Direct Observation of β-Fluoro-substituted 4-Methoxyphenethyl Cations by Laser Flash Photolysis

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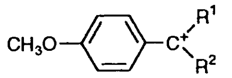
4-Methoxyphenethyl cations bearing β-fluorine substituents [4-$MeOC_6H_4C^+R^1R^2$ with R^1 = H, R^2 = CH_2F (**3**), R^1 = H, R^2 = CHF_2 (**4**), R^1 = H, R^2 = CF_3 (**5**), R^1,R^2 = CF_3 (**6**)] are observed as transient intermediates following 248 nm laser photolysis of chloride or bromide precursors $ArC(-X)R^1R^2$ in 2,2,2-trifluoroethanol (TFE) and TFE–water mixtures. Corresponding phenethyl radicals are also observed; successive fluoro-substitution has remarkably little effect on the Absorbance(cation):Absorbance(radical) ratio. Rate constants k_s for the decay of the cations have been directly measured, and compared with those of non-fluorinated analogues. In TFE–water mixtures the reactivity order is $ArCH^+CHF_2$ > $ArCH^+CH_2F$ > $ArCH^+CF_3$ > $ArCH^+CH_3$ (**1**) > $ArC^+(CH_3)_2$ (**2**) > $ArC^+(CF_3)_2$, but the differences are small, there being little more than a two-order of magnitude decrease across the series. This remarkably small effect of fluorine had previously been observed in an examination of azide:solvent partitioning ratios k_{az}:k_s. Rate constants k_{az} have also been obtained in this work, and, with the exception of **2** which reacts somewhat more slowly, these are constant, with values consistent with the azide:cation combination occurring at the diffusion limit for these cations, as had been assumed in the previous work. The small, complex effects of fluoro substitution on the reactivities of these cations have been explained by a model which has, as a key component, an effect of electron withdrawing substituents of forcing the positive charge away from the benzylic carbon to the oxygen of the 4-methoxy group. Evidence for a significant perturbation of the π electron density is available in the present work, in that the absorption maxima of the α-CF_3 and bis-α-CF_3 cations **5** and **6** are shifted 20 nm and 50 nm, respectively, to lower wavelengths than the corresponding α-methyl derivatives **1** and **2**. Studies of **6** in 100% aqueous solution reveal a second, slower, transformation following the decay of the cation. Product studies have previously indicated that a fraction of the hydration of this cation occurs at the 4-position of the aromatic ring, producing a quinone methide and products arising from such a species. An unobserved hemiacetal is an intermediate in this sequence. From spectral and kinetic considerations the second process observed with flash photolysis has been identified as representing the breakdown of the hemiacetal to the quinone methide. A complete rate–pH profile for this reaction has been obtained, from which a pK_a of 11.0 has been determined for the ionization of the hemiacetal.

There has been considerable interest in reactions generating carbocation intermediates bearing electron-withdrawing substituents attached at the positive centre.[1–4] Replacement of the α-methyl group with an α-trifluoromethyl in a benzylic-type cation $ArCH(CH_3)^+$ has a considerable thermodynamic destabilizing effect and results in large (10^7–10^9 fold) decreases in the rate constants for the formation of the cation in an S_N1 solvolysis reaction.[5–9] This substitution, on the other hand, has surprisingly little effect on the ratio $k_{az}:k_s$ for the partitioning of the intermediate cations between azide ion and the solvent in trifluoroethanol–water mixtures.[8,9] With the assumption that both $ArCH(CH_3)^+$ and $ArCH(CF_3)^+$ react with azide in a diffusion-limited reaction, with k_{az} ~ 5×10^9 dm^3 mol^{-1} s^{-1} ('azide-clock'),[10] this means that the trifluoromethyl substitution has little effect on the solvent rate constant k_s. This observation has now been extended to a number of systems producing intermediate cations of the structure 4-$CH_3OC_6H_4$-$C^+R^1R^2$ (**1**–**9**).[11–16]

Thus, the electrophilic reactivity of these cations is relatively independent of structure, and certainly shows no parallelism with thermodynamic stability. This contradictory situation has been rationalized on several grounds. A recent proposal[16] separates the substituent effects into polar and resonance contributions, and considers the differential effects of these on the kinetics and overall equilibrium in terms of the 'principle of non-perfect synchronization'.[17]

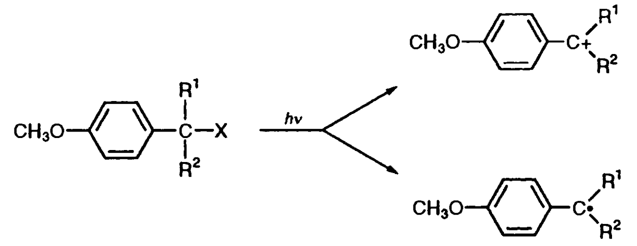


1; R^1 = H, R^2 = CH_3
2; R^1 = CH_3, R^2 = CH_3
3; R^1 = H, R^2 = CH_2F
4; R^1 = H, R^2 = CHF_2
5; R^1 = H, R^2 = CF_3
6; R^1 = CF_3, R^2 = CF_3
7; R^1 = H, R^2 = COOEt
8; R^1 = H, R^2 = OCH_3
9; R^1 = H, R^2 = N_3

This paper describes a laser flash photolysis (LFP) investigation of systems leading to the fluoro-substituted cations **3**–**6**. LFP has seen considerable recent application for the study of cationic intermediates.[18–30] The technique provides absolute rate constants for the reactions of transient cations with the solvent and with added nucleophiles. Using a series of triarylmethyl and diarylmethyl cations, it has been employed to establish the validity of the azide-clock method,[24] and one objective of the present work was to verify that this approach does apply to fluoro-substituted cations. Such ions have in fact not been reported even under stable ion conditions, so that this work also represents their first direct observation. An LFP study of diphenylmethyl and fluoren-9-yl cations substituted at the positive centre with an electron-withdrawing $COOCH_3$ substituent has recently appeared.[30]

Results and Discussion

Transient Cations.—Precursors for **3**–**6** were the chlorides or bromides **10**–**13**, with photolysis experiments being conducted with 248 nm irradiation in 2,2,2-trifluoroethanol (TFE) and TFE–water mixtures. The halides **11**–**13** were stable over > 30 min at ambient temperature in these solvents, permitting detailed transient spectra to be obtained. The retarding effect of the fluoro-substituents on the ground-state solvolysis provides an important advantage here. 4-Methoxybenzyl chloride and its α-methyl derivatives undergo rapid solvolysis in TFE–water mixtures, and thus cannot be studied by the LFP technique.* The monofluoro-substituted **10** proves to be an intermediate case, with half-lives of the order of 1–10 min sufficient for kinetic studies at a single wavelength, but not for the construction of a transient spectrum.



10; $R^1 = H, R^2 = CH_2F, X = Cl$
11; $R^1 = H, R^2 = CHF_2, X = Cl$
12; $R^1 = H, R^2 = CF_3, X = Br$
13; $R^1 = CF_3, R^2 = CF_3, X = Br$

Transient absorption spectra obtained with compound **12** in TFE are shown in Fig. 1. There are two overlapping bands, whose kinetics of decay indicate that they represent different intermediate species. The band at higher wavelength decays with exponential kinetics that are unaffected by oxygen [Fig. 1(*c*)], but accelerated by added nucleophiles such as primary amines [Fig. 1(*b*)] and azide (see later). The band at shorter wavelength is unaffected by nucleophiles, but quenched by oxygen, in fact so rapidly that this band is not observed in the oxygen-saturated solution [Fig. 1(*c*)]. In the absence of oxygen, the decay is not exponential, but can be fit by a second-order kinetic treatment. Such observations have been made previously with various benzylic-X species—triarylmethyl and diarylmethyl acetates and 4-cyanophenolates,[19,20] diarylmethyl halides (in acetonitrile)[23] and naphthylmethyl phosphonium salts.[27] The two transients can be identified as the cation **5**, the species quenched by nucleophiles, and the corresponding radical, the species quenched by oxygen. Corroborating evidence for these assignments is available from the positions of the bands. Benzylic radicals,[31] including the 4-methoxyphenethyl radical,[32] typically have a strong absorption band with λ_{max} in the region 280–300 nm. Benzylic cations, on the other hand, absorb at slightly higher wavelengths, the 4-methoxyphenethyl cation, for example, having λ_{max} at 340 nm.[25]

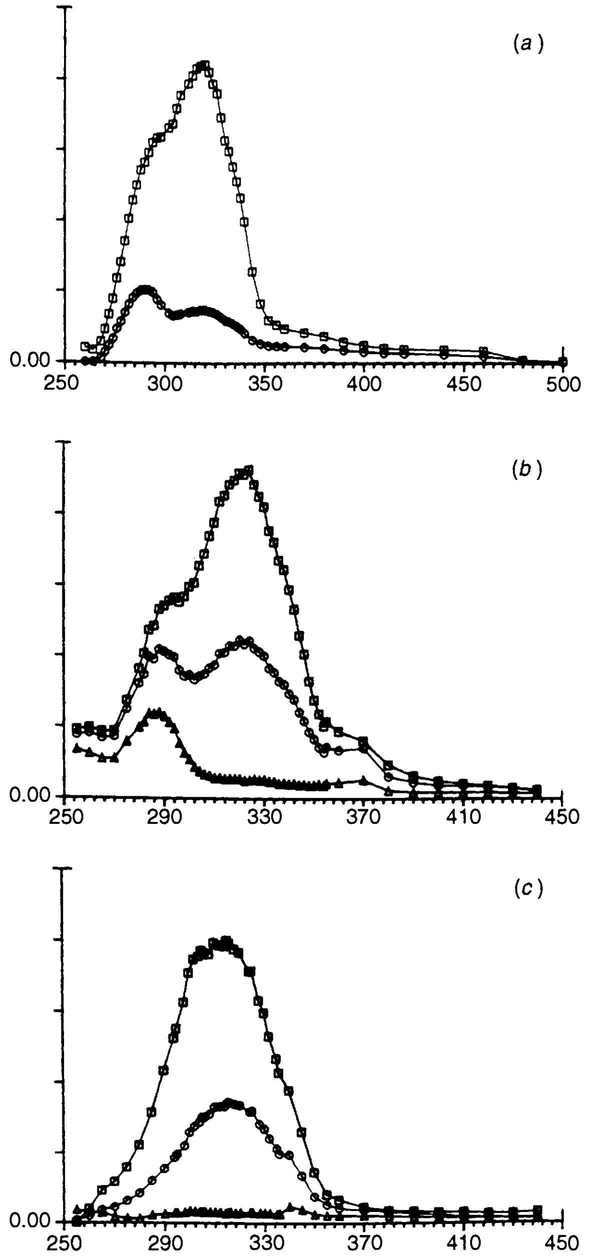


Fig. 1 Transient absorption spectra obtained with 2,2,2-trifluoro-1-(4-methoxyphenyl)ethyl bromide (**12**) following irradiation at 248 nm in 2,2,2-trifluoroethanol. (*a*) Argon-saturated solution: □, 35–40 ns after laser pulse and ○, 1.9–2.0 μs; (*b*) argon-saturated solution with 0.07 mol dm^{-3} 2-methoxyethylamine: □, 35–40 ns; ○, 90–100 ns and △, 1.9–2.0 μs; (*c*) oxygen-saturated solution: □, 35–40 ns; ○, 0.9–1.00 μs and △, 90–100 μs. The '*y*' axis plots arbitrary units of Δ Absorbance, although the scale will be the same for each of (*a*)–(*c*).

Similar behaviour is observed with **11** (Fig. 2) and **13** (Fig. 3), 248 nm irradiation resulting in a relatively strong signal for the transient cation, with an overlapping signal for the radical at slightly shorter wavelength. As with **12**, the signal for the latter is completely quenched within the 20 ns laser pulse in oxygen-saturated TFE. Although quantum yields cannot be measured since the extinction coefficients of these intermediates are unknown, in terms of absorbance, the increased fluoro-substitution in the series **11**–**13** has remarkably little effect on the amount of cation that forms, as well as on the cation : radical ratio.

Table 1 lists λ_{max} for the cations and radicals observed in the present study, along with values previously obtained for analogues without the fluorine substituents. Overall, there is little effect of α-substitution on the radical spectra, but a more pronounced effect for the cation. As noted in a previous study,[25] α-methylation results in a ~20 nm bathochromic shift relative

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* Unpublished. As with diarylmethyl halides[23] which also undergo rapid solvolysis, LFP studies can be conducted in 100% acetonitrile, with transient cations (and radicals) being observed.

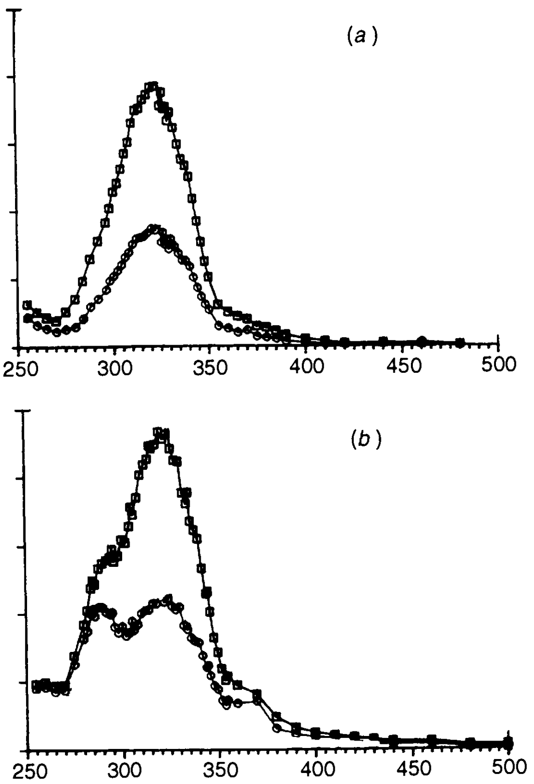


Fig. 2 Transient absorption spectra following 248 nm irradiation of 2,2-difluoro-1-(4-methoxyphenyl)ethyl chloride (**11**) in 2,2,2-trifluoroethanol: (*a*) oxygen saturated solution; (*b*) argon-saturated solution: □, 35–40 ns and ○, 0.9–1.00 μs after laser pulse

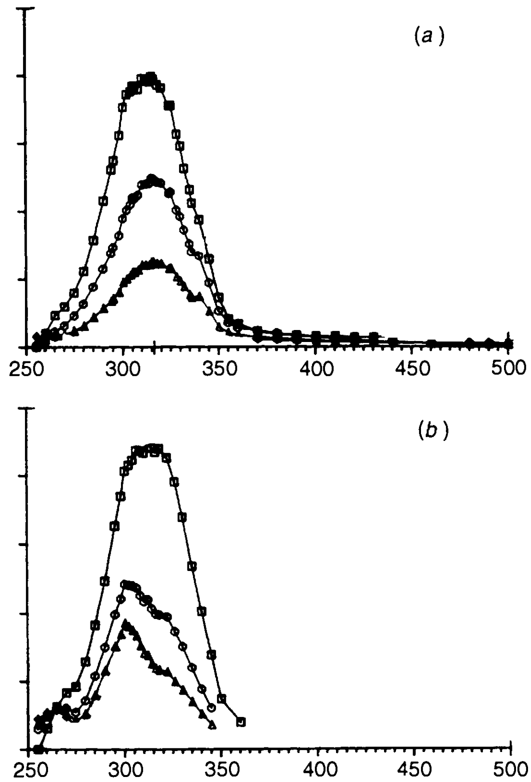


Fig. 3 Transient absorption spectra following 248 nm irradiation of 1,1,1,3,3,3-hexafluoro-2-(4-methoxyphenyl)-2-propyl bromide (**13**) in 2,2,2-trifluoroethanol: (*a*) oxygen-saturated solution: □, 35–40 ns; ○, 9–10 μs and △, 19–20 μs after laser pulse; (*b*) argon-saturated solution: □, 35–40 ns; ○, 24–25 μs and △, 48–50 μs after laser pulse

Table 1 Absorption maxima of methoxybenzyl cations and radicals

System Ar = 4-$CH_3OC_6H_4$	$\lambda_{max}(R^+)$/nm	$\lambda_{max}(R^{\bullet})$/nm
$ArCH_2$	320[a]	290[b]
$ArCHCH_3$	340[a]	300[b]
$ArC(CH_3)_2$	360[a]	
$ArCHCHF_2$	325	290
$ArCHCF_3$	320	295
$ArC(CF_3)_2$	310	300

[a] Ref. 25. [b] Ref. 32.

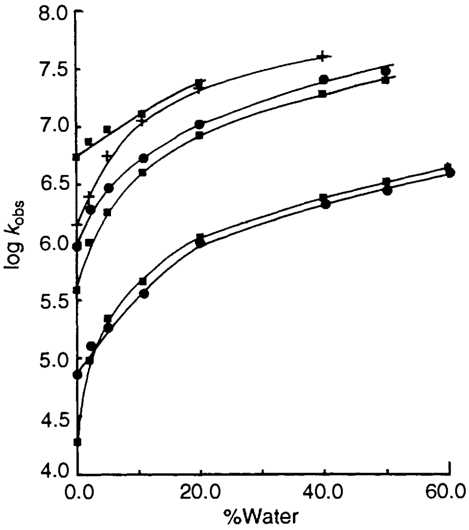


Fig. 4 Observed rate constants (s^{-1}, 20 °C) for the decay of 4-methoxybenzyl cations in TFE–water (v/v) mixtures. From the top: ■, $ArCH^+CHF_2$; +, $ArCH^+CH_2F$; ●, $ArCH^+CF_3$; ■, $ArCH^+CH_3$; ■, $ArC^+(CH_3)_2$; ●, $ArC^+(CF_3)_2$.

to the parent 4-methoxybenzyl cation. Introduction of trifluoromethyl on the other hand has little effect. In fact, there is a small ~ 10 nm hypsochromic shift for the bis-CF_3 cation **6** relative to 4-methoxybenzyl.

Kinetics.—Kinetic studies were carried out in oxygen-saturated solutions where the radical is rapidly quenched. In this way the signal for the radical transient does not interfere with that of the cation, and excellent exponential behaviour in the decay of the latter is observed. As is expected, this decay is accelerated with increasing water content in TFE–water mixtures. As shown in Fig. 4, plots of log *k versus* volume percent water are reasonably parallel above ~ 10% water, although the parallelism breaks down below this point. The actual reason for this is not clear.

Numerical values of the rate constants in 100% TFE and, where they could be measured, in 50:50 TFE–W are provided in Table 2. Overall, these show the same pattern of behaviour as deduced previously from $k_{az}:k_s$ ratios measured in 50:50 TFE–W, with the fluoro-substitution having only a small, and complex, effect on k_s. For the secondary cations the order in both TFE alone and in the mixed solvents is $ArCH^+CH_2F$ > $ArCH^+CHF_2$ > $ArCH^+CF_3$ > $ArCH^+CH_3$, but there is only a single order of magnitude difference across the series. The tertiary cations react at very similar rates in the mixed solvents with $ArC^+(CH_3)_2$ slightly faster than $ArCH^+(CF_3)_2$. In the TFE-rich mixtures, these cross over so that the former is slightly less reactive. This is likely due to the low of reactivity of $ArCH^+(CF_3)_2$ with trifluoroethanol, as has been observed in partitioning ratios based upon products in water–TFE

Table 2 Rate constants for the reactions of 4-methoxybenzyl cations (20 °C)

Cation	k_s/s^{-1} (TFE)[a]	$k_{az}/dm^3\ mol^{-1}\ s^{-1}$ (98:2 TFE–W)[a]	k_s/s^{-1} (1:1 TFE–W)[a]	$(k_{az}/k_s)/dm^3\ mol^{-1}$ (1:1 TFE–W)[b]	$k_{az}/dm^3\ mol^{-1}\ s^{-1}$ (1:1 TFE–W)[c]
$ArCH_2^+$	4.3×10^6			25	
$ArCH^+CH_3$	3.9×10^5	5.6×10^9	2.5×10^7	105	2.6×10^9
$ArC^+(CH_3)_2$	1.6×10^4	3.9×10^9	3.3×10^6	380	1.3×10^9
$ArCH^+CH_2F$	1.4×10^6	5.4×10^9	5.0×10^7 [d]	50	2.5×10^9
$ArCH^+CHF_2$	5.5×10^6	5.9×10^9		50	
$ArCH^+CF_3$	9.3×10^5	5.3×10^9	3.0×10^7	90	2.7×10^9
$ArC^+(CF_3)_2$	6.6×10^4	5.9×10^9	3.0×10^6	1100	3.3×10^9 3.0×10^9 [a]

[a] Direct measurement with flash photolysis. [b] Determined for ground-state solvolysis reaction through common-ion inhibition or analysis of products in the presence of azide—ref. 16. [c] Calculated from $k_{az}:k_s$ using directly measured k_s. [d] Estimated by small extrapolation of plot of Fig. 4 (from 40% water).

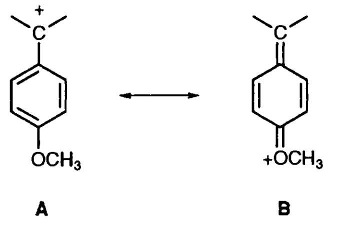
mixtures.[11] A possible explanation is that the transition state for the addition of TFE to $ArCH^+(CF_3)_2$ is destabilized by a combination of steric and electrostatic interactions between CF_3 groups.

As is expected, the cations are efficiently quenched by the addition of azide ions, significant rate accelerations being observed even at concentrations of azide of 0.1–1.0 mmol dm^{-3}. Plots of k_{obs} *versus* the azide concentration are excellently linear. Values of the second-order rate constants k_{az} determined as the slopes of these plots in a solvent of 98:2 TFE–water are given in Table 2. For five of the cations (**1**, **3**–**6**) k_{az} is, to within experimental error, constant at $(5.6 \pm 0.3) \times 10^9$ dm^3 mol^{-1} s^{-1}. This likely represents the diffusion limit for this type of cation in this solvent. As we have shown previously,[24] rate constants calculated for the diffusional encounter of azide anion and carbenium ions through the use of the Debye–Smoluchowski equation are larger than the observed limiting k_{az}. The limiting k_{az} also depend on cation structure, being about 40% larger for diarylmethyl cations as compared with triarylmethyl. These differences can be explained through models based upon non-productive collisions.

For 1:1 TFE–water, the solvent employed in the thermal studies of these cations, k_{az} has been calculated by combining the $k_{az}:k_s$ partition ratios with values of k_s directly obtained with flash photolysis. The velocity of the solvent decay in this mixture makes the direct measurement of k_{az} difficult, since the rates are approaching the apparatus limit even without the azide. In the case of the more slowly reacting **6**, direct measurement has been possible, and the k_{az} so obtained shows good agreement with the calculated number. As in the 98:2 mixture, the cations appear to have reached a limiting k_{az}, in this case at $(2.7 \pm 0.3) \times 10^9$ dm^3 mol^{-1} s^{-1}. This lower number reflects a combination of changes in the viscosity and relative permittivity of the solvent.

In both solvents, the 4-methoxycumyl cation **2** has k_{az} which is somewhat smaller than the limit observed with the others. This likely represents a situation where the bond-forming step has become partially rate-limiting, so that the reaction is not entirely encountered-controlled. The difference with the limiting k_{az} is, however, not large. Overall, therefore, the conclusion is that the assumption in the azide-clock approach of a constant k_{az} is valid for this class of cation. In addition, the use of 5×10^9 dm^3 mol^{-1} s^{-1} for this constant produces k_s values in 1:1 TFE–water which are a factor of about two larger than the actual numbers. The 4-methoxycumyl cation is somewhat less reactive relative to the others than predicted by the $k_{az}:k_s$ ratios.

This study obviously verifies the previous conclusions based on the $k_{az}:k_s$ ratios, namely that fluoro-substitution has little effect on the reactivities of these cations, despite the significant thermodynamic destabilizing effect. This has been explained by a model where the polar and resonance effects of the fluoro substituents operate in opposite directions.[16] Thus, the introduction of the electron-withdrawing group destabilizes the cation through a polar effect, but this is offset somewhat by increased resonance interaction with the 4-methoxy ring substituent, this interaction being augmented as the electron-withdrawing properties of the fluorine force the charge away from the benzylic carbon onto the oxygen of the 4-methoxy group.



(1)

To explain the thermodynamic trends, the polar effect must be considered to be more important on the overall equilibrium. The kinetic trends are explained by a model, based upon literature precedence,[10,20,33,34] where there is an imbalance in the expression of these effects in the transition state. In the nucleophile–cation combination direction, there is substantial loss of the resonance interaction at the transition state, but less of a change in the polar interaction. With the greater overall importance of the latter, the consequence is that the opposing changes in polar and resonance effects on proceeding from the starting cation to the transition state almost cancel, so that the effects on k_s are small.

A key component of the above explanation is that delocalization of the π-electrons in these cations is dependent on the substituents present at the benzylic carbon, electron-withdrawing substituents for example, resulting in an increased positive charge at the 4-methoxy group, as in contributor **B** of eqn. (1). A prediction is that the absorption spectra of these cations should also be sensitive to the nature of the substituents. Indeed, as seen in Table 1, this does seem to be the case. Most notable is the observation that the absorption maxima of the α-CF_3 and bis-α-CF_3 derivatives **5** and **6** are shifted 20 nm and 50 nm, respectively, to lower wavelengths than the corresponding α-methyl derivatives.

Quinone Methide Formation.—Previous evidence for the importance of the resonance contributor **B** of eqn. (1) has been the observation of products of nucleophilic substitution of the methoxy group in the solvolysis reactions involving the cations **5** and **6**.[11,35–37] These products arise from nucleophilic addition at C4 of the aromatic ring, followed by loss of methanol. In water, a quinone methide is an intermediate, and indeed the species **15** has been observed and characterized, and its further reactions studied.[11,37]

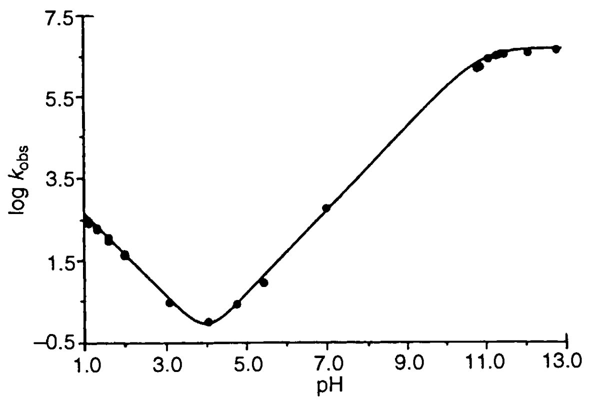
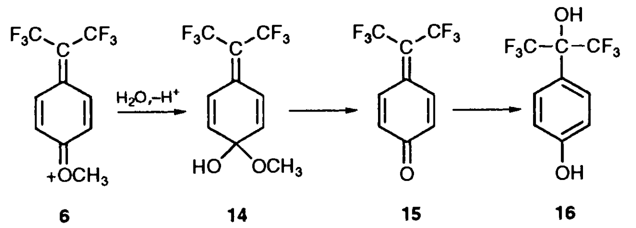
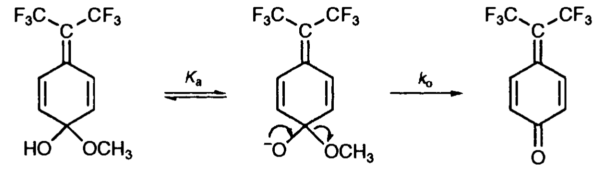


Fig. 5 Rate–pH profile for the breakdown of the hemiacetal **14** in aqueous solution. Rate constants were obtained by following the formation of the quinone methide at 280 nm. The curve is drawn according to eqn. (2), using parameters given in the text.



The cation **6** is observed on irradiation of its precursor **13** even in aqueous solution, although the decay at 2 × 10^7 s^{-1} is reaching the apparatus limit. At the completion of this decay a new, relatively weak, absorbance centred at 260 nm has appeared. This is not stable, and more slowly evolves, resulting in a third, more strongly absorbing, species with λ_{max} at 280 nm. This species, which is, in fact, not itself stable at very long times, is the quinone methide **15** previously identified.[11,37] The 260 nm transient can thus be identified as the hemiacetal **14**, the precursor of this species.

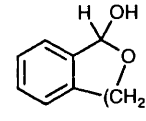
The breakdown of the hemiacetal to the quinone methide is thus a slower process than the hydration of the cation, the usual situation for such systems.[21,38–41] With the ease of access into the present system with flash photolysis, it is possible to obtain a full rate–pH profile for the hemiacetal breakdown. This is shown in Fig. 5, and takes the form expected for such a process,[21,38–41] with catalysis by H^+ and OH^-, and kinetic saturation in base due to ionization of the hemiacetal OH.



The rate constants can be fit to the rate law given in eqn. (2) where k_H is the catalytic coefficient for H^+, K_a is the dissociation

$$k_{obs} = k_H[H^+] + \frac{k_o K_a}{K_a + [H^+]} \qquad (2)$$

constant for the hemiacetal and k_o is the rate constant for the breakdown of ionized hemiacetal. Non-linear least-squares fitting of k_{obs} provides $k_H = 3.4 \times 10^3$ dm^3 mol^{-1} s^{-1}, $k_o = 4.3 \times 10^6$ s^{-1}, and $pK_a = 11.0$. This represents one of the few direct measurements of a dissociation constant for a hemiacetal, in fact the first such measurement for an acyclic version where the expulsion of alkoxide is irreversible (in water). Measurements have been made for cyclic hemiacetals, such as α- and β-D-glucose (pK_a = 12.5 and 12.2 respectively)[42] and the benzaldehyde derivatives **17** and **18** (12.3 and 12.4).[43] As seen in



17, *n* = 1
18, *n* = 2

the comparison with the above numbers, the hydroxy group in **14** is about an order of magnitude more acidic than in these previous examples. This may be related to the presence of the electron-withdrawing CF_3 groups.

Experimental

2-Fluoro-1-(4-methoxyphenyl)ethyl chloride (**10**),[11] 2,2-difluoro-1-(4-methoxyphenyl)ethyl chloride (**11**),[11] 2,2,2-trifluoro-1-(4-methoxyphenyl)ethyl bromide (**12**),[16] and 1,1,1,-3,3,3-hexafluoro-2-(4-methoxyphenyl)-2-propyl bromide (**13**)[11] have been described previously. Solutions employed in the flash photolysis experiments were prepared by adding a small amount of a stock solution (~0.1 mol dm^{-3}) of **10**–**13** in acetonitrile to the appropriate TFE–water mixture to give a final concentration of ~1 × 10^{-4} mol dm^{-3}. The 4-methoxyphenethyl cation **1** was generated by photoprotonation of 4-methoxystyrene,[19,25] and above 20% water in TFE, by the photoheterolysis of 4-methoxyphenethyl acetate.[19] The 4-methoxycumyl cation **2** was generated by photoprotonation of 4-methoxy-α-methylstyrene.[25] Flash photolysis experiments were carried out with 248 nm irradiation employing a Lambda-Physiks excimer laser. The details of this equipment have been described elsewhere.[18–20]

Acknowledgements

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