

Reactivities of 9-Arylfluoren-9-yl and 1-(4-Dimethylaminophenyl)ethyl Cations in Water and Trifluoroethanol Studied by Laser Flash Photolysis

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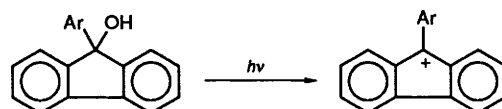
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9-Arylfluoren-9-yl cations have been observed as transient intermediates upon 248 nm laser photolysis of 9-arylfluoren-9-ols in 2,2,2-trifluoroethanol (TFE) and 1:4 (v/v) acetonitrile–water. Quantum yields for the formation of the cations were measured and found to lie in the range 0.5–0.8. Rate constants for the decay of the cations in the two solvents parallel each other, a plot of $\log k_{\text{TFE}}$ versus $\log k_{\text{w}}$ being linear with a slope of 1.00. These rate constants are approximately two orders of magnitude larger than those observed in the same solvent for the corresponding monosubstituted triarylmethyl cations. Substituent effects in the two series are similar. For both the hydration reaction and the overall equilibrium, a two-parameter treatment dissecting the substituent contributions into resonance and polar effects shows that the former are more important in the triarylmethyl series, while the latter are more important in the fluorenyl series. Twisting of the 9-aryl ring out of coplanarity with the fluorenyl ring is the likely cause of the diminished resonance interaction in this system. The 1-(4-dimethylaminophenyl)ethyl cation has been observed in TFE and 1:1 TFE–W, being generated by photoprotonation of 4-dimethylaminostyrene. Rate constants for decay are about 50 times smaller than those previously estimated by a clock method. The failure of the latter approach is associated with the rate constant for the clock nucleophile becoming significantly less than diffusion control for this highly stable cation. An extended $\log k_{\text{w}}-pK_{\text{R}}$ correlation is constructed. This shows a series of reasonably parallel lines associated with different families. In considering cations with the same pK_{R} , the order of inherent reactivity is 9-unsubstituted-9-xanthylium \sim cyclic dialkoxy-carbocation $>$ phenyltropylium $>$ diarylmethyl \sim 9-arylxanthylium $>$ triarylmethyl \sim 9-arylfluoren-9-yl. The $\log k_{\text{w}}-pK_{\text{R}}$ data for each family are reasonably satisfied by a linear relationship, with a slope $d(\log k_{\text{w}})/dpK_{\text{R}}$ of 0.6 ± 0.1 . The triarylmethyl and 9-arylfluoren-9-yl cations form a contiguous series covering 26 pK_{R} units. The data for these indicate that there is probably a gentle downward curvature in the correlation, particularly at the high reactivity end. This is consistent with a Hammond effect on the transition state such that it becomes more cation-like in the hydration direction for more reactive cations.

We have reported the use of laser flash photolysis to investigate triarylmethyl,^{1–4} diarylmethyl,^{3–5} and xanthylium⁶ cations in aqueous acetonitrile and 2,2,2-trifluoroethanol (TFE) solutions. This technique not only detects the transient cation as an intermediate in the appropriate photochemical reaction employed, but also it provides a direct measure of rate constants for the decay of the cation in the solvent and for its reactions with added nucleophiles. Previously, highly stabilized examples of carbocations had been subjected to such direct measurements,^{7,8} but only selectivity data (relative rate constants) had been obtained for less stable derivatives. Rate constant ratios have been converted into absolute reactivities through the assumption that one of the nucleophiles combines with the cation at the diffusion limit.^{9–12} This assumption has been validated by flash photolysis for the case of azide as the ‘clock’ nucleophile.³

As part of our continuing study of benzylic-type cations, we consider in this paper the reactivities of a series of 9-arylfluoren-9-yl cations, these ions being generated photochemically from the corresponding alcohol precursors.

The fluoren-9-ol system has proved to have some unusual photochemical features. As demonstrated initially by Wan and co-workers, the parent fluoren-9-ol^{13,14} and the 9-methyl¹⁴ and 9-phenyl derivatives¹⁴ undergo a relatively efficient photo-substitution in aqueous methanol resulting in the production of the corresponding 9-methoxyfluorene. A mechanism has been proposed involving C–OH heterolysis of the excited singlet alcohol leading to an intermediate fluoren-9-yl cation. Alcohols



such as diphenylmethanol do not undergo this photoreaction, or do so considerably less efficiently.¹⁴ This has led to the suggestion that the efficient cation formation in the fluorenyl case is associated with an enhanced reactivity of excited states leading to systems with internal cyclic arrays containing $4n \pi$ systems.^{13–15}

Ground state fluoren-9-yl cations are however destabilized. This can be seen in kinetic data for solvolysis reactions, those involving fluoren-9-yl cations as intermediates proceeding several orders of magnitude more slowly than those of analogues that do not contain the $4n \pi$ system.^{16–18} Differences in stability are also evident in comparisons involving pK_{R} data, values for triphenylmethyl, $pK_{\text{R}} = -6.6$,^{19,20} and diphenylmethyl, -13.3 ,¹⁹ each being 4 log units more positive than those of fluorenyl analogues, 9-phenylfluoren-9-yl, -10.8 ,²¹ and fluoren-9-yl itself, -17.3 .²² The latter cation cannot in fact be observed in concentrated acid,²³ and the pK_{R} value is estimated from electrochemical data. The parent fluoren-9-yl cation, moreover, is extremely short-lived in aqueous solution, decaying within the laser pulse (lifetime < 25 ps) when generated from the alcohol in a picosecond flash photolysis apparatus.²⁴ This lifetime is increased to 30 μs in the relatively

Table 1 9-Arylfluoren-9-yl cations. λ_{\max} values for transient in TFE and stable cation in 96% H_2SO_4 , quantum yield for formation of cation in TFE, and rate constants ($20 \pm 1^\circ\text{C}$) for the decay in TFE and 1:4 acetonitrile–water, and for the reaction with bromide ion in TFE

Subst.	$\lambda_{\max}/\text{nm}^a$	$k_{\text{TFE}}/\text{s}^{-1}{}^b$	$k_{\text{Br}}/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}{}^c$	$k_w/\text{s}^{-1}{}^d$	ϕ_{TFE}^e
4-MeOC ₆ H ₄	540 450sh 365 (TFE) 545 460sh 360 (H ₂ SO ₄)	1.8×10^2	1.2×10^8	1.7×10^5	0.5
3-MeOC ₆ H ₄	600 480 450sh 370 (TFE) 620 495 460sh 360 (H ₂ SO ₄)	1.6×10^4	4.7×10^8	1.6×10^7	0.8
4-MeC ₆ H ₄	500 470sh 365 (TFE) 515 490sh 370 (H ₂ SO ₄)	4.1×10^3	1.5×10^8	4.4×10^6	0.6
3-MeC ₆ H ₄	480 450sh 360 (TFE) 485 460sh 370 (H ₂ SO ₄)	9.5×10^3	3.4×10^8	1.1×10^7	0.6
C ₆ H ₅	490 355 (TFE) 490 460sh 355 (H ₂ SO ₄)	1.5×10^4	6.8×10^8	1.5×10^7	0.6
4-ClC ₆ H ₄	500 370 (TFE) 505 375 (H ₂ SO ₄)	1.6×10^4	1.0×10^9	1.8×10^7	0.6
3-ClC ₆ H ₄	490 460sh 375 (TFE) 500 465sh 380 (H ₂ SO ₄)	4.2×10^4	1.0×10^9	3.6×10^7	0.5
4-CF ₃ C ₆ H ₄	500 450 375 (TFE) 508 453 380 (H ₂ SO ₄)	1.0×10^5	1.8×10^9	$>5 \times 10^7$	0.5
3-CF ₃ C ₆ H ₄	500 450 380 (TFE) 505 455 380 (H ₂ SO ₄)	8.2×10^4	1.7×10^9	$\sim 5 \times 10^7$	0.5

^a At $\lambda > 300$ nm. There is a band near 260 nm, but this is partly obscured in the flash photolysis experiments by the absorbance of the precursor in this region. ^b First-order rate constant for the decay in TFE. ^c Second-order rate constant for the reaction with bromide in TFE, bromide present as its tetrabutylammonium salt. ^d First-order rate constant for decay in 1:4 acetonitrile–water. ^e Quantum yield for the formation of cation in TFE for 248 nm irradiation.

non-nucleophilic solvent 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP).²⁵ The diphenylmethyl cation, in contrast, is 2–4 orders of magnitude kinetically more stable, with lifetimes of 750 ps in 1:1 water–acetonitrile²⁶ and *ca.* 0.1 s in HFIP.²⁷

One of the objectives of the present study was to probe how the reactivity of the fluoren-9-yl cation is attenuated by the introduction of aryl groups at the 9-position. The 9-arylfluoren-9-yl cations in fact prove to be sufficiently stable to be studied by nanosecond flash photolysis in aqueous solutions. The availability of $\text{p}K_{\text{R}}$ data^{21,28} for some of these cations also means that additional data points can be placed at the high reactivity end of a $\log k_w - \text{p}K_{\text{R}}$ rate–equilibrium correlation for carbenium ion–carbinol equilibration.^{2,8,29,30} As part of the consideration of this relation we also report a direct measurement of the rate constant for the decay of the 1-(4-dimethylaminophenyl)ethyl cation. Phenethyl cations of this type have been investigated previously by the clock method, but there were concerns that the assumption of diffusion control in the clock nucleophile is not valid in the case of the highly stabilized dimethylamino derivative.

Results

9-Arylfluoren-9-yl Cations.—Flash photolysis experiments were carried out with 248 nm irradiation of 0.1–0.5 mmol dm^{-3} solutions of 9-arylfluoren-9-ols in TFE or 4:1 water–acetonitrile. Transient absorption spectra for six derivatives are shown in Fig. 1. Strong signals are observed, with maxima at several wavelengths. These absorptions represent in each case essentially a single transient, in that the rate constants for decay are identical across the entire spectrum. This decay is exponential, and bromide, added in concentrations of 0.1–3 mmol dm^{-3} as the tetrabutylammonium salt, increases the rate constant with a linear dependence in $[\text{Bu}_4\text{NBr}]$. Oxygen on the other hand has no effect, either on the decay rate or on the shape of the

absorption bands. These observations of quenching by nucleophiles with no effect of oxygen are consistent with the identity of the transients as cations. In these cases there is no ambiguity, since each of the 9-arylfluoren-9-yl cations can be prepared as a stable solution by dissolving the fluoren-9-ol in concentrated acid, and the spectra are essentially identical with those obtained by flash photolysis. There is one minor difference, a weak absorption near 380 nm in the spectra obtained with flash photolysis. Being very small, this signal is most apparent after the completion of the decay of cation. It is unaffected by oxygen, and possibly represents the cation radical of the 9-arylfluoren-9-ol. As is observed with fluoren-9-ol itself,²⁵ the cation radical can arise from photoionization in the laser pulse.

Table 1 provides λ_{\max} and rate constant data. It can be noted that the rate constants refer to the reaction of free ground state cations. This point has been discussed in detail in previous studies of cations generated by flash photolysis.^{2,5,25} A key indicator with the present systems is the excellent agreement between the spectra of the transients and those of the ground state cations in concentrated acid.

Table 1 also gives absolute quantum yields for the formation of the cations upon 248 nm irradiation in the solvent TFE. These values were calculated by measuring the initial cation absorbance following irradiation at the λ_{\max} in the region around 500 nm. The reference was the initial absorbance of the hydrated electron obtained by irradiation of potassium iodide in water under identical conditions of 248 nm absorbance, laser dose and cell configuration. The measurements were carried out with varying laser intensity, the absorbance of the electron being linear in this quantity, with plots of absorbance *versus* laser dose for the fluoren-9-yl cations displaying downward curvature. The latter is likely due to an ‘inner filter’ effect.^{6,31} The 9-arylfluoren-9-yl cations do absorb at 248 nm, so that once significant amounts are formed, they intercept part of the exciting light.

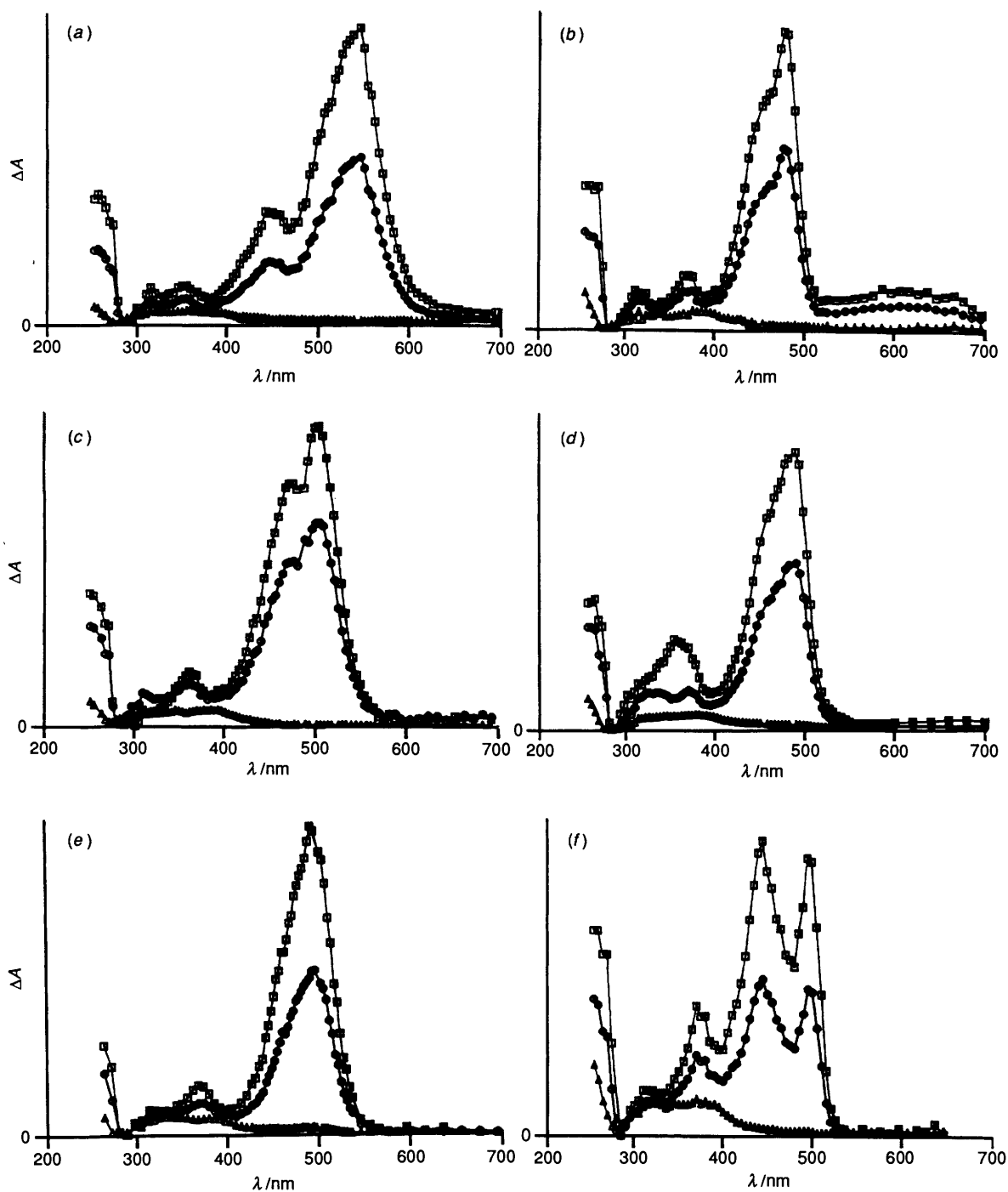


Fig. 1 Transient absorption spectra generated upon 248 nm laser flash photolysis of (a) 9-(4-methoxyphenyl)fluoren-9-ol in 4:1 water-acetonitrile, (b) 9-(3-methoxyphenyl)fluoren-9-ol in TFE, (c) 9-(4-methylphenyl)fluoren-9-ol in TFE, (d) 9-phenylfluoren-9-ol in TFE, (e) 9-(4-chlorophenyl)fluoren-9-ol in TFE, and (f) 9-(4-trifluoromethylphenyl)fluoren-9-ol in TFE. Spectra were recorded at times of (a) 500 ns (\square), 4.2 μ s (\circ), 50 μ s (Δ); (b) 530 ns (\square), 36 μ s (\circ), 500 μ s (Δ); (c) 450 ns (\square), 80 μ s (\circ), 3 ms (Δ); (d) 450 ns (\square), 24 μ s (\circ), 490 μ s (Δ); (e) 480 ns (\square), 24 μ s (\circ), 170 μ s (Δ); (f) 340 ns (\square), 8 μ s (\circ), 82 μ s (Δ).

$$\Phi(\text{FIOH} \rightarrow \text{FI}^+) = \left(\frac{S_{\text{FI}}}{S_{\text{e}}} \right) \left(\frac{\epsilon_{\text{e}}}{\epsilon_{\text{FI}}} \right) \Phi(\text{I}^- \rightarrow \text{e}_{\text{aq}}^-) \quad (1)$$

Eqn. (1) was employed for the calculation of quantum yields,³¹ where S_{FI} and S_{e} are the limiting slopes at zero laser dose of the absorbance-intensity plots and ϵ_{FI} and ϵ_{e} are extinction coefficients. Values of ϵ_{FI} were taken to be identical with ones measured in 96% H_2SO_4 . The value of ϵ_{e} at 650 nm was taken as $1.64 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$,³² with the absolute quantum yield for its formation from iodide taken as 0.29.³³ Considering the uncertainties in the extinction coefficient and quantum yield for the electron, coupled with the assumption

that the ϵ_{FI} is solvent independent, the accuracy of $\Phi(\text{FIOH} \rightarrow \text{FI}^+)$ is likely no better than ± 0.1 . Regardless of the error, the numbers in Table 1 attest to a very efficient photodehydroxylation that is relatively insensitive to the nature of the substituent in the 9-aryl ring. In contrast, 248 nm laser irradiation of triphenylmethanol under the same conditions produces little cation.

1-(4-Dimethylaminophenyl)ethyl Cation.—We have demonstrated previously that 4-methoxystyrene undergoes Markovnikov addition of the solvent when irradiated in TFE. The reaction involves protonation of the singlet excited state by the

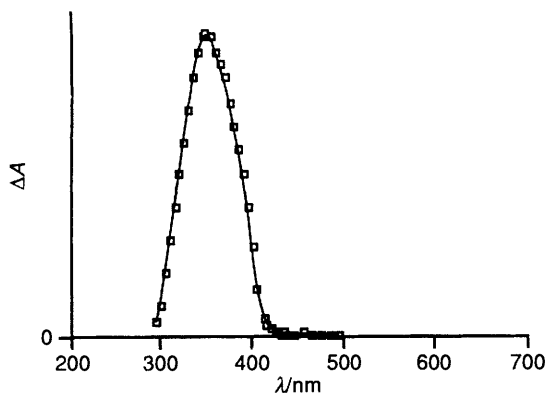


Fig. 2 Transient absorption spectrum generated upon 248 nm laser flash photolysis of 4-dimethylaminostyrene in TFE, recorded at 500 ns

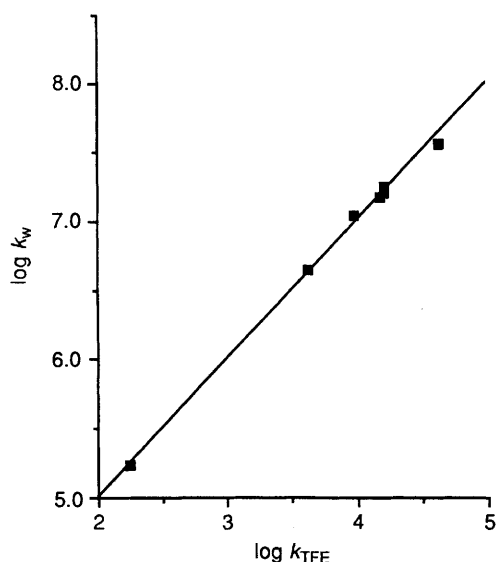
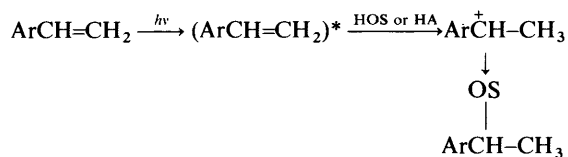


Fig. 3 Relationship between the observed rate constants for the decay of 9-arylfuoren-9-yl cations in 4:1 water-acetonitrile and in TFE. The linear regression line (correlation coefficient = 0.997) follows the equation $\log k_w = 3.00 + 1.00 \log k_{\text{TFE}}$. Data for 4-CF₃ and 3-CF₃ have been omitted since k_w values for these cations cannot be accurately measured.

solvent producing the 1-(4-methoxyphenyl)ethyl cation. This ion is readily observed with flash photolysis.^{5,34,35} Similar behaviour is found in water but the efficiency of the photoprotonation is low unless stronger acids are present.^{36,37} Moreover, the intermediate cation is too short-lived to be detected with nanosecond flash photolysis equipment. With styrene itself, the solvent HFIP is required for efficient photoprotonation, and for the intermediate, the parent phenethyl cation, to be observed.³⁵



In a similar manner, we now find that 1,4-dimethylaminostyrene undergoes photoprotonation in TFE, as well as in TFE mixtures with water, to give the 1-(4-dimethylaminophenyl)ethyl cation. The spectrum of the transient obtained upon 248 nm irradiation in pure TFE is shown in Fig. 2. Identification as a cation follows arguments similar to those employed previously,⁵ namely the observation of exponential decay kinetics with quenching by a good nucleophile, azide, and no

effect of oxygen. In addition the initial absorbance of the transient is linear in laser intensity, ruling out two-photon ionization to produce a cation radical. A stable spectrum of the 1-(4-dimethylaminophenyl)ethyl cation cannot be obtained, since attempts to generate this cation in acidic solutions result in protonation of the amino group.³⁸ However, the λ_{max} of the transient obtained with 4-dimethylaminostyrene is consistent with those of other phenethyl cations that have been studied by flash photolysis,³⁵ the order 4-Me₂N (360 nm) > 4-MeO (340 nm) > 4-Me (325 nm) > H (315 nm) being the same as that observed with triaryl- and diaryl-methyl cations.

Rate constants for the decay of the 1-(4-dimethylaminophenyl)ethyl cation were measured in 1:1 TFE-water, with values of $k_s = 4.0 \times 10^1 \text{ s}^{-1}$ being obtained for the decay in the solvent alone and $k_{\text{Az}} = 1.6 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the quenching by azide. Using the same solvent mixture, the ratio $k_{\text{MeOOCCH}_2\text{S}^-} : k_s = 2.5 \times 10^6 \text{ dm}^3 \text{ mol}^{-1}$ has been obtained through the analysis of products of a solvolysis reaction carried out in the presence of MeOOCCH₂S⁻.¹¹ A value of $k_s = 2 \times 10^3 \text{ s}^{-1}$ was then obtained from this ratio with the assumption that the thiol anion reacts with the cation at the diffusion limit, $5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The present, directly measured, results show that this assumption is not valid, a possibility that was mentioned in the original report. In fact, using our value of k_s , $k_{\text{MeOOCCH}_2\text{S}^-}$ is calculated as $1 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, well below the diffusion limit. Interestingly the latter rate constant is about an order of magnitude greater than k_{Az} , a difference expected on the basis of the N_+ values for the two nucleophiles.⁸

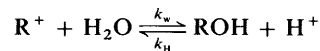
The failure of the 'clock' approach with the dimethylamino-substituted cation results from its inherent lack of reactivity, such that combinations with azide and thiolate are activation controlled. For the more reactive phenethyl cations such as the *p*-methoxy derivative considered by Richard, Rothenberg and Jencks,¹¹ the directly measured values⁵ of k_{Az} are indeed in the range $5\text{--}6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ typical of a diffusion-controlled reaction. Thus the other rate and equilibrium constants estimated by these authors with this assumption¹¹ are reasonable.

Discussion

Table 1 summarizes the rate constants for the decay of the 9-arylfuoren-9-yl cations in TFE and 1:4 acetonitrile-water. Wholly aqueous solutions could not be used owing to the insolubility of the alcohol precursor. However, rate constants for the decay of carbocations have been shown to be relatively constant upon going from 1:1 water-acetonitrile to 100% water,^{2,20} so that the rate constants obtained in 1:4 acetonitrile-water are considered to be good approximations of the values in water.

Interestingly, substituent effects on reactivity are independent of solvent, despite the fact that the cations undergo decay 10^3 times faster in the aqueous mixture as opposed to TFE. This is best seen in a plot of $\log k_{\text{TFE}}$ versus $\log k_w$ (Fig. 3), which is excellently linear with a slope of exactly 1.00.

For seven substituents, equilibrium constants K_R for the equilibrium involving the fluorenyl cation and fluorenone are available from the literature.^{21,28} These can be combined with



the decay rate constants k_w directly measured in this work to give rate constants k_{H} for the H⁺-catalysed conversion of the alcohol into the cation. These values are summarized in Table 2.

As shown in Table 3 the substitution of hydrogen by phenyl clearly has a significant retarding effect on the reactivity of the fluorene-9-yl cation, an almost 10^5 -fold reduction being observed

in the rate of decay in TFE solvent. Kinetic stabilization by phenyl is expected on both resonance and steric grounds. Table 3 also provides a comparison of this effect as seen with other benzylic-type cations. Consistent with the idea of 'resonance saturation',^{39,40} the exact magnitude of the effect is dependent on the nature of the cation, with the general trend that the more inherently stable the cation, the smaller the effect of an additional phenyl group. As shown by the final column in Table 3, qualitatively similar behaviour is observed on replacing phenyl by 4-methoxyphenyl, with the more stable

cations, especially the xanthylium cation, exhibiting a smaller effect.

Substituent Effects.—Fig. 4 shows correlations of $\log k_w$ for 9-arylfluoren-9-yl cations with the substituent constants σ^+ and σ^{C+} . The plot involving the former is not perfectly linear, the point for the 4-methoxy derivative deviating significantly from the correlation line. Moreover, this deviation occurs in a direction corresponding to the case where the cation-stabilizing effect of the π -donor is underestimated by the σ^+ scale. On the other hand, use of σ^{C+} , a substituent scale based upon the ^{13}C NMR chemical shifts of fully formed cations,⁴¹ provides a much better correlation.

This same situation was observed previously in correlations involving triarylmethyl cations.² Further insight comes from the application of the two-parameter Yukawa-Tsuno equation⁴⁰ (2) or the equivalent representation, eqn. (3), suggested

$$\log(k/k_0) = \rho_n[\sigma^n + r^+(\sigma^+ - \sigma^n)] \quad (2)$$

$$\log(k/k_0) = \rho_n\sigma^n + \rho_r(\sigma^+ - \sigma^n) \quad (3)$$

by Jencks and co-workers¹¹ where the product $r^+\rho_n$ is replaced with ρ_r .

Parameters obtained by fitting to these equations are given in Table 4, along with those previously obtained for mono-substituted triarylmethyl cations² and phenethyl cations.¹¹ The numbers for the last system employ the directly measured rate constant for the dimethylamino-substituted cation and are thus changed somewhat from those given in the original reference. There are several observations that are common to each cation type. The parameter r^+ of Yukawa-Tsuno was intended to range from 0 to 1, and thus allow for interactions of the reaction centre with π donors that were intermediate between those described by σ^+ and σ_n . However, the rate constant k_w requires r^+ values that are significantly greater than 1. This is essentially the same phenomenon just discussed, namely that π donors interact more strongly with a fully formed cationic centre than is indicated by their σ^+ values. For the rate constants k_H , on the other hand, values of r^+ do indeed fall in the correct range. The difference in the substituent interactions for the reactions in the forward and reverse directions is further revealed in the normalized parameters $\rho(\text{norm})$. These are calculated as $\rho(k):\rho(K)$ and provide a measure of the change that has occurred at the transition state.¹¹ For each of the cations, these parameters reveal a significant imbalance at the transition state, with greater than 50% of the resonance interaction having disappeared by the time the transition state has been reached in the direction of cation hydration, but less than 50% of the polar interaction. Obviously in the reverse, cation-forming direction, the opposite situation holds. This now appears to be a general phenomenon for such carbocation equilibria. The explanation¹¹ invokes a transition state in which in the hydration direction the incoming water molecule

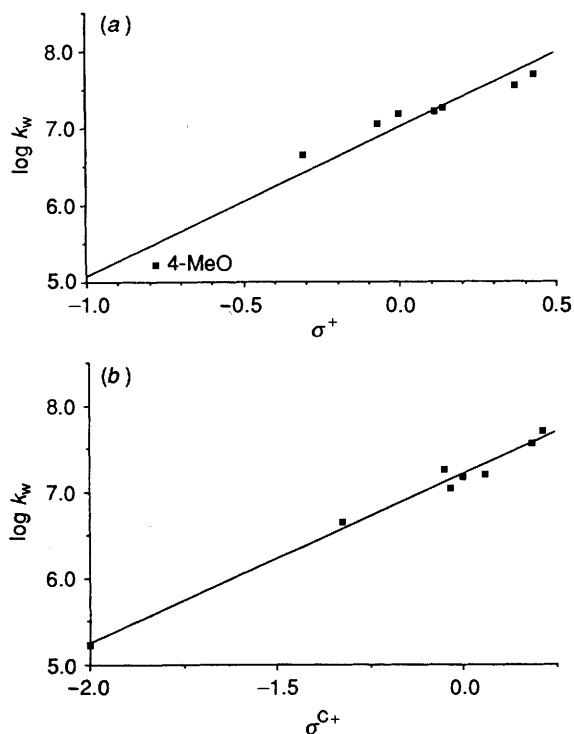


Fig. 4 Relationship between $\log k_w$ and substituent constants σ^+ and σ^{C+} for 9-arylfluoren-9-yl cations. Lines are based upon linear regression and have slopes of +1.9 (σ^+) and 1.0 (σ^{C+}).

Table 2 Rate and equilibrium constants for the hydration of 9-arylfluoren-9-yl cations in water

Aryl subst.	k_w/s^{-1} ^a	$k_H/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ^b	$\text{p}K_R$
4-MeO	1.7×10^5	3.9×10^{-3}	-7.64 ^c
4-Me	4.4×10^6	1.6×10^{-3}	-9.43 ^c
H	1.5×10^7	2.2×10^{-4}	-10.82 ^c
3-MeO	1.6×10^7	1.2×10^{-4}	-11.11 ^c
4-Cl	1.8×10^7	1.4×10^{-4}	-11.11 ^d
3-Cl	3.6×10^7	8.9×10^{-6}	-12.6 ^c
3-CF ₃	5×10^7	3.5×10^{-6}	-13.16 ^c

^a Rate constant at 20 °C directly measured in 4:1 water-acetonitrile (from Table 1). ^b k_w/K_R . ^c Ref. 21. ^d Ref. 28.

Table 3 Relative rate constants for the decay of carbocations^a

Cation type	$\left(\frac{k_s(\text{R} = \text{C}_6\text{H}_5)}{k_s(9\text{-C}_6\text{H}_5\text{X}^+)}\right)^b$	$\left(\frac{k_s(\text{R} = \text{H})}{k_s(\text{R} = \text{C}_6\text{H}_5)}\right)$	$\left(\frac{k_s(\text{R} = \text{C}_6\text{H}_5)}{k_s(\text{R} = 4\text{-MeOC}_6\text{H}_4)}\right)$
9-R-Xanthylium ^c	1.00	1.0×10^3	2
(4-MeOC ₆ H ₄)(C ₆ H ₅)C ⁺ -R ^d	6.0×10^1	1.6×10^3	16
(C ₆ H ₅) ₂ C ⁺ -R ^e	6.5×10^3	8.7×10^3	107
4-MeOC ₆ H ₄ CH ⁺ -R ^f	8.7×10^4	3.6×10^3 ^g	86 ^g
9-R-Fluorenyl ^h	6.5×10^5	5.9×10^4 ^g	83 ^g

^a At 20 °C, in acetonitrile-water solvent, unless otherwise specified. ^b Rate constants of the cation with R = C₆H₅ relative to 9-phenylxanthylium ion. ^c Ref. 6. ^d Ref. 2 for R = Ar. Ref. 26 for R = H. ^e Ref. 5 for R = Ar. Ref. 35 for R = H. ^f For TFE solvent. ^g This work for R = Ar. E. Hilinski, personal communication for the rate constant in TFE for R = H.

Table 4 Parameters obtained from two-parameter analysis of rate and equilibrium constants for benzylic-type cations

Parameter	Ar- ⁺ CHCH ₃ ^a	Ph ₂ C ⁺ -Ar	9-Ar-fluoren-9-yl	9-Ar-9-xanthylum
$\rho_n(k_w)$	+2.7	+1.3	+1.3	+0.4 ^b
$\rho_r(k_w)$	+6.1	+4.7	+2.8	+0.4 ^b
$r^+(k_w)$	2.3	3.6	2.2	1.0
$\rho_n(k_H)$	-4.9	-2.7	-4.2	
$\rho_r(k_H)$	-4.4	-1.8	-0.7	
$r^+(k_H)$	0.9	0.7	0.2	
$\rho_n(K_R)$	+7.6	+4.0	+5.5	
$\rho_r(K_R)$	+10.5	+6.5	+3.6	
$r^+(K_R)$	1.4	1.6	0.7	
$\rho_n(\text{norm})$	0.36	0.33	0.23	
$\rho_r(\text{norm})$	0.61	0.72	0.76	

^a In 1:1 TFE-W. Parameters for k_w and K_R have been calculated with the directly measured rate constant for the *p*-dimethylamino compound, and thus differ from those given in the original reference.¹¹ In that work the observed rate constant for decay of the *p*-dimethylamino-substituted cation in 1:1 TFE-W was estimated as $2 \times 10^3 \text{ s}^{-1}$. As demonstrated by direct measurement, the actual rate constant is 50 times smaller. Thus the values of k_{H_2O} and K_{eq} given for 4-N(CH₃)₂ in Table VII of ref. 11 are 50 times too high.^b There is very little effect of aromatic substituent. A single parameter plot of $\log k_w$ versus σ has a slope of +0.5 and is of equal statistical significance.

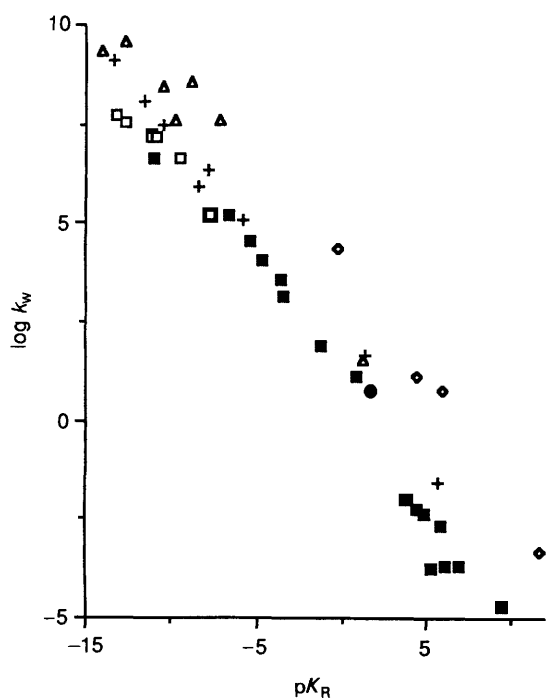
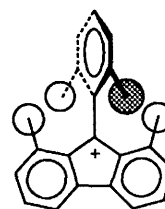


Fig. 5 Rate-equilibrium correlation for the addition of water to carbocations. Cation types are as follows: \diamond , xanthylum ions unsubstituted in the 9-position (ref. 8); \blacksquare , triarylmethyl cations (ref. 8 for $pK_R > 0$, ref. 2 for $pK_R < 0$); \triangle , 1-arylethyl cations (ref. 11; the point for the 4-dimethylamino-substituted cation is based upon the rate constant directly measured in this work, and a value of pK_R calculated with this rate constant); \bullet , 9-phenylxanthylum cation (ref. 6); +, diarylmethyl cations (ref. 2); \square , 9-arylfluoren-9-yl cations (rate constants measured in this work; pK_R values from refs. 21 and 28).

localizes the fractional positive charge on the central carbon, so that the resonance interaction with π donors decreases at a more rapid rate than the polar interaction.

Table 4 also reveals some interesting trends in a comparison of ρ values for the various types of cation. The values of both ρ_n and ρ_r are largest for the phenethyl system, this being true for the rate constants in each direction, as well as the overall equilibrium constant. These cations of course contain only one aryl ring, and thus are the least stable, so that interactions with substituents are the most important. At the other extreme lie the xanthylum ions, where the effects of substituents in the 9-aryl ring are very small. Here the cations are highly stable even in the

absence of the 9-aryl ring, so that interactions with substituents are highly attenuated. The triarylmethyl and fluorenyl cations are of intermediate stability and, as expected, have intermediate ρ values. A comparison of these two systems shows that the ρ_r values are larger for triarylmethyl, while ρ_n are larger (or equal, for k_w) for 9-arylfluoren-9-yl. The most likely explanation for the former lies in the orientation of the aryl ring with respect to the plane described by the formal cationic centre. Triarylmethyl cations are non-planar,⁴² a consequence of interactions of *ortho* hydrogens in a fully planar structure. For example, the crystal structure of the perchlorate salt of the parent cation shows that each phenyl ring is twisted about 32°.⁴³ The fluoren-9-yl cations are constrained to have a planar arrangement of the fluorenyl ring system. This means that on substituting a third phenyl group at the 9-position, severe steric interactions are introduced involving the *ortho* hydrogens of this ring and the hydrogens at positions 1 and 8 of the fluorene. Thus, the phenyl ring is undoubtedly twisted well out of the plane, likely by considerably more than 30°. In fact an MM2 calculation shows that the 9-phenyl ring is twisted by 70°.



Such a large deviation from planarity obviously has a significant effect on the ability of *para* substituents to interact in a conjugative manner with the positive charge, with the result that the values of the resonance parameter ρ_r are lower. The larger ρ_n values indicate a stronger polar interaction in the 9-arylfluoren-9-yl cations. As discussed previously the fluoren-9-yl cation is inherently unstable. Thus substituents can have a significant effect. The greater polar interaction in particular could be considered to be a compensation for the smaller resonance interaction caused by the twisting of the aryl ring.

Rate-Equilibrium Correlation.—Fig. 5 shows a plot of $\log k_w$ versus pK_R , including the new data obtained in this work for the 9-arylfluoren-9-yl cations, and also a point for the 1-(4-dimethylaminophenyl)ethyl cation based upon the directly measured rate constant. As suggested in the original construction by Taft and co-workers,²⁹ a single correlation clearly

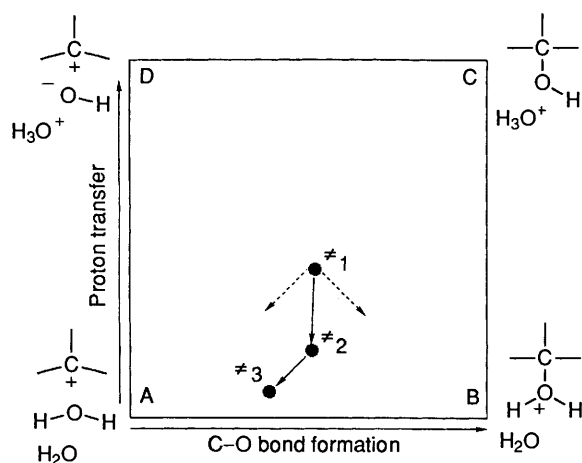


Fig. 6 Reaction-coordinate diagram for the addition of water to carbocations. The x and y axes represent C–O bond formation and proton transfer to a second water, respectively. The point \neq_1 is a transition state for a relatively stable cation, and the dashed arrows represent the effects parallel to and perpendicular to the reaction coordinate for a structural change that results in a less cation, with the point \neq_2 the resultant transition state. For highly reactive cations, the transition state moves as indicated from \neq_2 to \neq_3 .

does not exist, but the data are better accommodated by a separation into families of structurally related ions. In considering cations with the same pK_R , the order of inherent reactivity is 9-unsubstituted-9-xanthylium \sim cyclic dialkoxy-carbocation (not shown in Fig. 5) $>$ phenyltropylium (not shown) $>$ diarylmethyl \sim 9-arylxanthylium $>$ triarylmethyl \sim 9-arylfluoren-9-yl. In simple terms this order corresponds to an increasing steric hindrance to the addition of water. That is, the inherent barrier for the addition of water to a carbocation would appear to be lower, the less the steric congestion in the transition state.

As shown in Fig. 5, the data for the various families form a series of reasonably parallel lines. There is a small amount of scatter even within each family. This scatter is particularly apparent for the less stable cations, whose values of pK_R are based upon acidity function measurements that may cause some uncertainty.^{44,45} Whatever the cause, this scatter may mask a gentle downward curve. Such behaviour is most apparent for the series consisting of the triarylmethyl and 9-arylfluoren-9-yl cations. These two cation types seem to form a continuous series, and as drawn in Fig. 5, the data are better fit by a curve, particularly at the high reactivity end. A curved dependence is consistent with the transition state becoming more reagent-like as the reactivity of the cation increases. However, even if this curvature is a real phenomenon, it is very slight. Considering the large change in pK_R now covered in this correlation, the value of $d(\log k_w)/dpK_R$ is remarkably unchanged, being 0.6 ± 0.1 throughout.

The addition of water to carbocations is catalysed by added general bases,^{46,47} with the implication that the solvent reaction itself involves a second molecule of water simultaneously removing a proton.⁸ The reaction coordinate diagram for such a situation, with C–O bond making and proton transfer as the two coordinates, is shown in Fig. 6. Starting with a relatively stable cation whose transition state lies at the point arbitrarily represented by \neq_1 , a substituent change that results in a less stable cation is predicted to have the effects indicated by the dashed arrows. In the direction along the reaction coordinate (A \rightarrow C) the transition state will tend to move toward the cation corner A, while in the direction perpendicular to the reaction coordinate, the transition state will tend to move towards the protonated alcohol corner B. If these two effects are of a similar

magnitude, the result is a movement of the transition state towards the bottom edge, to the transition state represented by the point \neq_2 . If such were the case, there is actually very little change in the amount of C–O bond making at the transition state, and $d(\log k_w)/dpK_R$, which provides an approximate measure of this bond making, is relatively unchanged. The amount of proton transfer at the transition state, on the other hand, is predicted to change, and there is experimental evidence for this, in terms of decreasing values of Brønsted β values with increasing cation reactivity.^{46,47} Movement parallel to the proton transfer coordinate cannot continue forever. As the transition state approaches the bottom edge of Fig. 6, it is predicted to slide towards the cation corner, as indicated by the movement to the point \neq_3 .⁴⁶ This situation now corresponds to decreasing C–O bond making at the transition state, and consequently decreasing $d(\log k_w)/dpK_R$. This may be the picture that is most appropriate for the more reactive cations, particularly the fluorenyl cations.

Stability of Fluoren-9-yl Cations.—While it is clear that fluoren-9-yl cations are destabilized relative to analogues without the five-membered ring, the actual extent of this effect is not enormous. The pK_R values for such cations show 4–5 log units of destabilization relative to acyclic analogues, and, as demonstrated in this work, the solvent reactivities of 9-arylfluoren-9-yl cations are only two orders of magnitude greater than those of corresponding triarylmethyl cations. There is a question as to whether the central ring imparts 4π antiaromatic character, and such an explanation has been invoked for the significantly enhanced heterolytic reactivity of fluoren-9-ols that is observed upon irradiation.^{13,14} However, this cannot be an important factor in the ground state. This same conclusion has recently been reached by Amyes, Richard and Novak on the basis of an examination of reactivities determined using the azide clock approach, coupled with detailed theoretical calculations.⁴⁵ These workers found that the fluoren-9-yl cation shows none of the characteristics of destabilized 4π systems such as the cyclopentadienyl carbocation. At the theoretical level, there is a 8–10 kcal mol⁻¹ destabilization relative to diphenylmethyl that can be accounted for by a combination of a smaller amount of π -stabilization coupled with Van der Waals and ring strain.

Experimental

9-Arylfluoren-9-ols were prepared by reacting the appropriate arylmagnesium bromide with fluorenone as previously described.^{21,28} 4-Dimethylaminostyrene was a gift from Prof. J. Wirz. Water was purified with a Millipore-Q system. 2,2,2-Trifluoroethanol was dried over 4A molecular sieves and distilled under nitrogen through a 40 cm Vigreux column prior to use. Solutions used in the laser flash photolysis experiments were prepared by adding a small amount of a stock solution (0.1–1 mol dm⁻³) of the substrate in acetonitrile or trifluoromethanol to the appropriate solvent such that the absorbance of the final solution at 248 nm was 0.5–2.0 cm⁻¹. This corresponds to concentrations in the range $1\text{--}5 \times 10^{-4}$ mol dm⁻³. Flash photolysis experiments were carried out by irradiating at 248 nm with a Lambda-Physiks excimer laser (KrF). Details of this equipment have been described elsewhere.^{1,2,6}

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