Detection and Characterization of a Transient Zwitterion, the 9-Carboxylate-9-fluorenyl Cation, and Its Conjugate Acid[1]

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Abstract: Laser flash photolysis of 9-hydroxy-9-fluorenecarboxylic acid in hexafluoro-2-propanol (HFIP) generates a transient with λ_{max} at 495 nm that reacts with nucleophiles such as methanol and bromide and is insensitive to oxygen. In the presence of 0.15 M trifluoroacetic acid, a different transient with λ_{max} at 560 nm that also reacts with nucleophiles is formed. The 495 and 560 nm species are identified as a zwitterion (the 9-carboxylate-9-fluorenyl cation) and its conjugate acid (the 9-carboxy-9-fluorenyl cation), respectively. The assignment of the zwitterion is supported by the observation of infrared absorptions in the carboxylate region that are quenched by nucleophiles with rate constants similar to those obtained by UV−visible detection. Both the zwitterion and its protonated form are observed at intermediate acid concentrations, leading to an estimate of 1×10^{-2} M^{-1} for the equilibrium constant for the ionization of the 9-carboxy-9-fluorenyl cation in HFIP. Absolute rate constants for reaction of the zwitterion with alcohols, anionic nucleophiles, and substituted aromatics are reported and compared to data for other 9-fluorenyl cations.

There has been considerable recent interest in the generation of carbocations substituted with electron-withdrawing groups.[3−14] Despite initial assumptions concerning the intrinsic instability of these species, "electron-deficient" carbocations are now well-established intermediates in solvolysis reactions and have been generated under stable ion conditions. Several arylmethyl and diarylmethyl carbocations with either α-ester or trifluoromethyl groups have also been generated photochemically, and their reactivity toward nucleophiles has been measured directly using laser flash photolysis techniques.[15−17] The results for diphenylmethyl, 9-fluorenyl, and benzyl cations all indicate that α-ester-substituted cations are kinetically more stable than their hydrogen-substituted analogues.[12,15,17] By contrast, the replacement of the α-methyl hydrogens in the 4-methoxyphenethyl cation with fluorines leads to modest increases in reactivity, despite the fact that replacement of an α-methyl group with an α-trifluoromethyl has a large thermodynamic destabilizing effect.[16,18] The relatively small effect of fluorine substituents has been explained by a model in which the electron-withdrawing substituent forces positive charge away from the benzylic carbon to the 4-methoxy group. A number of theoretical studies have also addressed the relative importance of resonance stabilization and neighboring group participation in stabilizing cations substituted with formally electron-withdrawing groups.[19−21]

The 9-fluorenyl cation has not been observed in strong acid solution, even at low temperature, and has traditionally been considered to be thermodynamically unstable due to its antiaromatic (4n π) character.[22] However, this cation and a number of its 9-substituted derivatives have recently been characterized by laser flash photolysis experiments in nonnucleophilic solvents such as hexafluoro-2-propanol.[15,23−25] Most of the time-resolved experiments have used the appropriate 9-hydroxyfluorene as the cation precursor based on the efficient photodehydroxylation observed for a variety of 9-fluorenyl alcohols.[26−28] These studies have prompted a reexamination of the question of the antiaromatic nature of the 9-fluorenyl cation.[29] In fact, the thermodynamic stabilities of the 9-fluorenyl and 9-methyl-9-

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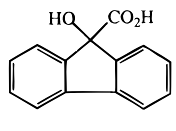
fluorenyl cations as measured by pK_R values for their reactions with water are only 5.5 and 2.5 kcal/mol lower than those of the analogous diphenylmethyl cations. These results combined with *ab initio* calculations of the structures and energies of 9-fluorenyl and diphenylmethyl cations have led to the hypothesis that there is little, if any, antiaromatic destabilization of the 9-fluorenyl cation.[29]

Our earlier work on the 9-carbomethoxy- and 9-*N*,*N*-dimethylthioformamidyl-9-fluorenyl cations[15,30] has prompted us to examine the photolysis of 9-hydroxy-9-fluorenecarboxylic acid (**1**) as a potential source of an α-carboxy-substituted carbocation for kinetic studies. This substrate belongs to a family of synthetic plant growth regulators known as morphactins that consist of substituted 9-fluorenecarboxylic acids.[31] The morphactins have widespread use as herbicides and plant growth regulators, and several biological studies indicate that their activity is light-dependent.[31−34] We report herein that photolysis of **1** in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) generates a transient zwitterion, **2**, which has been characterized using both UV−visible and IR spectroscopy, and which is converted to its protonated form **3** in the presence of trifluoroacetic acid (TFA). Related zwitterions have been proposed as intermediates in some nucleophilic substitutions and polyesterifications.[35−39] The closed form of the zwitterion (α-lactone, eq 1) has been detected spectroscopically but in most cases is only stable in matrices at low temperature. For example, when R = phenyl the zwitterion is thought to predominate even at −100 °C, although the α-lactone can be observed at lower temperatures.[37,40,41] This indicates that only a small energy barrier separates the cyclic isomer from its ionic form.[37] By contrast, α-lactones with perfluoroalkyl groups are considerably more stable and can in some cases be observed at room temperature.[39,42] This work provides the first direct detection of the transient zwitterionic isomer of an α-lactone at room temperature.



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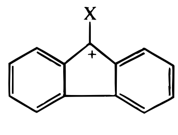
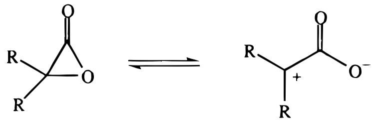


2, X = CO_2^-
3, X = CO_2H
4, X = CO_2CH_3
5, X = CH_3
6, X = H



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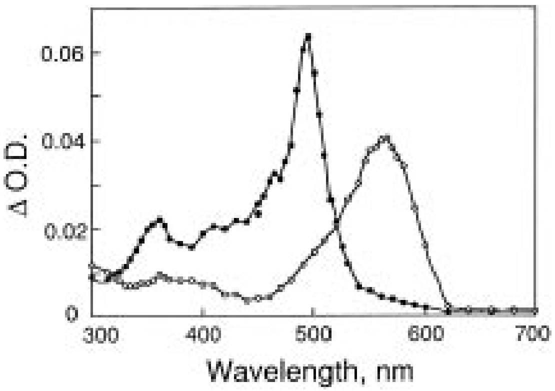
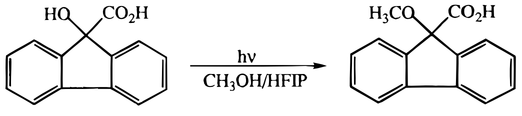


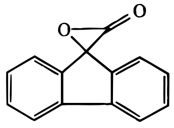
Figure 1. Transient absorption spectra measured after 308 nm laser excitation of 5 × 10^{-4} M 9-hydroxy-9-fluorenecarboxylic acid in HFIP (●, 1.6 μs) and 0.15 M TFA/HFIP (○, 0.8 μs).

Results and Discussion

Steady State Photolysis. Photolysis of an aerated solution of **1** in 10% methanol/HFIP at 300 nm gave one major product at conversions up to ~30%. This was identified as the methyl ether **7** (eq 2) by comparison of LC−MS and ^{1}H NMR data for the photolysis mixture with an authentic sample of **7**. Continued irradiation led to the formation of additional products, including 9-fluorenone and unidentified products of higher molecular weights. Irradiation of a number of 9-alkoxy-9-fluorenes has been shown to generate radical-derived products, which may account for the formation of additional photolysis products at high conversion.[28,43] Irradiation of the α-lactone **8**, which may be in equilibrium with zwitterion **2**, could provide an alternate explanation for the formation of 9-fluorenone since a number of related α-lactones have been shown to undergo thermal and photochemical decarbonylation.[38−40]



1 **7** (2)



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Irradiation of **1** in HFIP gave a product with LC and LC−MS data consistent with the formation of the hexafluoro-2-propyl ether. Thus steady state photolysis of **1** in alcohols is consistent with the formation of a carbocation that is trapped by solvent to give the corresponding ether as the primary product.

Laser Flash Photolysis: UV−Visible Detection. Laser excitation (308 nm, 8 ns/pulse) of 5 × 10^{-4} M **1** in HFIP generates the transient spectrum shown in Figure 1. The observed transient has λ_{max} at 495 nm, is formed within the laser pulse, and decays with first-order kinetics with a lifetime

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Table 1. Rate Constants for Reaction of 9-Substituted Fluorenyl Cations with Nucleophiles in HFIP at 20 °C[a]

	k_q, $M^{-1}\,s^{-1}$			
nucleophile	**2** ($X = CO_2^-$)	**4** ($X = CO_2CH_3$)	**5** ($X = CH_3$)	**6** (X = H)
methanol	$(1.6 \pm 0.1) \times 10^6$ $(2.4 \pm 0.6) \times 10^{6\,d}$	$6.7 \times 10^{6\,b}$	$(4.8 \pm 0.6) \times 10^{5\,c}$	$1.8 \times 10^{7\,b}$
ethanol	$(9.7 \pm 0.2) \times 10^5$	$4.6 \times 10^{6\,b}$	$(4.2 \pm 0.3) \times 10^{5\,c}$	$1.3 \times 10^{7\,b}$
2-propanol	$(5.4 \pm 0.1) \times 10^5$	$2.3 \times 10^{6\,b}$	$\leq 1 \times 10^5$	$7.9 \times 10^{6\,b}$
water	$\leq 1 \times 10^5$	$2.4 \times 10^{5\,b}$	$\leq 5 \times 10^4$	$1.5 \times 10^{6\,e}$
bromide	$(2.4 \pm 0.1) \times 10^6$ $(2.2 \pm 0.5) \times 10^{6\,d}$	$3.5 \times 10^{9\,b}$	$(4.5 \pm 0.1) \times 10^9$	$9.6 \times 10^{9\,b}$
chloride	$(4.7 \pm 0.2) \times 10^5$	$(4.7 \pm 0.1) \times 10^9$	$(8.4 \pm 0.3) \times 10^8$	$(9.9 \pm 0.3) \times 10^9$

[a] Unless otherwise noted all rate constants were measured by using UV/visible detection of the cation. Cations were generated by 308 (**2**, **4**, **6**) or 266 nm (**5**) irradiation of the corresponding alcohol. [b] Reference 15. [c] Plots are curved at high nucleophile concentrations. [d] IR detection at 1575 cm^{-1}. [e] Reference 24.

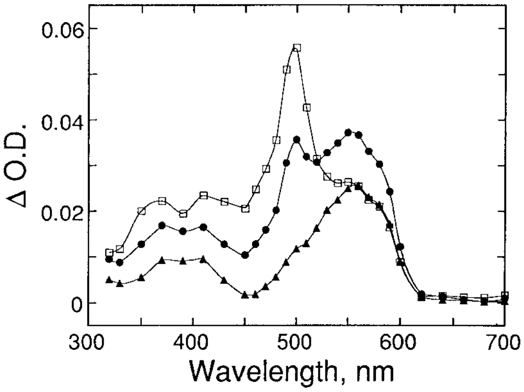

Figure 2. Transient absorption spectra measured at various times after 308 nm excitation of 1×10^{-3} M 9-hydroxy-9-fluorenecarboxylic acid in 0.065 M TFA/HFIP: (□), 80 ns; (●), 400 ns; (▲), 3.5 μs.

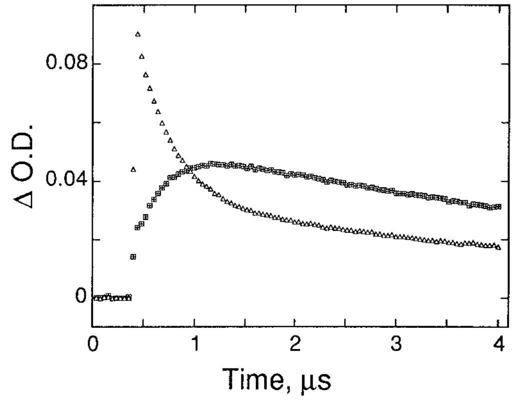

Figure 3. Transient decay and growth at 490 (△) and 560 (□) nm, respectively, following 308 nm excitation of 1×10^{-3} M 9-hydroxy-9-fluorenecarboxylic acid in 0.065 M TFA/HFIP.

of ~20 μs. The spectrum shown in Figure 1 has a weak absorption at 360 nm that decays with the same kinetics as the 495 nm band and is, thus, assigned to the same species. A weak long-lived residual absorption also contributes to the spectrum between 300 and 460 nm. The 495 nm transient is unaffected by oxygen but reacts with nucleophiles, consistent with its assignment to a cationic species. For example, plots of the observed rate constants for decay of the 495 nm transient as a function of nucleophile concentration gave rate constants of 1.6×10^6 and 2.4×10^6 $M^{-1}\,s^{-1}$ for reaction with methanol and bromide, respectively (Table 1). The lifetime of this transient is also sensitive to the concentration of the precursor alcohol; a plot of the observed rate constant for the decay as a function of [**1**] gives a rate constant of 2.6×10^7 $M^{-1}\,s^{-1}$.

A different transient spectrum with λ_{max} at 560 nm and a lifetime of ~10 μs is obtained upon 308 nm excitation of **1** in HFIP containing 0.15 M TFA (Figure 1). This species also exhibits cationic behavior in that it is insensitive to oxygen and reacts with nucleophiles. Rate constants of 7.2×10^6 and 4.0×10^9 $M^{-1}\,s^{-1}$ were measured for reaction of the 560 nm transient with methanol and bromide, respectively, in 0.15 M TFA/HFIP. At lower concentrations of TFA the transient spectra clearly show the presence of both the 495 and 560 nm species. For example, Figure 2 shows the transient spectra obtained in the presence of 0.065 M TFA at three different times after the laser pulse. Under these conditions a substantial fraction of the 495 nm signal decays with apparent first-order kinetics with an observed rate constant of 2.9×10^6 s^{-1}, whereas the 560 nm signal grows in with a similar rate constant of 3.1×10^6 s^{-1}. Both the 560 nm transient and the residual signal at 495 nm then decay on a somewhat longer time scale (Figure 3). The relative amounts of the two transients and the kinetics for their growth and decay depend on the concentration of TFA, as discussed in more detail below.

Excitation of **1** in HFIP with a 35 ps 266 nm laser pulse results in the formation of the same 495 nm transient that is observed in the nanosecond experiment. The transient is formed within the laser pulse, and no additional species are detected in the 400−700 nm region after 5 ns. The same 495 nm transient was generated by nanosecond laser flash photolysis in mixtures of HFIP and 2,2,2-trifluoroethanol (TFE). The observed rate constant for its decay increased with increasing percent of TFE, with an observed lifetime of ~100 ns in 80% TFE/HFIP. Plots of the observed rate constant vs percent TFE showed pronounced positive curvature. Attempts to generate **2** in HFIP in the presence of other strong acids such as perchloric, sulfuric, methanesulfonic, and hydrochloric were unsuccessful; in most cases the problems appeared to be related to decomposition of the precursor alcohol, **1**.

Both the radical cation $\mathbf{1}^{\bullet+}$ and the 9-carboxy-9-fluorenyl radical were generated independently in order to confirm that these two species were distinguishable from the two transients observed upon laser irradiation of **1**. Thus, 355 nm irradiation of chloranil in acetonitrile containing 1×10^{-3} M **1** leads to efficient quenching of the initially formed chloranil triplet at 520 nm. The quenching results in electron transfer to generate the chloranil radical anion at 450 nm[44] and $\mathbf{1}^{\bullet+}$ with λ_{max} at 650 nm, in good agreement with the spectra for a number of substituted fluorene radical cations.[15,45] The 9-carboxy-substituted radical was generated by hydrogen abstraction from 9-fluorenecarboxylic acid using *tert*-butoxyl radical generated by 355 nm photolysis of di-*tert*-butyl peroxide in nitrogen-saturated 1:1 peroxide/acetonitrile. The radical has λ_{max} at 555 nm, with a shoulder at 525 nm, in good agreement with the spectrum of the 9-carbomethoxy-9-fluorenyl radical[15] and is

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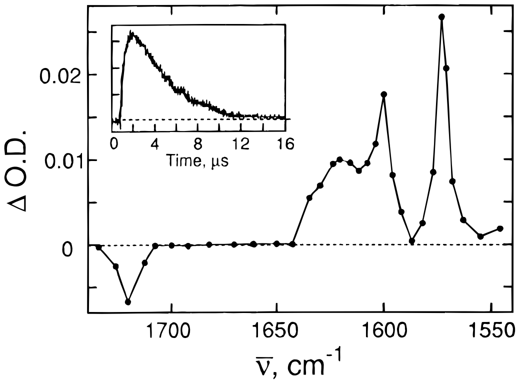

Figure 4. Time-resolved infrared spectrum obtained 1 μs after 308 nm excitation of 4 × 10^{-3} M 9-hydroxy-9-fluorenecarboxylic acid in HFIP. The inset shows the time-resolved absorbance trace at 1575 cm^{-1}; a first-order fit of this decay yields a lifetime of 5.4 μs.

clearly distinguishable from either of the two transients obtained upon photolysis of **1**.

Laser Flash Photolysis: IR Detection. The photolysis of **1** was also examined using laser flash photolysis with infrared detection. Excitation of **1** ((4−8) × 10^{-3} M in HFIP) results in bleaching of the carbonyl band of the starting material at 1721 cm^{-1} and the production of transient absorptions between 1625 and 1575 cm^{-1} (Figure 4). The lifetime is the same within experimental error at both 1620 and 1575 cm^{-1}, indicating that a single species is responsible for the observed IR signals. Further, this lifetime depends on the concentration of **1** and is in reasonable agreement with the lifetime for the 495 nm transient at the same concentration of **1** in the UV−visible experiments. For example, at 0.004 M **1**, the 495 nm transient decays with an observed rate constant of 1.4 × 10^5 s^{-1} similar to the value of ∼1 × 10^5 s^{-1} measured in the infrared experiment. The rate constants for the infrared measurements are in general slightly lower than those based on UV−visible detection, probably as a result of differences in experimental conditions for the two.

The IR signals decay more rapidly in the presence of nucleophiles such as methanol or bromide and are insensitive to oxygen. For example, the measured rate constant for quenching of the 1575 cm^{-1} signal by methanol of 1.2 × 10^6 M^{-1} s^{-1} agrees well with that measured using UV−visible detection (Table 1). The IR signals at 1600 and 1620 cm^{-1} are quenched by methanol with similar kinetics, further confirming that all three bands belong to the same species. The 1575 cm^{-1} transient reacts with bromide with a measured rate constant that is also in good agreement with that obtained by UV−visible detection (Table 1). Bromide quenching leads to the production of additional long-lived signals between 1600 and 1640 cm^{-1} that complicate the kinetic analysis in this region.

Attempts to carry out the IR experiments in the presence of sufficient concentrations of TFA to generate predominantly the 560 nm transient were unsuccessful due to strong IR absorptions of TFA in the region of interest. The use of other acids that are suitable for IR experiments was also unsuccessful, as noted above. No transients were observed in HFIP between 1855 and 1988 cm^{-1}, the typical region for absorptions due to α-lactones.[41,42,46] Note that this region is not shown in the spectrum in Figure 4 since independent experiments using two different laser diodes for the IR detection system were required to monitor the entire carbonyl range.

Assignment of Transients. The above observations are consistent with the assignment of both the 495 and 560 nm transients to cationic species. Our initial hypothesis was that zwitterion **2** and its protonated form **3** were responsible for the 495 and 560 nm transients, respectively. The effects of added TFA are consistent with the formation of two cationic species that are in acid−base equilibrium. This assignment is also supported by the following spectroscopic and kinetic evidence. The spectrum for **3** has λ_{max} at 560 nm and is virtually identical to the spectrum of the corresponding 9-carbomethoxy-9-fluorenyl cation (**4**) which also has λ_{max} at 560 nm.[15] The observed λ_{max} of 495 nm for the α-carboxylate-substituted cation **2** is in good agreement with data for most other 9-fluorenyl cations. For example, the parent cation and its 9-alkyl and 9-aryl analogues have absorption maxima between 480 and 540 nm.[23−25] Similarly the 9-*N*,*N*-dimethylthioformamidyl-9-fluorenyl cation has λ_{max} at 520 nm.[30] A similar shift to longer wavelength upon substitution of hydrogen by an α-carbonyl group has also been observed for substituted diphenylmethyl cations.[9]

Additional support for the assignment of the 495 nm transient to zwitterion **2** is provided by the IR results. The IR and UV−visible transients detected in HFIP are obviously the same species, based on their observed lifetimes and quenching behavior. More importantly, the observed IR transient has strong absorption in the region expected for a carboxylate anion. For example, a variety of carboxylate anions have strong infrared absorptions between 1650 and 1540 and 1450 and 1360 cm^{-1} for the asymmetric and symmetric C−O stretches, respectively.[47]

The kinetic results for reactions of the 495 and 560 nm transients with nucleophiles are consistent with their assignment to **2** and **3**, respectively. As noted above, there is a large difference between the observed rate constants for reaction of the two species with bromide while those for methanol are quite similar. The rate constant of 4 × 10^9 M^{-1} s^{-1} for reaction of the 560 nm transient with bromide is comparable to values (Table 1) reported for other 9-fluorenyl cations (e.g., 3.5 × 10^9 M^{-1} s^{-1} for **4**). By contrast, the 495 nm transient assigned to **2** is 3 orders of magnitude less reactive, a result that may be explained on the basis of electrostatic repulsion between the carboxylate group and the incoming anionic nucleophile. Such effects are not important for quenching by neutral nucleophiles such as alcohols, and the rate constants for methanol quenching of **2** and **3** are both similar to that for **4** (6.7 × 10^6 M^{-1} s^{-1}). Our apparent rate constant for reaction of **2** with bromide may, in fact, be only an upper limit since it probably includes a contribution from reaction of a small equilibrium concentration of **3** with bromide ion.

The evidence in favor of assignment of the two transients to zwitterion **2** and its protonated form **3** is compelling. Nevertheless, it is important to show that other potential intermediates are inconsistent with the available experimental data. For example, the assignment of one of the two transients to the radical cation of the precursor ($\mathbf{1}^{\bullet+}$) would be consistent with the observed reactivity toward nucleophiles and insensitivity toward oxygen. However, this possibility can be eliminated by the fact that $\mathbf{1}^{\bullet+}$ generated by photosensitized electron transfer has λ_{max} at 650 nm, in agreement with the known spectra for substitued fluorenyl radical cations.[15,45] The 9-carboxy-substituted fluorenyl radical can also be ruled out on the basis of an authentic spectrum for this radical generated by hydrogen abstraction from 9-fluorenecarboxylic acid.

Photodecarboxylation of arylacetic acids is a well-known reaction and could be a potential complication in the photolysis

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of alcohol **1**.[48-51] However, the parent 9-fluorenecarboxylic acid does not undergo efficient photodecarboxylation ($\Phi < 0.01$) to give anion-derived products in either acetonitrile or in acidic solution.[48] Similarly, assignment of either of the two transients to a carbene (fluorenylidene) or the 9-fluorenyl cation formed by its protonation can be ruled out on the basis of the known spectroscopic and kinetic properties of these two species. For example, 9-fluorenylidene has λ_{max} at 470 nm in acetonitrile and reacts rapidly with both oxygen (1.4×10^9 M^{-1} s^{-1})[52] and methanol (6.3×10^8 M^{-1} s^{-1})[53] and the 9-fluorenyl cation has λ_{max} at 515 nm[24] and reacts with methanol more rapidly (1.8×10^7 M^{-1} s^{-1})[15] than do either **2** or **3**. Furthermore, attempts to protonate fluorenylidene in HFIP have been reported to be unsuccessful.[54]

The importance of the α-lactone in the room-temperature photolysis of alcohol **1** must also be considered. It is clear that the relative importance of the zwitterionic and cyclic α-lactone forms shown in eq 1 is dependent on a number of factors, including the temperature, substituents, and solvent polarity. Although α-lactone **8** would not be detectable in our transient experiments based on UV−visible detection, it should be readily observable in the transient IR experiments. The failure to observe any IR absorptions in the expected α-lactone region (1855−1988 cm^{-1})[41,42,46] suggests that this species is not present to a significant extent. This is supported by the fact that the transient absorptions assigned to zwitterion **2** and cation **3** are comparable in magnitude to those observed previously for **4** (and assuming that the 9-substituent does not affect the quantum yield for photodehydroxylation). A significant equilibrium concentration of **8** would lead to substantially reduced yields of **2** and/or **3**. Thus, there is no direct evidence that α-lactone **8** is formed by photolysis of alcohol **1**, although it is difficult to conclusively eliminate the possibility that a small equilibrium concentration of the cyclic form is present. These results are consistent with earlier observations for the related diphenylmethyl system, for which the α-lactone could only be observed at temperatures lower than −100 °C.[37,40,41]

Reactions of 2 with Nucleophiles. As noted above the transients assigned to zwitterion **2** and cation **3** reacted with nucleophiles such as methanol and bromide. The reactivity of **2** toward a series of alcohols and anions was evaluated by measuring the rate constant for its decay as a function of the concentration of added nucleophile. The rate constants for reaction with nucleophiles are summarized in Table 1, along with data for the parent 9-fluorenyl cation (**6**) and its 9-methyl and 9-carbomethoxy derivatives (**5**, **4**). The latter cations have all been characterized previously using laser flash photolysis techniques, and most of the rate constants for addition of nucleophiles are available in the literature.[15,24] In some cases, the data for these cations had not been determined; these rate constants were measured by monitoring the decay of cations **4**, **5**, and **6** at their respective maxima of 560, 510, and 515 nm as a function of nucleophile concentration.

The rate constants for addition of alcohols to **2** decrease in the order methanol > ethanol > 2-propanol, as observed previously for other 9-fluorenyl cations. In each case, the carboxylate-substituted cation is slightly less reactive than the carbomethoxy-substituted analogue but more reactive than the methyl-substituted cation. All three cations are less reactive than the parent 9-fluorenyl cation with typical decreases of 1−2 orders of magnitude in rate constant. As noted above, zwitterion **2** is relatively unreactive toward bromide and the data in Table 1 show that the same is true of other anionic nucleophiles such as chloride. For both halides the rate constants are $\leq 2.4 \times 10^6$ M^{-1} s^{-1} and may include a contribution from reaction with a small equilibrium concentration of the protonated cation, **3**. Cations **4**, **5**, and **6** show the same reactivity order with anions as with alcohols with decreasing rate constants in the order H > CO_2CH_3 > CH_3.

Table 2. Rate Constants for Reaction of Zwitterion **2** and the 9-Fluorenyl Cation **6** with Aromatics in HFIP at 20 °C

	k_q, M^{-1} s^{-1}	
aromatic	**2**	**6**
anisole	$(2.9 \pm 0.1) \times 10^6$	1.7×10^9 [a]
mesitylene	$(6.4 \pm 0.2) \times 10^5$	1.9×10^9 [a]
diphenylmethane	$\leq 5 \times 10^4$	$(4.9 \pm 0.1) \times 10^6$
benzhydrol	$(6.5 \pm 0.2) \times 10^6$ [b]	$(1.3 \pm 0.x) \times 10^8$ [b]

[a] Reference 55. [b] Plots are curved at higher concentrations.

The rate constants for reaction of **2** with a number of substituted aromatics were also measured and are listed in Table 2, along with data for the 9-fluorenyl cation, **6**. The data demonstrate that the parent 9-fluorenyl cation is more reactive toward all the aromatics than is zwitterion **2** although the changes in rate constant are much more pronounced for simple substituted benzenes than for diphenylmethane and benzhydrol. The reaction of **2** with both anisole and mesitylene is likely to occur via addition to the aromatic ring to give products derived from a cyclohexadienyl cation, as has been observed previously for the 9-fluorenyl cation.[24,55] Transient absorption spectra measured in the presence of anisole and mesitylene provided no evidence for the formation of additional transient products as a result of the reaction of zwitterion **2** with the aromatic substrate.[56] Although cyclohexadienyl cations have been detected by laser flash photolysis in the addition of **6** to anisole and mesitylene, they were not observed for less reactive aromatic substrates ($k_q \leq 10^7$ M^{-1} s^{-1}), presumably due to rapid reactions of the cyclohexadienyl cations. The product cyclohexadienyl cations formed by addition of **2** to substituted benzenes may be relatively short-lived as a result of rapid intramolecular proton transfer from the aromatic ring to the carboxylate group and are thus unlikely to be detectable in our transient experiments.

Zwitterion **2** is relatively unreactive toward diphenylmethane, and only an upper limit for the rate constant of $\leq 5 \times 10^4$ M^{-1} s^{-1} could be estimated. The measured rate constant of 4.9×10^6 M^{-1} s^{-1} for reaction of **6** with diphenylmethane is a factor of 2 slower than that measured previously for toluene.[55] Both ring addition and hydride transfer[57,58] are potential reaction pathways in this case, but the relatively slow rate constant makes

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[56] Competitive absorption by the quencher at the laser wavelength is a problem at high concentrations of some of these aromatics. Spectra were recorded at 0.14 M anisole, which corresponds to ~80−90% quenching of **2**. However, **2** still has a lifetime of several microseconds under these conditions, which may make it difficult to detect transients with similar or shorter lifetimes. Spectra for mesitylene and benzhydrol could only be measured at concentrations for which there was considerably less quenching of the initial zwitterion.

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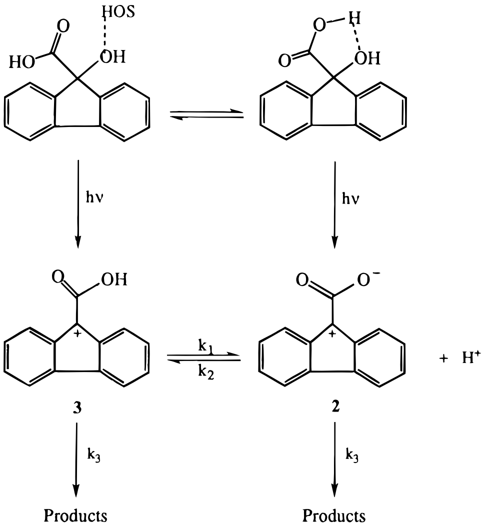
Scheme 1



it difficult to obtain transient evidence that could distinguish between these two possibilities. Both **2** and **6** react with benzhydrol with zwitterion **2** reacting ~20 times more slowly than **6**. This is in contrast to the fact that **6** is ~3 orders of magnitude more reactive than **2** toward addition to the aromatic ring of anisole and mesitylene and suggests that reactions such as nucleophilic addition or hydride transfer may also be important. Quenching of **6** with benzhydrol does lead to additional transients in the 400−500 nm region that may be related to either ring addition or hydride transfer.[59] The transient experiments do not allow us to draw any conclusions as to the reaction mechanism for **2** since spectra can only be measured at relatively low concentrations of benzhydrol.[56]

Estimation of pK_a for 3. As noted above, zwitterion **2** is the only transient observed upon laser irradiation of **1** in HFIP alone, whereas only the protonated cation **3** is formed in the presence of concentrations of TFA of ≥0.15 M. At lower acid concentrations both are formed (Figure 2). Under these conditions, the zwitterion decay no longer follows simple monoexponential kinetics but shows both a fast and a slow component. The fast component increases with increasing acid concentration and the decay kinetics match those for the growth of **3** at 560 nm (Figure 3). The decay kinetics for **3** match those for the slow component in the decay of **2**, indicating that the kinetics reflect the decay of an equilibrium mixture of the two species. These results are consistent with a mechanism in which the starting material is either intramolecularly or intermolecularly hydrogen-bonded, with the former predominating in HFIP alone and the latter increasing in concentration with increasing [TFA] (Scheme 1; SOH = HFIP or TFA). The pK_a's of the solvent HFIP, TFA, and **1** of 9.3, 0.2, and ~4[60,61] are consistent with these assumptions. Photolysis of the intramolecularly hydrogen-bonded form gives the zwitterion directly, consistent with the fact that this intermediate is the only species observed in HFIP and is formed within a 35 ps laser pulse. Photolysis of the intermolecularly hydrogen-bonded form at high TFA concentrations gives cation **3**. At intermediate acid concentrations, both **2** and **3** are generated within the laser pulse and some of the initial zwitterion is protonated in a slower step to give **3**.

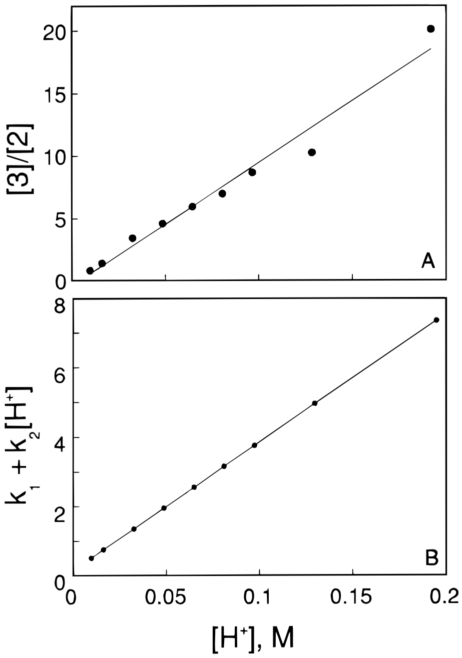


Figure 5. Plot of the ratio [**3**]/[**2**] at equilibrium (A) and the calculated value of $k_1 + k_2[H^+]$ as a function of acid concentration in HFIP (B).

The equilibrium constant (K, eq 3) for the interconversion

$$K = k_1/k_2 = [\mathbf{2}][H^+]/[\mathbf{3}] \qquad (3)$$

of **2** and **3** has been estimated by measuring the ratio of the amounts of **2** and **3** at equilibrium ([**2**]/[**3**]) as a function of the acid concentration. The ratio of the equilibrium concentrations can be estimated from the relative optical densities at 490 and 560 nm if the ratio of the molar absorption coefficients for the two species is known. This ratio has been estimated from the relative optical densities at 490 and 560 nm for matched samples of alcohol **1** in HFIP and 0.15 M TFA/HFIP. It has been assumed (1) that **2** and **3** are the exclusive products of photolysis in HFIP alone and in the presence of acid, respectively, and (2) that the quantum yields for cation formation for the two samples are identical. The ratio of optical densities at the two wavelengths for any given acid concentration for which both species are formed can then be used to calculate concentration ratios, after correction for the fact that both transients contribute to the signal at each wavelength. The ratio of optical densities at 490 and 560 nm reaches a constant value at a certain time delay after the laser pulse, giving the equilibrium value for [**2**]/[**3**] at each acid concentration. An equilibrium constant of 1.0×10^{-2} M is estimated from the reciprocal of the slope of the plot of [**3**]/[**2**] vs [H$^+$] (Figure 5).

A second approach for determining the equilibrium constant is based on measuring the individual rate constants k_1 and k_2 for the ionization of **3**. These rate constants could not be directly extracted from the kinetic data obtained for **2** and **3**. However, it was possible to obtain the sum $k_1 + k_2[H^+]$ at each acid concentration by curve fitting the decay traces obtained for zwitterion **2** at 490 nm (as outlined in the Experimental Section). A plot of $k_1 + k_2[H^+]$ vs [H$^+$] gave an excellent linear correlation (Figure 5), with values of $k_1 = (1.5 \pm 0.5) \times 10^5$ s^{-1} and $k_2 = 3.7 \times 10^7$ M^{-1} s^{-1} obtained from the intercept and slope, respectively. This gives an estimate of 4×10^{-3} M

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for the equilibrium constant. Similar curve fitting of the 560 nm data for **3** gave values of $k_1 = (8.5 \pm 1.2) \times 10^5$ s^{-1}, $k_2 = 4.4 \times 10^7$ M^{-1} s^{-1}, and $K = 1.9 \times 10^{-2}$ M. Values of k_1 are subject to large errors when k_2 is comparable or larger than k_1, thus resulting in a substantial variation in both k_1 and K in comparing the two sets of data. Nevertheless, the average estimate of 1.1×10^{-2} M for the equilibrium constant for the acid dissociation of **3** compares favorably with the value of $K = 1 \times 10^{-2}$ M obtained above from equilibrium concentration measurements.[62]

Conclusions

Photolysis of alcohol **1** in HFIP generates transient zwitterion **2**, which has an absorption maximum at 495 nm and reacts rapidly with alcohols but is insensitive to oxygen. The assignment of the 495 nm transient to zwitterion **2** is confirmed by a time-resolved infrared experiment in which a species that absorbs in the carboxylate region and that matches kinetically the UV−visible transient is observed. Consistent with this, steady state photolysis of **1** in methanol leads to the formation of the expected nucleophilic trapping product, ether **7**. This work provides the first direct detection at room temperature of the type of zwitterionic intermediate that is thought to be responsible for the efficient polyesterifications observed for reactions involving α-lactone intermediates.[37,39,63] However, the experiments do not provide any direct evidence for the intervention of the cyclic α-lactone in the room-temperature photochemistry of alcohol **1**. In the presence of TFA the zwitterion is protonated to give its conjugate acid, cation **3**, which has λ_{max} at 560 nm. Both are formed at intermediate acid concentrations, and experiments in the presence of variable concentrations of TFA lead to an estimated pK_a (in HFIP) of ∼2 for **3**, substantially lower than the pK_a of the parent hydroxycarboxylic acid **1** (∼4 in water). Similar increases in acidity have been observed for radical cations of *p*-aminobenzoic acid and various methoxylated benzoic acids which yield transient radical zwitterions upon deprotonation.[64−66]

Both zwitterion **2** and cation **3** react with alcohols more slowly than the parent 9-fluorenyl cation, indicating that both α-carboxyl and carboxylate groups lead to kinetic stabilization of the 9-fluorenyl cation. This is more pronounced in the additions of **2** and **6** to substituted benzenes, for which the rate constants vary by 3 orders of magnitude. Reactions of zwitterion **2** with anionic nucleophiles are also several orders of magnitude slower than those for other 9-fluorenyl cations, although in this case the difference in reactivity is largely due to electrostatic effects. Similar rate constants are measured for the addition of both zwitterion **2** and the 9-fluorenyl cation to several substituted diphenylmethanes, although there are several possible mechanisms for these reactions.

Experimental Section

General Information. 9-Hydroxy-9-fluorenecarboxylic acid and 9-fluorenol were commercial samples (Aldrich) and were recrystallized twice from ethanol twice before use. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was distilled under a dry nitrogen atmosphere from a mixture of anhydrous sodium bicarbonate and 4A molecular sieves and then redistilled over molecular sieves through a 30 cm Vigreux column. Solvents used in all the HPLC experiments were of spectroscopic grade (Ominsolv). All other solvents and reagents were of highest purity available and were used as received from commercial sources.

Melting points are uncorrected. UV−visible spectra were measured on a Varian Cary 3 double-beam spectrophotometer. Proton and carbon-13 NMR spectra were recorded in $CDCl_3$ on a Bruker AM-200 or an AMX-500 instrument. Chemical shifts are reported in parts per million relative to tetramethylsilane as an internal standard. HPLC experiments were run on a HP 1090 liquid chromatograph equipped with a HP ODS Hypersil column (5 μm, 200 × 2.1 mm) and a UV detector. LC−MS experiments were carried out on a HP 1090 liquid chromatograph with a HP ODS-2 column (5 μm, 250 × 4.6 mm) linked to a HP 5988 mass spectrometer with a thermospray interface.

Steady State Photolysis of 1. (a) NMR. 9-Hydroxy-9-fluorenecarboxylic acid (**1**) (50 mg) was dissolved in a mixture of HFIP/methanol (1 mL, 9:1 v/v), and the solution was photolyzed at 300 nm in a Rayonet photoreactor for 20 min. The solvent was evaporated under vacuum. A 200 MHz ^{1}H NMR spectrum of the residual material in $CDCl_3$ consists of a singlet (2.92 ppm), a very broad peak (6.2 ppm), and a multiplet in the aromatic region (7.25−7.70 ppm). The broad peak at 6.2 ppm was assigned to alcoholic/acidic protons by a deuterium exchange experiment with D_2O. Addition of an authentic sample showed that the signal at 2.92 ppm is due to the methoxy group of 9-methoxy-9-fluorenecarboxylic acid (**7**). In the particular experiment described here, the ratio of the MeO signal at 2.95 ppm and aromatic protons at 7.25−7.70 ppm indicated ∼20% conversion of the starting material **1** to the ether.

(b) HPLC/LC−MS. A solution prepared as described above was photolyzed for varying times, and aliquots were periodically withdrawn and examined by HPLC. As photolysis in the HFIP/methanol (9:1 v/v) mixture proceeded, the peak due to starting material **1** decreased in intensity and a new peak with a longer retention time was formed. The chemical ionization (ammonium acetate) mass spectrum of the new peak had *m/z* 258 ($M + NH_4^+$, $M = CH_3OC_{13}H_8CO_2H$). This peak was assigned to **7** by co-injection of an authentic sample. Longer photolysis times (>30 min) resulted in the formation of 9-fluorenone and unidentified products with longer retention times.

When the photolysis was carried out in HFIP alone, a similar new peak was detected by HPLC; the chemical ionization (ammonium acetate) mass spectrum of this peak had *m/z* 394 ($M + NH_4^+$, $M = (CF_3)_2CHOC_{13}H_8CO_2H$). Based on the above results, the new peak was assigned to 9-(1,1,1,3,3,3-hexafluoro-2-propanoxy)-9-fluorenecarboxylic acid. At longer photolysis times (>30 min), 9-fluorenone and unidentified products with longer retention times were also detected.

Preparation of 9-Methoxy-9-fluorenecarboxylic acid (7). 7 was prepared by saponification of methyl 9-methoxy-9-fluorenecarboxylate,[67,68] which was synthesized by MeI/Ag_2O O-methylation[69] of methyl 9-hydroxy-9-fluorenecarboxylate.[70] A solution of methyl 9-methoxy-9-fluorenecarboxylate (0.5 g, 2 mM) in carbon tetrachloride (10 mL) and an aqueous solution of sodium hydroxide (2 M, 25 mL) was refluxed for 24 h. After cooling to room temperature, the organic layer was removed and the aqueous layer was further washed with carbon tetrachloride (2 × 25 mL). Aqueous hydrochloric acid (1 M) was added to the aqueous layer until the pH was <3. A white solid precipitated out and was extracted with chloroform (3 × 20 mL). After drying over magnesium sulfate, the solvent was removed at reduced pressure to give **7** as a white solid (0.26 g, 55%). NMR and HPLC experiments indicated that **7** prepared in this manner was at least 97% pure, mp 182−5 °C, lit.[68] mp 188 °C: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.27−7.70 (m, 8H, aromatic), 2.92 (s, 3H, OMe); (lit.[68] ^{1}H NMR ($CDCl_3$) δ 2.9 (s, 3H)): FABMS for $C_{15}H_{12}O_3$ *m/z* 253 [$M - H + 2Li^+$], 247 [$M + Li^+$] (using 3-nitrobenzyl alcohol as the matrix, positive mode).

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Laser Flash Photolysis. (a) UV−Visible. Sample solutions were prepared with optical density (OD) of 0.3−0.4 at the excitation wavelength (266 or 308 nm) and were contained in 7 × 7 or 7 × 3 mm^2 quartz cells (quenching experiments) or in 7 × 7 mm^2 flow cells connected with Teflon tubing to a sample reservoir equipped with a Teflon stopcock for controlling the flow rate. The nanosecond laser system has been described previously.[71] For these experiments, either a Lumonics HY750 Nd:YAG laser (266 nm, 10 ns pulses, ≤50 mJ/pulse) or a Lumonics EX-530 excimer laser (XeCl, 308 nm, 6 ns pulses, ≤40 mJ/pulse) was used for sample excitation. A Continuum YG-601-C Nd:YAG laser (266 nm, 35 ps pulses, 6 mJ/pulse) was used for the picosecond experiments.[72]

(b) Infrared. The system has been described.[73] For these experiments, samples were contained in quartz flow cells with a 1 mm path length and were excited at 308 nm with a Lumonics EX-510 excimer laser (XeCl, 308 nm, 6 ns pulses, ≤ 40 mJ/pulse).

Computational Details. Scheme 1 was used to obtain the time-dependent expressions for the concentrations of **2** and **3**. In order to simplify the kinetic analysis it was assumed that the initial concentration of **3** was negligible relative to **2** (i.e., $[\mathbf{3}]_0 = 0$). However, inclusion of a fixed initial concentration of **3** (i.e., $[\mathbf{3}]_0 > 0$) did not alter the measured values for k_1 and k_3. The time-dependent expressions for **2** and **3** are given by eqs 4 and 5, respectively. The observed optical

$$[\mathbf{2}] = \frac{[\mathbf{2}]_0(k_1 e^{-k_3 t} + k_2[\mathrm{H}^+]e^{-(k_2[\mathrm{H}^+]+k_1+k_3)t})}{k_1 + k_2[\mathrm{H}^+]} \tag{4}$$

$$[\mathbf{3}] = \frac{[\mathbf{2}]_0(k_2[\mathrm{H}^+]e^{-k_3 t} - k_2[\mathrm{H}^+]e^{-(k_2[\mathrm{H}^+]+k_1+k_3)t})}{k_1 + k_2[\mathrm{H}^+]} \tag{5}$$

density at 490 nm, OD_{490}, is given by eq 6, which corrects for any

$$\mathrm{OD}_{490} = \epsilon_{\mathbf{2},490}[\mathbf{2}] + \epsilon_{\mathbf{3},490}[\mathbf{3}] \tag{6}$$

overlap of absorption. The terms $\epsilon_{\mathbf{2},490}$ and $\epsilon_{\mathbf{3},490}$ refer to the molar absorptionf coefficients of species **2** and **3**, respectively, at 490 nm. The time dependence for the measured optical density at 490 nm is a double-exponential function of the form given by

$$\mathrm{OD}_{490} = a\mathrm{e}^{-bt} + c\mathrm{e}^{-dt} \tag{7}$$

where

$$a = \frac{[\mathbf{2}]_0}{k_1 + k_2[\mathrm{H}^+]}(k_1\epsilon_{\mathbf{2},490} + k_2[\mathrm{H}^+]\epsilon_{\mathbf{3},490})$$

$$b = k_3$$

$$c = \frac{[\mathbf{2}]_0}{k_1 + k_2[\mathrm{H}^+]}(k_2[\mathrm{H}^+]\epsilon_{\mathbf{2},490} - k_2[\mathrm{H}^+]\epsilon_{\mathbf{3},490})$$

$$d = k_2[\mathrm{H}^+] + k_1 + k_3$$

Equation 7 was used to curve fit the data obtained for the decay of the signal assigned to zwitterion **2** using a curve-fitting program (Sigma Plot Version 1.02 for Windows, Jandrel Corp.) The data points for two time windows were merged to obtain a single decay profile for curve fitting; the double-exponential function gave an excellent fit to the data, and the values for b and d obtained for various acid concentrations were used to obtain k_1 and k_2 as discussed in the text.

Acknowledgment. We thank Dr. Norman Schepp for help with the picosecond laser flash photolysis experiment and Professor S. Filseth for valuable suggestions on the kinetic analysis of the data. E.L.-R. thanks the Natural Sciences and Engineering Research Council for support of this work.

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