9-(4-methoxyphenyl)-fluorene > triphenylmethane, which bears no simple relationship to, for example, the sequence of pK_{R^+} values of the corresponding carbenium ions. A combination of electronic and steric effects would appear to be necessary to account for the observations.

Kinetic Deuterium-isotope Effects.—Values of the kinetic deuterium-isotope effect for all the systems studied are in Table 8. It is immediately apparent that the values are quite low and well below the maximum predicted on the simple basis of the zero-point vibrational energy difference of the reactant hydride donor and its deuterio-analogue. In general, k_H/k_D increases as ΔpK_{R^+} decreases, but it may be noted that the reverse trend is found for the three reactions in which 9-(4-methoxyphenyl)fluorene was the donor. The relationship between k_H/k_D and ΔpK_{R^+} is displayed in the Figure. For purposes of direct comparison, points for 4,4′-dimethoxydiphenylmethane as donor have been corrected for the secondary isotope effect of the non-transferred deuterium. Neglecting three of the values, referring to hydride transfer between 9-(4-methoxyphenyl)fluorene and 9-phenylfluorenyl cation and its 4′-chloro-analogue and between triphenylmethane and 9-(4-phenylphenyl)fluorenyl cation (for the high values of which we can offer no explanation), the points trace a roughly parabolic curve reaching a maximum value of k_H/k_D of *ca.* 4 when ΔpK_{R^+} is around zero. The results do not permit a more precise estimate of the position of the maximum to be made, but the fact that equilibrium isotope effects are generally close to unity [17] suggests that the full curve of k_H/k_D *versus* ΔpK_{R^+} should be symmetrical about the ordinate through ΔpK_{R^+} 0. It is recognised that the evidence for a maximum in k_H/k_D would be stronger had values been obtained for negative ΔpK_{R^+}, but for experimental reasons this was not possible.

The present results thus fall into a pattern very similar to that described by Stewart and Toone [4] for the transfer of hydride ion from formate anion to triphenylmethyl cations, the first observation of an isotope-effect maximum is hydride transfer. However, the maximum in the present case appears to be much broader than that previously reported and indicated by the broken line in the Figure. Such differences can be understood in terms of Marcus theory,[2,18] according to which the isotope effect is given by equation (12). Here ΔG^o is the free energy change for the reaction and $\Delta G_o^\ddagger$ is the geometric mean of the so-called intrinsic barriers to hydride and deuteride transfer, representing that part of the total free energy

$$\ln\frac{k_H}{k_D} = \ln\left(\frac{k_H}{k_D}\right)_{\text{max.}}\left[1-\left(\frac{\Delta G^o}{4\Delta G_o^\ddagger}\right)^2\right] \qquad (12)$$

barrier remaining when the reactants have been brought together in the reaction complex in which they have the correct geometry for reaction to take place. Least squares analysis of Stewart and Toone's results yields an intrinsic barrier $\Delta G_o^\ddagger$ of 2.5 kcal mol^{-1} while the results in the Figure yield a value of 3.5 kcal mol^{-1}. Hydride transfer between di- or tri-arylmethanes and 9-aryl-



Dependence of kinetic hydrogen-isotope effect (k_H/k_D) on ΔpK_{R^+} for intermolecular hydride transfer to 9-arylfluoren-9-yl cations. Hydride donors: ○ triarylmethane; ● 4,4′-dimethoxydiphenylmethane; ☐ 9-(4-methoxyphenyl)fluorene. The full curve is that calculated according to equation (12) with $(k_H/k_D)_{\text{max.}}$ 3.91 and $\Delta G_o^\ddagger$ 3.5 kcal mol^{-1}. The broken curve refers to hydride transfer from formate ion to triarylmethyl cations and is adapted from the work of Stewart and Toone [4] fluorenyl cations is thus an intrinsically slower process than between formate ion and triarylmethyl cations. It is not clear whether this is to be attributed to the electrostatic differences between the two reaction series, to the greater steric compressions likely to be generated in the present reaction series, or to some other cause.

Tritium Isotope Effects.—It may be noted from the results in Table 5 that the pattern of tritium kinetic isotope effects is much the same as for deuteride transfer. Thus k_H/k_T increases as ΔpK_{R^+} decreases except for the reaction of 4,4′-dimethoxydiphenylmethane with 9-(2-methylphenyl)fluorenyl cation where steric compressions in the transition state may be particularly high. Significantly the observed values are in good agreement with those derived from the observed deuterium isotope effects by application of the Swain–Schaad relation when allowance is made for the secondary deuterium isotope effect and for the combined uncertainties.

Deuterium–Tritium Isotope Effects and the Origin of Isotope-effect Maxima.—It was our intention at the outset of the investigation to determine the values of k_D/k_T for a series of reactants having a wide variation in ΔpK_{R^+} in the hope that this would shed light on the question of whether isotope-effect (k_H/k_D) maxima arise from variation in the correction for quantum mechanical tunnelling or simply from transition-state symmetry and its effect on the transition-state zero-point energy difference in hydride and deuteride transfer. Since the tunnelling corrections for D and T are very small compared to that for H, k_D/k_T should be invariant with change in ΔpK_{R^+} if tunnelling is responsible for the variation in k_H/k_D. Otherwise, k_D/k_T should vary in the same way as k_H/k_D although the effect should be muted by the greater masses of deuterium and tritium.[1,14]

The relevant results are in Table 9 for hydride transfer from 4,4′-dimethoxydiphenylmethane and its isotopically substituted analogues to four arylfluorenyl cations. The small variation in k_H/k_D means that high precision is necessary if a distinction is to be made between the two explanations. In fact the observed values of k_Dk_T are almost invariant within the probable error of the determinations, but the uncertainties embrace the whole of the variation predicted by simple application of the Swain–Schaad relation to the observed values of k_H/k_D. The invariance of k_D/k_T cannot therefore be taken as evidence that quantum mechanical tunnelling is responsible for the changes in k_H/k_D. Two other aspects of the results in Table 10 may be noted. First, the value of k_D/k_T calculated from the observed k_H/k_D for hydride transfer to 9-phenylfluorenyl cation is less than the observed value (although just within the combined probable errors); if tunnelling were occurring in hydrogen-transfer the reverse would have been expected. Tunnelling, if responsible for the high values of k_H/k_D and k_H/k_T in the sterically hindered reaction involving hydride transfer to the 9-(2-methylphenyl)fluorenyl cation, should be eliminated in k_D/k_T, yet the value is the highest of the four that have been measured.

TABLE 9

Values of k_D/k_T observed and calculated for hydride transfer from 4,4′-dimethoxydiphenylmethane to substituted 9-phenylfluorenyl cations

Substituent	$(k_H/k_D)_{obs.}$[a,b]	$(k_D/k_T)_{obs.}$[a]	$(k_D/k_T)_{calc.}$[a,c]
	2.62 ± 0.10	1.64 ± 0.09	1.53 ± 0.03
4-Me	3.29 ± 0.10	1.63 ± 0.08	1.69 ± 0.02
4-OMe	3.39 ± 0.03	1.65 ± 0.07	1.72 ± 0.01
2-Me	3.50 ± 0.09	1.75 ± 0.08	1.74 ± 0.02

[a] Uncertainties are probable errors. [b] Corrected for secondary isotope effects. [c] Calculated from the values in column 1 using the Swain–Schaad relation.

It is to be concluded that for these systems, the measurements of k_D/k_T do not permit identification of the origin of the isotope-effect variation, thus bearing out predictions based on previous experiments on other reactions[19a] and on theory.[19b] It remains to be seen whether, in systems where much larger variations of k_H/k_D are found as substituents and ΔpK change, a high enough precision of measurements can be achieved to distinguish tunnelling (k_H/k_T = constant) from transition-state zero-point energy differences (k_D/k_T shows an upward trend as ΔpK tends to zero).

EXPERIMENTAL

Materials.—Triphenylmethane was a commercial sample purified by sublimation and recrystallisation from ethanol, m.p. 93 °C. α-Deuteriotriphenylmethane was obtained by reduction of triphenylmethyl chloride using lithium aluminium deuteride–aluminium chloride in ether,[20] m.p. 93 °C; ^1H n.m.r. spectroscopy showed the product to be >99% deuteriated at the α-position. Tritiated triphenylmethane was obtained by decomposition of the Grignard reagent from triphenylmethyl bromide using tritiated water, the

TABLE 10

M.p.s of substituted 9-phenylfluorenols and 9-phenylfluorenes

Substituent(s) in phenyl group	Fluorenol			Fluorene		
	M.p. (°C)	Lit. m.p. (°C)	Ref.	M.p. (°C)	Lit. m.p. (°C)	Ref.
	110	108	21	148	149	26
4-CH_3	86.5—87 [a]	83	22	128—129	128	27
4-OCH_3	87—88	87—88	23	122	122—123	28
4-C_6H_5	140—141	141—142	24	224—225	225	26
2-CH_3	122—123	121—123	24	89—90 [d]	129—130	29
2-OCH_3	123—125 [b]	110	24			
2,6-$(CH_3)_2$	98—98.5 [c]	90—93	25			
2,4,6-$(CH_3)_3$	113—114	111—112	25			

[a] Found: C, 88.4; H, 6.1. $C_{20}H_{16}O$ requires C, 88.2; H, 5.9%. [b] Found: C, 83.4; H, 5.7. $C_{20}H_{16}O_2$ requires C, 83.3; H, 5.6%. [c] Found: C, 88.3; H, 6.6. $C_{21}H_{18}O$ requires C, 88.1; H, 6.3%. [d] Found: C, 93.8; H, 6.2. $C_{20}H_{16}$ requires C, 93.7; H, 6.3%.

product being recrystallised from ethanol to constant activity. Oxidation to triphenylmethanol showed that $>99.7\%$ of the activity was associated with the α-position.

4-Methoxytriphenylmethane was prepared by treating a solution of diphenylmethanol in an excess of nitromethane–anisole (1 : 1 v/v) with a catalytic amount of 72% perchloric acid and heating at 100 °C for 3 h. Nitromethane and acid were washed out and the excess of anisole steam-distilled. Distillation of the residue gave a fraction, b.p. 200—208 °C at 3 mmHg, which solidified, giving, after recrystallisation from petroleum, needles, m.p. 65 °C. The α-deuterio-analogue was prepared similarly from α-deuteriodiphenylmethanol obtained by sodium borodeuteride reduction of benzophenone. The product was $>95\%$ α-deuteriated.

4,4′-Dimethoxydiphenylmethane was prepared by refluxing 4-methoxybenzyl alcohol in anisole containing a catalytic amount of toluene-*p*-sulphonic acid using a Dean and Stark apparatus, m.p. 50 °C. The αα-dideuterio-analogue was prepared similarly from αα-dideuterio-4-methoxybenzyl alcohol obtained by lithium aluminium deuteride reduction of methyl 4-methoxybenzoate; ^{1}H n.m.r. spectroscopy showed $>99\%$ α-deuteriation. α-Deuterio-4,4′-dimethoxydiphenylmethane was prepared by lithium aluminium deuteride reduction of the diarylmethanol in dry ether and found spectroscopically to be $> 99\%$ monodeuteriated. The α-tritiated compound was obtained in the following way. 4-Methoxytoluene was tritiated in the C-methyl group by decomposing the Grignard reagent from 4-methoxybenzyl chloride with tritiated water. After separation from 4,4′-dimethoxybiphenyl, the product was distilled and treated with lead tetra-acetate in acetic acid at 80 °C for 3 h. Removal of the acetic acid and extraction into ether gave, after column chromatography on silica, tritiated 4-methoxybenzyl alcohol which was converted into 4,4′-dimethoxydiphenylmethane as indicated above. Oxidation with potassium dichromate in acetic acid showed that $>99.9\%$ of the activity was associated with the α-position.

9-Arylfluoren-9-ols were all prepared by reaction of fluorenone with the appropriate arylmagnesium bromide. Reduction with lithium aluminium hydride–aluminium chloride gave the corresponding 9-arylfluorenes. M.p.s are in Table 10, together with microanalytical data where appropriate.

Trifluoracetic acid was distilled from sulphuric acid through a 1 m helix-packed column immediately before use, b.p. 72 °C. Acetic acid was analytical reagent grade and was also fractionated before use.

Carbenium Ions.—Table 1 gives the principal absorption maxima of the 9-arylfluoren-9-yl cations generated from the corresponding alcohols in trifluoracetic acid containing 6% v/v acetic acid.

Values of pK_{R^+} were determined in aqueous sulphuric acid (containing 3% acetic acid) using the equation $pK_{R^+} = H_R + \log Q$ where H_R is the known value of the acidity function for the acid solution and Q is the spectrophotometrically determined ionisation ratio $[R^+]/[ROH]$. Several determinations, typically four, were made at different acidities and the average values are given in Table 1.

Kinetics.—Reactions were followed spectrophotometrically in the visible region either by repetitive scanning of the absorption peaks of the reactant and product carbenium ions or at fixed wavelength usually that of maximum absorption of the 9-arylfluorenyl cation. Reactions were almost always carried out in the presence of a large excess of hydride-ion donor under which conditions the reactions showed clean first-order kinetic behaviour for three or more half-lives. All reactions were carried out in duplicate, agreement of rate coefficients being within 2%.

Measurement of Tritium Kinetic Isotope Effects.—Reactions in which 9-arylfluorenyl cations reacted with tritiated hydride donors were carried out at concentrations close to those used in the direct kinetic determination of the deuterium kinetic isotope effect. This involved the use of rather large volumes of solvent (typically 300 ml). After an appropriate reaction time which could be accurately monitored spectrophotometrically, the reaction mixture was quenched with water and a known amount of inactive product 9-arylfluorene was added. The amount added was usually about ten times that of tritiated hydride donor originally present. The 9-arylfluorene was then isolated and recrystallised to constant activity. It was established by control experiments that (i) the hydride donor does not exchange its tritium label under the reaction conditions, and (ii) that there is no loss of tritium from the 9-arylfluorenes during the work-up.

Deuterium Analyses.—For the experimental determination of the secondary deuterium isotope effect on hydride transfer from 4,4′-dimethoxydiphenylmethane it was necessary accurately to determine the deuterium content of mixtures of Ar_2CH_2 and Ar_2CHD and of the product 9-arylfluorene ArFlH and ArFlD. In each case solutions of known concentration of the deuteriated compound were prepared containing small accurately known quantities of a standard compound, triphenylmethane. Comparison of peak areas (averages of ten-fold integration) in the ^{1}H n.m.r. spectrum obtained on a Perkin-Elmer R34 spectrometer (220 MHz) then yielded the protium content of the deuterated compound.

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