three to four times to a freeze–thaw procedure with highest purity N_2 (deoxygenated, dried, and passed over potassium-coated charcoal). The CH_2Cl_2 solvent or solution was added to the dimeric σ complex, and the reaction mixture was flushed with highest purity N_2 or O_2 for the period given in Table II (25 °C, strict exclusion of light). After completion of the reaction, the solvent was evaporated at ambient temperature, the residue was dried, and the percentage composition of the products was determined by UV and ^{1}H NMR as described in A.

UV Spectroscopic Determination of the Half-Periods of the Dimeric σ Complexes 2b–d at Ambient Temperature (for Results, See Table IIIA). (A) With Exclusion of Light. Purified acetonitrile was purged for 60 min with highest purity N_2 in a 1-cm UV cuvette covered with aluminum foil and equipped with a stopcock; **2** was added with continued N_2 flushing, the stopcock was closed, and UV measurement commenced immediately. The initial concentration of **2** was determined retrospectively from the three isosbestic points between 550 and 230 nm, and the progress of the reaction was followed by monitoring extinction at 400 nm.

(B) With Intermittent Exposure to Daylight. The reaction was carried out as described in A, with the closed cuvette intermittently being exposed to daylight (1–2 s each time).

^{1}H NMR Spectroscopic Determination of the Half-Periods of the Dimeric σ Complexes 2b–d, with or without π Donors Added (at 30 °C, with Exclusion of Light (for Results, see Table IIIB). To a solution of 0.1 mmol of the dimeric σ complexes (perchlorates) (**2b**, R = CH_3, 798 mg; **2c**, R = C_2H_5, 826 mg; **2d**, R = $CH(CH_3)_2$), 854 mg) in CD_3CN/CH_2Cl_2 (1:1 v/v, 1 mL) was added 0.15 mmol of **1** (**1a** = 43 mg, **1b** = 45 mg, **1c** = 49 mg, and 1,3,5-tripiperidin-1-ylbenzene, 49 mg), respectively. Decomposition of the educts **2** (30 °C, with exclusion of light) was followed by ^{1}H NMR, and the individual percentage composition was calculated from the integrals.

Flash Photolysis Measurements. A conventional flash photolysis apparatus[9a] was used to follow the decay of radicals **1c**$^{•+}$ produced by excitation (λ_{exc} > 400 nm) of ca. 10^{-5} M solution of **2c** (X = ClO_4) in acetonitrile (Merck reagent grade); observation at λ_{obs} = 800 nm, pathlength of the cuvette 10 cm. Oxygen was removed by bubbling pure nitrogen (O_2 content < 6 ppm) for 30 min. The influence of oxygen on the decay of **1c**$^{•+}$ was studied in air-saturated solution.

A home-built laser flash apparatus with signal averaging[9b] (time resolution ca. 0.25 μs) was used to measure the quantum yield of photodissociation of **2c** and the transient spectra of intermediates and to follow the reaction between **1c**$^{•+}$ and **1a** or **1c**, respectively (concentrations of **1a**, from 5×10^{-4} to 1×10^{-2} M); optical pathlength of the (flow through) cuvette 1 cm, concentration of **2c** ca. 10^{-4} M.

Acknowledgment. We express our thanks to P. Fischer for helpful discussions and also for the translation of this contribution. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Laser Flash Photolysis of 9-Fluorenol. Production and Reactivities of the 9-Fluorenol Radical Cation and the 9-Fluorenyl Cation

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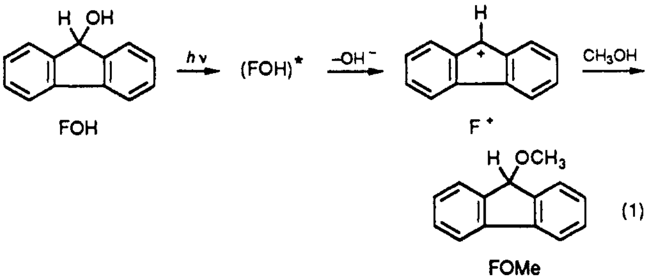
Abstract: Two recent flash photolysis investigations of 9-fluorenol (FOH) in aqueous methanol have reached conflicting conclusions regarding the spectrum and lifetime of the 9-fluorenyl cation (F^+). Gaillard, Fox, and Wan (GFW) (*J. Am. Chem. Soc.* **1989**, *111*, 2180) attributed to F^+ a transient at 640 nm with lifetimes in the microsecond range, while Mecklenburg and Hilinski (MH) (*J. Am. Chem. Soc.* **1989**, *111*, 5471) concluded that F^+ was the transient they observed at 515 nm which formed and decayed in <20 ps. MH ascribed the 640-nm transient to the 9-fluorenol radical cation ($FOH^{•+}$). In the present study $FOH^{•+}$ has been produced in aqueous trifluoroethanol and in aqueous acetonitrile by reacting FOH with $SO_4^{•-}$ produced by 248-nm photolysis of the $S_2O_8^{2-}$ ion. The $FOH^{•+}$ so formed has absorptions with λ_{max} at 395, 595, and 645 nm and decays with lifetimes of 10–100 μs. We conclude therefore that the 640-nm transient is $FOH^{•+}$, and not F^+. $FOH^{•+}$ forms in the direct photolysis by two-photon ionization, a conclusion reached on the basis of the quadratic dependency of the 640-nm absorbance on the intensity of the exciting light. The radical cation of fluorene has been produced in aqueous acetonitrile as well, both by photoionization and by reaction with $SO_4^{•-}$; this species has λ_{max} at 365, 590, and 645 nm, and a lifetime similar to that of $FOH^{•+}$. The 515-nm transient is observed as a relatively long-lived species (30 μs) upon photolysis of FOH in 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP). This transient is not quenched by oxygen, its decay is accelerated by nucleophiles such as water and trifluoroethanol, and 1,1,1,3,3,3-hexafluorisopropyl 9-fluorenyl ether is obtained as the only product of photolysis. We conclude therefore that the 515-nm transient is the ground-state 9-fluorenyl cation, which has also been observed by MH in aqueous methanol where its lifetime is <20 ps. The remarkably weak nucleophilicity of HFIP is further demonstrated by kinetic and product experiments that show that F^+ undergoes electrophilic substitution of benzene in competition with capture by this solvent.

Wan and co-workers have found that 9-fluorenol (FOH) undergoes an efficient photosolvolysis in methanol or aqueous methanol resulting in the production of 9-methoxyfluorene (FOMe).[2a,b] A mechanism was proposed with an intermediate 9-fluorenyl cation (F^+) produced by photoheterolysis of excited FOH. The relative ease of formation of the cation even with the poor leaving group OH^- was attributed to the enhanced reactivity of excited states leading to $4n$ π systems.[2]



(1)

This work has prompted investigations employing time-resolved methods. Gaillard, Fox, and Wan (GFW), using nanosecond laser

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[1] (a) University of Toronto. (b) Max-Planck-Institut.

[2] (a) Wan, P.; Krogh, E. *J. Chem. Soc., Chem. Commun.* **1985**, 1027. (b) *J. Am. Chem. Soc.* **1989**, *111*, 4887. (c) Wan, P.; Krough, E.; Chak, B. *J. Am. Chem. Soc.* **1988**, *110*, 4073.

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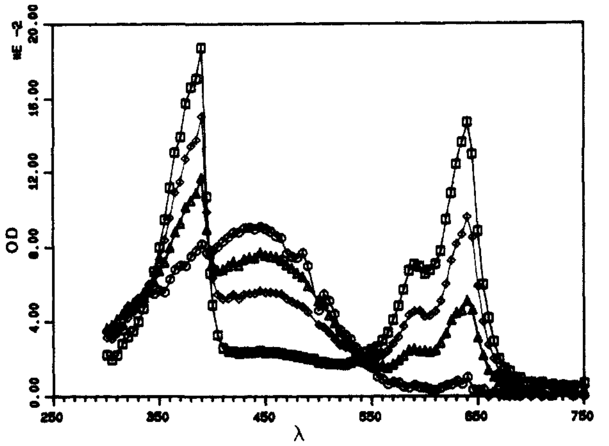

Figure 1. Absorption spectra upon 248-nm photolysis of 0.2 mM FOH and 0.1 M $(NH_4)_2S_2O_8$ in 1:1 trifluoroethanol–water. Points were recorded at times after the end of the pulse of 5 ns (circles), 300 ns (triangles), 600 ns (diamonds), and 2 μs (squares). Optical densities (OD) given in Figures 1–4 are in arbitrary units.

flash photolysis equipment, observed a transient at 640 nm upon photolysis of FOH and proposed that this was due to F^+.[3] This species had lifetimes ranging from 0.6 to 7.5 μs in 100% MeOH to 1:9 MeOH–H_2O. It was claimed that support for the assignment as cation was the observation of a similar transient absorption upon pulse radiolysis of 9-chlorofluorene in isooctane containing a small amount of CCl_4. The analogy was drawn here to triphenylmethyl chloride, which produces the readily identifiable triphenylmethyl cation under similar conditions.[4,5] GFW also noted that there is an absorption with a maximum at 660 nm when FOH is dissolved in concentrated sulfuric acid.[3,6]

More recently, Mecklenburg and Hilinski (MH), employing a picosecond flash photolysis apparatus, reported a transient with λ_{max} at 515 nm and a lifetime of less than 20 ps in aqueous methanol and suggested that this was F^+.[7] The same transient was observed with 9-chlorofluorene as precursor, and a similarly absorbing, but slightly longer lived species, was obtained with 9-methyl-9-fluorenol. MH suggested that the 640-nm transient of GFW was the *radical* cation of 9-fluorenol ($FOH^{\bullet+}$). They generated a species with λ_{max} at 635 and 590 nm which was attributed to $FOH^{\bullet+}$ by reaction in acetonitrile of FOH with excited chloranil. They also noted the similarity with a literature spectrum for the radical cation of fluorene itself.[8]

We have been studying the reactivities of various carbocations generated in aqueous solution by flash photolysis.[9] The xanthylium cation has a lifetime of 43 μs in 1:4 acetonitrile–water[9b] while the diphenylmethyl cation is too short-lived (<10 ns) to be observed in this solvent with our nanosecond laser apparatus.[9d] Both these cations have structural features found in F^+, and each are formed thermally from the alcohol more easily in acid solutions,[10] in particular the xanthylium cation which is stable in 10% H_2SO_4. Thus, unless there is a dramatic difference between thermodynamic and kinetic stability, the lifetime of the transient observed by GFW seemed inconsistent with our results. In consequence we have conducted an investigation into the 9-fluorenol system. We report here further evidence that the 640-nm species is the radical cation. We also show that the 515-nm species can be generated as a relatively long-lived transient upon photolysis of FOH in the weakly nucleophilic alcohol 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP) and that this species exhibits reactivities characteristic of a carbocation.

After submission of this manuscript we were informed of further experiments by Gaillard and Fox, who now agree that the 640-nm transient is $FOH^{\bullet+}$. They have shown that this transient forms in a two photon process as we have done and have also generated $FOH^{\bullet+}$ independently.[11]

Radical Cation of 9-Fluorenol. Our approach to this species is based on the reaction of FOH with photochemically generated $SO_4^{\bullet-}$. This involved the photolysis of aqueous solutions containing 0.1–0.4 mM FOH and 0.1 M $(NH_4)_2S_2O_8$. With such concentrations the majority of the light is absorbed by the $S_2O_8^{2-}$ ion, which undergoes homolysis to give the one electron oxidant $SO_4^{\bullet-}$.[9e] Figure 1 shows a typical experiment; the spectrum immediately after the laser pulse is that of $SO_4^{\bullet-}$, which has a broad absorption band with λ_{max} at 450 nm.[12] This disappears, with the buildup of absorbance in the regions 350–400 nm and 550–650 nm, with new λ_{max} at 395, 595, and 645 nm and reasonable isosbestic points at 345, 400, and 545 nm.[13] The rates for this process are dependent upon the concentration of FOH, with second-order rate constants of 6×10^9 M^{-1} s^{-1} in 1:1 trifluoroethanol–water and 4×10^9 M^{-1} s^{-1} in 1:4 acetonitrile–water. At longer times the new absorption bands decay at the same rate, with no significant absorption appearing at >300 nm. The decay is not perfectly exponential, but appears to involve a combination of first-order and second-order processes.[14] Approximate lifetimes in the two solvent systems investigated were 10–100 μs. The overall behavior, both in terms of appearance and disappearance of transients and rates for these processes, was the same in argon- and oxygen-saturated solutions. This is in agreement with the behavior of radical cations, which are typically unreactive toward oxygen.

The 595, 645 nm absorptions are very similar to those observed by MH and assigned to $FOH^{\bullet+}$ for the reaction in acetonitrile of FOH and excited chloranil.[7] The overall pattern including the band at lower wavelength is similar to that observed with fluorene itself, upon both photoionization and reaction with $SO_4^{\bullet-}$ in aqueous solutions (next section) and upon reaction with $NO_3^{\bullet}$ in acetonitrile.[15] The two bands at higher wavelength have previously been reported for reaction of fluorene with excited chloranil in acetonitrile.[8] That these bands represent the radical cations and not products of their further reaction can be deduced by consideration of the absorption spectra that would be expected for these products. For example, deprotonation at H9, a well-documented reaction of benzylic-type radical cations,[16] would produce from the fluorene radical cation the 9-fluorenyl radical, which has an absorption with λ_{max} at 500 nm.[3,17] The other common reaction of benzene-type radical cations in aqueous solutions is a nucleo-

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(10) The generation of F^+ from FOH in sulfuric acid solutions has been questioned by Olah and co-workers; they were unable to generate the cation from several precursors in superacids.[10b] (b) Olah, G. A.; Prakash, G. K. S.; Liang, G.; Westerman, P. W.; Kunde, K.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1980**, *102*, 4485.

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(13) These isosbestic points are best seen in the experiment in 1:1 trifluoroethanol–water. In aqueous acetonitrile, the decay of the radical cation is somewhat faster and deviations from isosbestic behavior are observed.

(14) (a) Second-order decay processes are frequently observed with radical cations of aromatic compounds.[14b,c] (b) Parker, V. D. *Acc. Chem. Res.* **1984**, *17*, 243. (c) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55.

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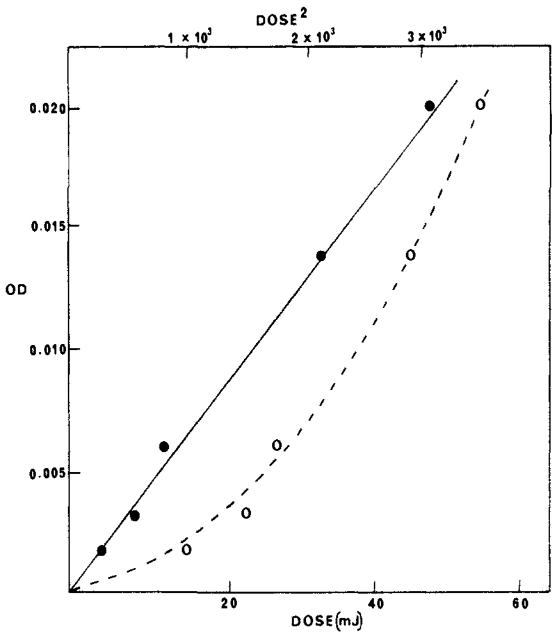

Figure 2. Dependence of the optical density of the transient at 640 nm on the intensity of the 248-nm light in the photolysis of 0.3 mM 9-fluorenol in 1:10 acetonitrile–water. The dose delivered by the laser was attenuated by calibrated neutral density filters. The optical density was measured in a cell with a 4-mm path length for the window 100–200 ns after the laser pulse. The open circles show the dependency plotted against the first power of the intensity, the closed circles against the square of the intensity.

philic ring substitution leading to cyclohexadienyl radicals,[9c,18] but these do not absorb above 400 nm.[9c,19] The nature of the products of the further reaction of the radical cations of fluorene and 9-fluorenol are at present unknown. Deprotonation from H9 does not appear to be an important reaction, since with the fluorene system the 9-fluorenyl radical is not observed in argon-saturated solutions after the decay of the radical cation.

We also investigated the direct photolysis of 9-fluorenol in methanol–water and in acetonitrile–water and observed the 640-nm transient reported by GFW. We find clear evidence that this species arises from a two-photon process.[20] As shown in figure 2, a plot of the optical density at 640 nm immediately after the laser pulse is approximately linear with the square of the intensity of the light delivered to the solution, while a plot against the first power of the intensity is curved significantly upward. We therefore support the conclusion of MH that this band represents the radical cation of 9-fluorenol and propose that it arises in these laser experiments from two photon ionization. One further important conclusion relates to the pulse radiolysis experiments of GFW. It is well-established with triphenylmethyl chloride that the Ph_3CCl radical cation is an intermediate, and that this undergoes C–Cl fragmentation to produce the Ph_3C^+.[5] It now appears that the transient observed by GFW was a radical cation, in this case of 9-chlorofluorene. This does not undergo fragmentation, presumably because the carbenium ion so produced is considerably less stable.

Radical Cation of Fluorene. In order to provide further support for the assignment of the spectrum of $FOH^{\bullet+}$ we have generated the radical cation of fluorene itself, a molecule that cannot undergo C–O cleavage. With this compound in aqueous acetonitrile, relatively strong signals for the radical cation could in fact be obtained by direct photolysis. Figure 3A shows the result with an oxygen-saturated solution, where a relatively clean spectrum of the radical cation is produced. This has bands with λ_{max} at 365, 590, and 645 nm, in positions similar to those observed with $FOH^{\bullet+}$, the most significant difference being a 30-nm shift in the band at low wavelengths. The dependency on laser dose is again parabolic, evidence for two-photon ionization. As shown by the spectrum at intermediate time in Figure 3A the bands decay at the same rate, leaving little residual absorption above 300 nm. As with $FOH^{\bullet+}$ the decay cannot be fit by a simple exponential, but appears to follow a combination of first- and second-order kinetics. The approximate lifetime in 2:3 acetonitrile–water is 20 μs, similar to $FOH^{\bullet+}$. Figure 3B shows the result obtained with the same solution irradiated after saturation with argon. In this experiment the 365-nm band of the radical cation lies under a more intense signal. This can be assigned to the triplet of fluorene,[4] which is quenched in the oxygen-saturated solution.[21] Experiments employing $SO_4^{\bullet-}$ in aqueous acetonitrile and $NO_3^{\bullet}$ in 100% acetonitrile[15] to generate the radical cation were also carried out with fluorene. The same transient (365, 590, 645 nm) was formed. The bimolecular rate constant for the reaction of fluorene and $SO_4^{\bullet-}$ in 2:3 acetonitrile–water is 2.5×10^9 M^{-1} s^{-1}.

Under the same conditions (optical density at 248 nm, solvent, laser intensity) photolysis of fluorene results in considerably more radical cation (10–50 times) formed by biphotonic photoionization than does photolysis of 9-fluorenol (assuming the same extinction coefficients for the two radical cations). This is probably a reflection of the difference in the lifetimes of the excited states of the two species. Wan and Krogh have recently concluded that fluorescence lifetimes of 9-fluorenol in aqueous acetonitrile are of the order of 20 ps, while those of fluorene itself are in the ns range (5.6 ns in 4:1 acetonitrile–water).[2b] They argued that this difference is caused by the additional deactivation pathway—photoheterolysis—available to the alcohol. For an electron ejection by a two-photon process, the probability must be greater with a longer lived excited state, since there is more opportunity for a second photon to be absorbed in the laser pulse before deactivation occurs.

9-Fluorenyl Cation. In recent experiments, we have realized that carbocations can be remarkably long-lived in the solvent HFIP.[22] We therefore investigated this solvent to see if the 515-nm band that MH attributed to F^+ could be observed with nanosecond equipment. Indeed photolysis of FOH in this solvent produced a strongly absorbing signal with λ_{max} at 515 nm with a lifetime of 30 μs. A typical series of spectra are illustrated in Figure 4. There is a clearly defined shoulder on the 515-nm band at 480 nm; this shoulder is also apparent in the spectrum reported by MH although less well defined. Our spectra show two additional bands at lower wavelengths (λ_{max} of 260 nm[23] and 340 nm) which decay with the same kinetics and therefore must represent the same intermediate. All the absorptions are formed with a linear dependency upon laser dose, and thus the process generating the intermediate is monophotonic. The decay is exponential, and as seen in Figure 4, there is no residual absorbance. Oxygen has no effect on the decay, but decay is accelerated by nucleophiles such as water, strong evidence that the intermediate has cationic character. Experiments were also performed with excitation at 308 nm, and an identical behavior was observed.

We therefore conclude that the transient at 515 nm seen by MH in aqueous methanol is the 9-fluorenyl cation. Moreover, since this same transient is observed in the solvent HFIP at times in the microsecond regime, it must be a ground-state cation. Such a conclusion was reached by MH on the basis of a comparison of the spectrum of the transient 9-methyl-9-fluorenyl cation with one obtained in sulfuric acid. Wan and Krough have discussed

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(20) (a) Radical cations of simple benzene derivatives have previously been generated by biphotonic ionization in aqueous solution.[9c,20b,c] (b) Steenken, S. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 113. (c) Steenken, S.; Warren, C. J.; Gilbert, B. C. *J. Chem. Soc., Perkin Trans. 2* **1990**, 335.

(21) The triplet *is* observed in the experiment in the oxygen-saturated solution, but it decays within 40 ns. In the argon-saturated solution the triplet and the radical cation decay at similar rates.

(22) McClelland, R. A.; Steenken, S. To be published.

(23) This absorption occurs in the same region where the precursor FOH absorbs. Since the quantity measured in our experiments is the change in optical density, the absolute intensity of the band must be higher and there may be a slight shift in the true λ_{max}.

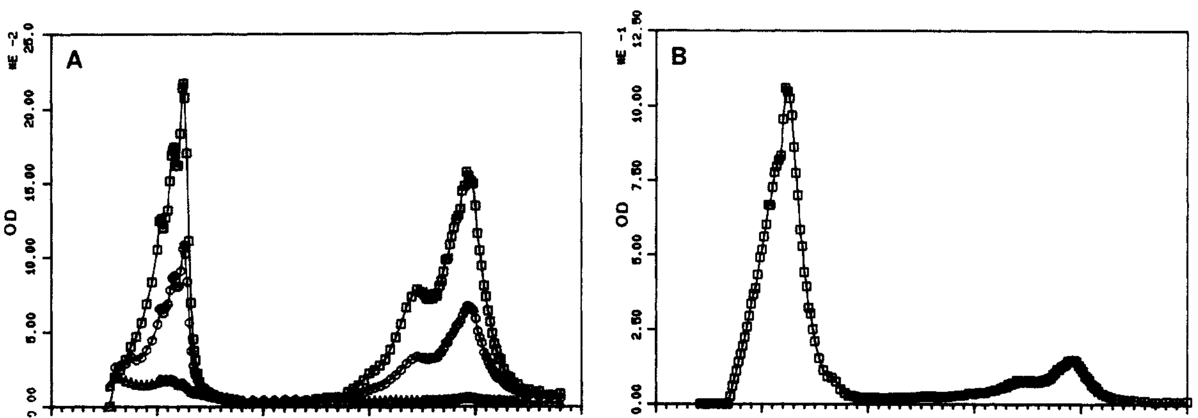

Figure 3. Absorption spectrum observed on 248-nm photolysis of 0.3 mM fluorene in 2:3 acetonitrile–water with oxygen saturation (A) and argon saturation (B). The solutions also contained 1% CH_2Cl_2 to scavenge electrons. Spectra were obtained at times after the pulse of 80 ns (squares in A and B), 20 μs (circles), and 100 μs (triangles). Note that the optical density scales in A and B are different and that the initial optical densities at 645 nm are similar in the two experiments.

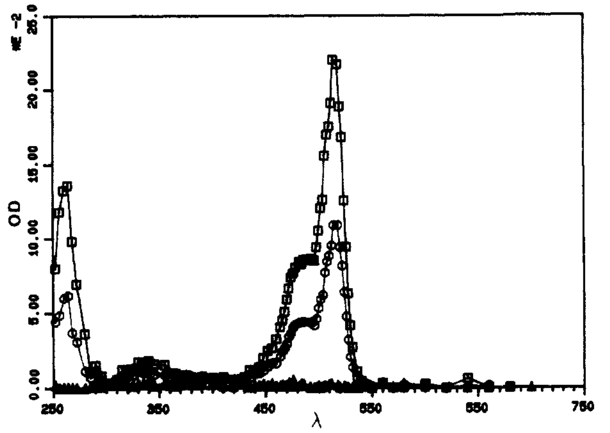

Figure 4. Absorption spectrum (argon or oxygen saturation) observed on 248-nm photolysis of 0.3 mM 9-fluorenol in 1,1,1,3,3,3-hexafluoroisopropyl alcohol. Spectra were recorded at times of 1 μs (squares), 40 μs (circles), and 400 μs (triangles).

the possibility that the photoheterolysis of 9-fluorenol proceeds on the excited-state surface to produce initially an excited-state fluorenyl cation.[2b] However the evidence of MH is that the 515-nm band, now assigned also to the ground-state cation, forms promptly (<20 ps), with no indication of the intermediacy of an excited precursor.

Product analysis provides confirmation of the intermediacy of F^+. Photolysis of FOH in HFIP at 254 nm in a Rayonet reactor results in essentially quantitative conversion to 1,1,1,3,3,3-hexafluoroisopropyl 9-fluorenyl ether ($FOCH(CF_3)_2$), this being the only product observed by gas chromatography and NMR spectroscopy even after 90% of the original FOH has dissappeared. The GC experiment also shows the absence (<1%) of fluorene, 9,9′-bifluorene, and fluorenone, products that would arise from the 9-fluorenyl radical upon homolysis of FOH (or the ether).[2b] The relative unimportance of homolysis is also seen in the close similarity of the transient spectra in argon- and oxygen-saturated solutions. There is no additional absorbance around 500 nm in the former that would be characteristic of the radical. A further interesting feature of the photolysis in HFIP is that the ether product does not undergo photohomolysis, at least during the time required to convert 90% FOH. This contrasts with the situation in 50% aqueous methanol, where the ether, 9-methoxyfluorene, readily undergoes photohomolysis as it forms from FOH, such that its maximum yield is only 30%.[2b] The behavior in HFIP may reflect a more efficient photoheterolysis of FOH, or a less efficient photohomolysis of the ether. Both are in fact likely, the greater polarity of HFIP favoring heterolysis and the homolysis being disfavored because of the production of the less stable $(CF_3)_2CHO^\bullet$ radical.

Table I. Rate Constants at 20 °C for the Decay of the 9-Fluorenyl Cation in 1,1,1,3,3,3-Hexafluoroisopropyl Alcohol Containing Water and Trifluoroethanol

$[H_2O]$	% H_2O[a]	k, s^{-1} [b]	% TFE[a]	k, s^{-1} [b]
0	0	3.4×10^4	0	4.0×10^4
0.05	0.1	1.3×10^5	4.4	1.9×10^5
0.10	0.2	1.9×10^5	9.5	6.4×10^5
0.14	0.3	2.4×10^5	13.6	1.5×10^6
0.30	0.5	4.1×10^5	17.2	3.0×10^6
0.55	1.0	7.8×10^5	28.4	8.6×10^6
1.67	3.0	2.9×10^6	42.0	2.7×10^7
4.1	7.4	1.6×10^7		
6.5	11.7	4×10^7		

[a] Volume percent. [b] Uncertainties in the rate constants are ±3%, with a larger uncertainty for $k > 10^7$ s^{-1}.

The solvent HFIP clearly has a remarkable kinetic stabilizing effect for the 9-fluorenyl cation. To relate this behavior to that observed by MH in more reactive solvents, rate constants for solutions in HFIP containing water and trifluoroethanol have been measured. These are given in Table I. In each case the cosolvent was added to HFIP until the stage was reached where the rate of decay became too fast to be measured with our apparatus (>5 × 10^7 s^{-1}). The addition of either water or trifluoroethanol to HFIP accelerates the decay of the cation, but it is surprising how much can be added before the time-resolution limit is reached. In the case of water which was investigated at low concentrations, a plot of the rate constant versus $[H_2O]$ is approximately linear up to about 0.5 M, with a bimolecular rate constant of 1.5 × 10^6 M^{-1} s^{-1}. At higher concentrations, the rates increase more rapidly with added water, i.e. the rate constants are larger than expected on the basis of the initial behavior. This may be explained by a model where the water at low concentrations is tied up through hydrogen bonding with the OH of HFIP, but eventually a stage is reached where it becomes more free. MH reported rate constants for the decay of F^+ of >5 × 10^{10} s^{-1} in 9:1 water–methanol, and 3 × 10^{10} s^{-1} in 9:1 trifluoroethanol–water. The order of reactivity of alcohol solvents towards carbocations has now been established by both direct[9c] and indirect methods[24] to be methanol > water > trifluoroethanol. The present results illustrate the dramatic effect of adding a second CF_3 group. It should also be noted that even in supposedly 100% HFIP, we found that rate constants varied from one experiment to another, as is illustrated with the two entries in Table I.[25] This is undoubtedly related to water present in the solvent. HFIP samples employed in our experiments had water contents ranging from 0.05 to 0.1%, even

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(24) Richard, J. P.; Rothenburg, M. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1361.

(25) Reproducibility in replicate measurements in a single experiment was however excellent (±3%).

after drying by a literature procedure.[26] Considering that water has a significant accelerating effect, as shown in Table I, it is therefore unlikely that the rate constants that we have measured in the 100% HFIP reflect precisely the reactivity with the pure solvent. The possibility exists that in the dry solvent the rate could be lower by as much as a factor of 3.

Further evidence of the remarkably weak nucleophilicity of HFIP is that even benzene can compete with this solvent for F^+. This was initially indicated by transient experiments, which showed that the decay of F^+ is accelerated by benzene, with rate constants linear in benzene concentration up to 0.1 M and a bimolecular rate constant of 2×10^6 M^{-1} s^{-1}. Proof comes from product studies, which showed that upon photolysis of FOH in HFIP containing benzene 9-phenylfluorene is formed, along with the hexafluoroisopropyl ether as the only products.[27] The 9-phenylfluorene must arise from electrophilc substitution. The evidence for this is the absence of radical-derived products in any of the photolyses in HFIP coupled with the actual observation of benzene accelerating the decay of cation. *In conclusion, the 9-fluorenyl cation generated in HFIP undergoes electrophilic substitution of benzene in competition with capture by the solvent.*

This study reports the first direct measurement of a rate constant for the reaction of a carbocation intermediate in HFIP. From studies of ground-state solvolysis reactions this solvent is regarded as being weakly nucleophilic, but it is surprising how large the effect is, compared, for example, to trifluoroethanol, which is also considered to be weakly nucleophilic. Solvent nucleophilicty parameters N or N_{OTs} would suggest that there is a little over an order of magnitude difference between trifluoroethanol and the less reactive 97:3 HFIP–water.[26] The directly measured results for F^+ show that the difference between these two solvents is greater than 10^3 ($\sim 10^{10}$ s^{-1} in trifluoroethanol and 2.9×10^6 s^{-1} in 97:3 HFIP–water). Removing the last 3% of water to go to 100% HFIP results in a further decrease of 10^2.

There are two other comments regarding the kinetics. (i) At high laser doses the decay becomes faster, by as much as 50% at a dose of 80 mJ as compared to 3 mJ. Moreover, a close examination of the fit of the experimental data to the exponential equation reveals that there are slight deviations, unlike the situation at low laser intensities where excellent fits are obtained. We attribute this behavior to the presence of the anion which must accompany formation of the cation in the photoheterolysis. This anion is initially hydroxide, but this should react rapidly with the acidic OH of HFIP to generate the corresponding alkoxide ion. We suspect that at high laser doses some fraction of the cation reacts with this anion, and thus the decay is faster. Moreover since this anion is present at all times in concentrations equal to that of the cation this combination will follow second-order kinetics. (ii) There is also a dependency of the decay on the concentration of the precursor FOH, with the rate higher at higher concentrations. This can be attributed to a reaction of the cation with the excess FOH present after photolysis. A plot of rate constant versus [FOH] is reasonably linear,[28] giving a second-order rate constant of 5×10^6 M^{-1} s^{-1}. A simple interpretation is that this reaction involves combination with the alcohol group of FOH. However the experiment described above with benzene suggests that it could also be due to reaction with one of the aromatic rings.

Experimental Section

9-Fluorenol and fluorene were commercial samples and were recrystallized before use. Fluorenone, 9,9′-bifluorene, and 9-phenylfluorene were obtained commercially and used as received. 1,1,1,3,3,3-Hexafluoroisopropyl alcohol was treated at room temperature with 4A molecular sieves for 4 days, decanted on to fresh molecular sieves, and distilled under a nitrogen atmosphere through a 40-cm Vigreux column, with a considerable amount of the head and tail fractions being discarded.

The laser apparatus has been described.[9a] In brief, solutions were prepared with OD/cm of 0.5–3.0 at 248 nm, or 0.05 at 308 nm. These were photolyzed with ~20-ns pulses of 248-nm (KrF) or 308-nm (XeF) light from Lambda Physik excimer lasers. The optical signals were digitized simultaneously by Tektronix 7612 and 7912 transient recorders, which were interfaced with a DEC 11/73 computer, which process controlled the laser apparatus and (pre)analyzed the data. The kinetic experiments with benzene present were carried out with 308-nm irradiation.

Products in HFIP. (a) NMR. FOH (2 mg) was dissolved in 3 mL of HFIP and the solution photolyzed at 254 nm in a Rayonet reactor for 20 min. The solvent was removed on a rotary evaporator, the residual material dissolved in $CDCl_3$, and a 200-MHz NMR spectrum recorded. This revealed the presence of unreacted FOH, which is characterized by a singlet at 5.58 ppm for the 9-H proton and a multiplet from 7.2 to 7.7 ppm. New peaks appeared at 4.35 ppm (septet with $J = 5.9$ Hz), 5.84 ppm (singlet), and in the aromatic region overlapping with the FOH signals. The 4.35 ppm septet and 5.84 ppm singlet were in a 1:1 ratio. Addition of HFIP showed that the septet was not due to unremoved solvent. We therefore assign these new signals to 1,1,1,3,3,3-hexafluoroisopropyl 9-fluorenyl ether. In the particular experiment described here the ratio of the 9-H protons at 5.58 and 5.84 ppm indicated a 50% conversion of FOH to the ether.

(b) GC. The assignment of the ether structure was confirmed by GC/MS. A solution prepared as described above was photolyzed for varying times, aliquots were periodically withdrawn, the solvent was evaporated, and the residual was taken up in CH_2Cl_2. This solution was injected into a Varian 3400 gas chromatograph with FID detector and a Durabond-1 fused-silica open tubular column. As the photolysis proceeded, the peak due to FOH was replaced by a single peak with lower retention time. The electron-impact mass spectrum of this new peak had *m/e* 332 (70, P = $FOCH(CF_3)_2$), 181 (83, P–$CH(CF_3)_2$), 165 (100, P–$OCH(CF_3)_2$). High-resolution MS 332.0638, $C_{16}H_{10}F_6O$ requires 332.0635.

In this experiment the only new signal which was observed as the FOH disappeared is that for the ether, even after 90% loss of FOH. Co-injection of the photolyzed solution with authentic samples of fluorene, 9,9′-bifluorene, and fluorenone showed that these all had retention times different from those of FOH and $FOCH(CF_3)_2$.

(c) GC, with Benzene Added. Photolysis was carried out as described above, with 0.1 M benzene present. A peak at longer retention time appeared (in addition to the peak for $FOCH(CF_3)_2$). The new peak had a retention time identical with that of an authentic sample of 9-phenylfluorene. Correspondence with this substance was verified by GC/MS, the peak from the photolysis, and the authentic sample having identical mass spectral parent ions and fragmentation patterns.

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[26] Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.

[27] Quantitatively there is less 9-phenylfluorene formed than predicted from the rate acceleration. We are currently investigating this through a detailed examination of this system, as well as the reactivities with other aromatic and alkene carbon nucleophiles. One explanation is that the initial reaction of F^+ and the aromatic compound producing the cyclohexadienyl cation (or a π complex) is reversible.

[28] These experiments were carried out with FOH concentrations in the range 0.1–1 mM, and low laser intensities so that the depletion of FOH was minimal.