# Solvent-Dependent C–OH Homolysis and Heterolysis in Electronically Excited 9-Fluorenol: The Life and Solvation Time of the 9-Fluorenyl Cation in Water

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**Abstract:** The primary pathways of the photodecomposition of 9-fluorenol (FOH) were studied in polar and nonpolar solvents by use of laser flash-photolysis with a resolution time of 10 ps. In solvents of high polarity, that is, in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), 2,2,2-trifluoroethanol (TFE), formamide or water, the fluorenyl cation, $F^+$, forms by *heterolytic* C–O bond cleavage. In $H_2O$, the initial (10 ps) spectrum of $F^+$ has $\lambda_{max}$ at $<460$ nm. This absorption red-shifts with $\tau = 25$ ps to the "classical" spectrum with $\lambda_{max} = 510-515$ nm. This process is assigned to the solvation of the initial "naked" cation, or rather, the contact ion pair. The lifetime of the solvated fluorenyl cation in $H_2O$ (or $D_2O$) and TFE was measured to be $\tau = 20$ ps and 1 ns, respectively. In solvents of lower polarity such as alkanes, ethers and alcohols, the long-lived ($\tau_{1/2} \approx 1\ \mu s$) fluorenyl radical, $F^\bullet$, ($\lambda_{max} = 500$ nm) forms through *homolytic* C–O cleavage. In addition to the radical and the cation, the vibrationally relaxed excited singlet state of FOH is seen with its absorption at $\approx 640$ nm; its lifetime is strongly dependent on the solvent, from 10 ps for formamide to 1.7 ns for cyclohexane. The rate constant for singlet decay increases exponentially with the polarity of the solvent (as expressed by the Dimroth–Reichardt $E_T$ value) or with the Gutmann solvent acceptor number. The relaxation of $S_1$ to $S_0$ is accompanied by homolytic C9–O bond cleavage (except in HFIP, TFE, and water, where $S_1$ is not seen).

**Keywords:** carbocations · fluorene · photodissociation · picosecond spectroscopy · solvent effects

## Introduction

The photochemistry of 9-fluorenol (FOH) in aqueous methanol has been studied by Wan et al.[1–5] and from the several photo-products identified, the occurrence of photohomolysis and -heterolysis involving the C–O bond was identified. Mecklenburg and Hilinski,[6] by use of laser photolysis with picosecond time resolution, detected an absorption band at 515 nm on photolysis of FOH in $H_2O$:MeOH 1:1, and assigned it to the fluorenyl cation, $F^+$, and an additional band at 500 nm identified as the fluorenyl radical, $F^\bullet$, thus supporting the conclusions of Wan et al. on the occurrence of photoheterolysis as well as photohomolysis. Whereas the lifetime of $F^\bullet$ in this solvent is very long (>1 µs), the lifetime of $F^+$ was estimated to be $\tau < 20$ ps.

In contrast to this interpretation, Gaillard et al.[3] assigned a broad and long-lived (>6 µs) band with the maximum at 640 nm to the cation, $F^+$. This assignment, however, was corrected[7] on the basis of nanosecond laser flash-photolysis experiments in which $F^+$ was generated specifically in the weakly nucleophilic solvent 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) (in which the longevity of $F^+$, absorbing at 515 nm, is a record 30 µs).

Taking all these data together, it is evident that electronically excited FOH undergoes two different reactions, both involving the C9–OH bond, namely homo- and heterolytic cleavage. Furthermore, it appears that these reactions are strongly solvent dependent. Therefore, it was decided to study this phenomenon in a more systematic way, with the hope of shedding more light on the mechanism by which solvent influences the nature of a bond-breaking process. As far as heterolysis is concerned, it is evident that in order for solvation to influence the reaction, the solvation of the incipient ions must be very *rapid* so that the ionic path by which the scissile bond is *broken* is already preformed by the solvent. This implies that the solvent must play an *active* part in the early stages of the bond-breaking process.

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## Results and Discussion

**Fluorescence data**: The absorption[8] and fluorescence spectra of FOH in MeCN with their maxima at 270 and 320 nm, respectively, are shown in Figure 1.

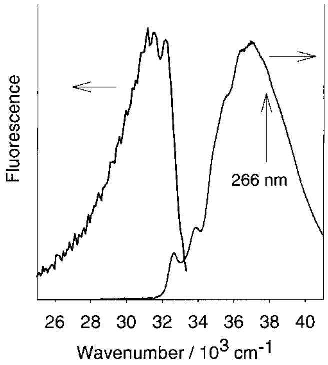


Figure 1. Absorption and fluorescence spectra of 9-fluorenol in MeCN.

The fluorescence emission of FOH in dioxane, alcohols, THF, or MeCN consists of a structured single band with $\lambda_{max} = 310-320$ nm (for an example, see Figure 1). The quantum yield of fluorescence of FOH in MeCN ($\lambda_{max} =$ 325 nm) is small, $\phi_f < 10^{-2}$, and in 80% $H_2O$/MeCN it is even smaller, $\phi_f < 10^{-3}$.[2] In HFIP, 2,2,2-trifluoroethanol (TFE), and $H_2O$ the steady-state fluorescence of FOH turned out to be below our detection limit; we estimate the quantum yield to be $\phi < 10^{-5}$. The lifetimes of the fluorescence were measured by the single-photon counting technique, and the lifetimes of $S_1$ were monitored by the $S_1 \rightarrow S_n$ transition at $\approx$640 nm (see section on absorption data).

It is known that the main photoproduct of UV photolysis of FOH in non and moderately polar solvents is fluorene.[2] In contrast to FOH, fluorene is a *strongly* fluorescing molecule with $\lambda_{max}$(emission) = 305 nm; the quantum yield in polar and nonpolar solvents being $\approx$0.7,[9] which is $\approx$100 times higher than that of FOH. Water has only a moderate quenching effect on the fluorescence. By going from neat MeCN to 4:1 (v/v) $H_2O$/MeCN the quantum yield decreases from 0.7 to 0.6, and the lifetime decreases from 6.7 to 5.6 ns.[2] On the basis of the high yield of fluorene and its strong fluorescence, it is evident that there is the danger that this photochemical product interferes in fluorescence lifetime measurements on FOH. In fact, the long fluorescence lifetimes of the order of several nanoseconds reported for FOH in, for example, MeOH,[3] are indicative of the presence of fluorene formed from FOH as a photochemical product.

Therefore, in order to get a more solid basis for judging the possible influence of fluorene on the FOH results, we also performed picosecond flash-photolysis experiments on fluorene.[10] Our results on the singlet state $S_1$ of fluorene were obtained (see section on adsorption data) from time-resolved absorption measurements and are shown in Table 1, together with data from the literature.

It is evident that the singlet lifetime is independent of the polarity of the solvent. This is probably the consequence of the nonpolar character of fluorene (dipole moment $\mu \approx$ 0.6[18–20]. This independence is in contrast to the behavior of FOH (see section on absorption data below).

Table 1. The lifetime $\tau_S$ of the singlet state $S_1$ of fluorene in various solvents.

| Solvent | $\tau_S$ [ns] | Reference |
|---|---|---|
| TFE | 4.8[a] | this work |
| MeOH | 2.9[a] | this work |
| $CH_2Cl_2$ | 3.3[a] | this work |
| MeCN | 2.5[a] | this work |
| MeCN | 6.7[b] | [2] |
| cyclohexane | 5.6[a] | this work |
| cyclohexane | 5.1[a] | [11] |
| cyclohexane | 5.9 ± 0.9[b] | [11] |
| cyclohexane | 3.36[b] | [12] |
| cyclohexane | 10[b] | [13, 14] |
| *n*-hexane | 7.5[b] | [15, 16] |
| hexane | 3.8 ± 0.1[b] | [17] |

[a] From transient absorption. [b] From fluorescence.

**Absorption data of transients**: The species formed photochemically from FOH depend strongly on the solvent. Therefore, the situation observed experimentally is described first for low and intermediate polarity solvents.

The absorption spectra (see, e.g., Figure 2a) of the transients observed on 266 nm photolysis of FOH in MeCN, alcohols, ethers, or hydrocarbons, consist of two species: 1) A species with a broad band with $\lambda_{max}$ at $\approx$ 640 nm and 2) a species characterized by a relatively wide band (or shoulder) with a maximum at $\approx$470 nm and a narrow band at $\lambda_{max} =$ 500 nm (the intensity of the 470 nm band is $\approx$50% of that of the 500 nm band). The first species, that is the one with the band at 640 nm, was assigned[6] to the $S_1 \rightarrow S_n$ transition of the excited singlet state of FOH, FOH($S_1$); this is in agreement with the fluorescence lifetime data obtained (see ref. [2] and Table 2).

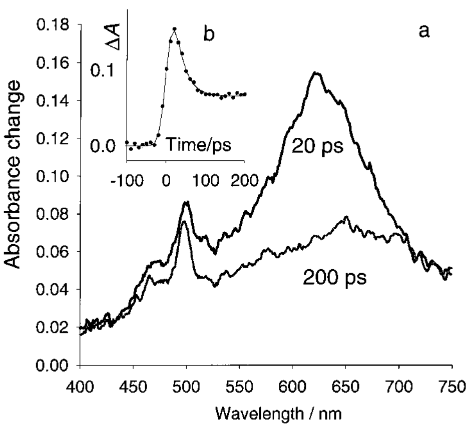


Figure 2. a) Absorption spectra of transients recorded at 20 and 200 ps after the 266 nm excitation pulse and b) the decay kinetics monitored at 630 nm in a solution of 9-fluorenol in methanol.

*The FOH singlet, FOH($S_1$)*: The lifetimes of FOH($S_1$) measured by the decay of the 640 nm band range from

Table 2. The lifetime of FOH($S_1$), $\tau_s$, in different solvents (air-saturated) as determined by the decay of the $S_1 \rightarrow S_n$ absorption signal.

| Solvent | Polarity[a]/$E_T^N$ | dielectric constant $\varepsilon_r$ | $\lambda_{max}$ of the $S_1 \rightarrow S_n$ transition | $\tau_s$ [ps][b] |
|---|---|---|---|---|
| 2,2,2,2′,2′,2′-hexafluoroisopropanol | 1.068 | 16.6 | not detected | < 10 |
| water | ≡ 1.000 | 78.3 | not detected | < 10 |
| 2,2,2-trifluoroethanol | 0.898 | 26.7 | not detected | < 10 |
| glycerol | 0.812 | 42.5 | 650 | 20 |
| formamide | 0.799 | 111.0 | 660 | 10 |
| ethylene glycol | 0.790 | 37.7 | 650 | 36 |
| MeOH | 0.762 | 32.66 | 630 | 30 (20[c]) |
| *N*-methylformamide | 0.722 | 182.4 | 650 | 40 |
| EtOH | 0.654 | 24.55 | 630 | 50 (20[c]) |
| *n*PrOH | 0.617 | 20.45 | 630 | 110 |
| *i*PrOH | 0.546 | 19.92 | 630 | 70 (200[c]) |
| MeCN | 0.460 | 35.94 | 620 | 130 – 160 (350[2], 400[c]) |
| dimethylformamide | 0.404 | 36.71 | 640 | 540 |
| *tert*-butanol | 0.389 | 12.47 | 630 | 150 – 290 |
| dichloroethane | 0.327 | 10.37 | 630 | 100 |
| dichloromethane | 0.309 | 8.93 | 630 | 30 |
| 1,2-dimethoxyethane | 0.231 | 7.2 | 630 | 1000 |
| THF | 0.207 | 7.58 | 645 | 1300 (1500[b,d]) |
| dioxane | 0.164 | 2.21 | 640 | 1200 (1200[b,d]) |
| dimethoxymethane | 0.157 | 2.65 | 630 | 800 (1100[b,d]) |
| cyclohexane | 0.006 | 2.02 | 625 | 1700 (1900[b,d]) |

[a] From ref. [22]. [b] This work. [c] From fluorescence. The fluorescence lifetime was measured with a streak camera (overall time resolution 10 ps, see ref. [23]). We thank T. Leichtner at the University of Leipzig for the measurements. [d] From fluorescence measurements by using the single-photon-counting technique with 0.8 ns time resolution.

1.3 ns for the less polar solvents cyclohexane, dioxane, or THF to 150 ps for MeCN and 20 – 60 ps for alcohols as solvents[21] (see Figure 2b) down to < 10 ps for TFE, HFIP, or water. The results are collected in Table 2.

As is evident from Table 2, the lifetimes of the singlet state, $\tau_S$, are in the range of 10 ps to > 1 ns depending on the solvent, the lifetimes being longer in nonpolar solvents and shorter in polar solvents. In the case of water, HFIP, and TFE, no absorption at 630 – 650 nm was observed. We assume that in these cases $\tau_S$ is much less than 10 ps, which is in agreement with the absence of steady-state fluorescence ($\phi < 10^{-5}$). In Figure 3 are plotted the logarithms of the rate constants[24] ($1/\tau_S$) for decay of $S_1$ versus the polarity of the solvent, as expressed by the Reichardt $E_T^N$-value. It is evident that the rate constant for the decay of the singlet increases exponentially with $E_T^N$ ($r = 0.974$). In Figure 3 there is also a plot of log $\tau_s$ versus the Gutmann solvent acceptor[25] number.[26] The fact that the correlation coefficient (0.949) is similar to that of the Reichardt plot indicates that—within the collective property "polarity"— it is the acceptor power of a solvent which influences the rate of the $S_1 \rightarrow S_0$ internal conversion.

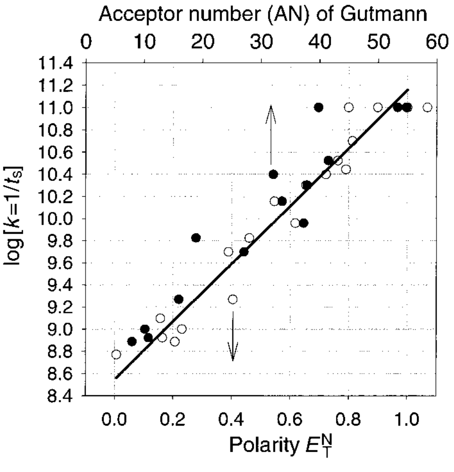


Figure 3. Dependence of the rate constant of the 9-fluorenol singlet decay on the polarity of the solvent.

The above dependence on the polarity/acceptivity can be qualitatively understood in terms of the energy gap law[27, 28] with the assumption that $S_1$ is more polar than $S_0$. The energy gap law states that the Franck – Condon factor and, therefore, the rate of the $S_1 \rightarrow S_0$ internal transition, $k_{ic}$, is a very sensitive function of the energy difference $\Delta E$ between the zero-point vibrational levels of the singlet states $S_1$ and $S_0$ [Eq. (1)].

$$k_{ic} = A \exp(-\Delta E/\hbar\omega) \tag{1}$$

In Equation (1), $A$ is proportional to the electronic matrix element for vibronic coupling between $S_1$ and $S_0$, and [29] $\omega$ is the frequency of the normal molecular vibration; both are weak functions of $\Delta E$. If $S_1$ is more polar than $S_0$, the energy difference will decrease as one goes from nonpolar to polar solvents and, therefore, $k_{ic}$ will increase. Note, that in contrast to the case of fluorene, whose singlet-state lifetime is *not* solvent dependent (Table 1), the strong solvent dependence of the lifetime of FOH($S_1$) indicates that it is the polar C9–OH group in FOH ($\mu = 1.89$ D)[30] through which FOH($S_1$) is stabilized by interaction with the solvent. Based on the Gutmann plot (Figure 3), in protic solvents it is probably stabilized by interaction with the solvent molecules as proton donors to the O at C9 of FOH (see Scheme 3 later).[31] This leads to a decrease of $\Delta E$ and, thus, an increase in $k_{ic}(S_1 \rightarrow S_0)$.

In agreement with this, in the solvents THF or dioxane the (relatively long-lived) FOH excited singlet state was observed to be quenched on addition of $HClO_4$ or HFIP to the solution. A corresponding decrease was observed with respect to the fluorescence intensity at 310 nm. In Figure 4 it is shown that the *rate of decay* of FOH($S_1$) depends on [HFIP] as described by the Stern – Volmer equation which, with approximately the same slope, also describes the dependence of the *quantum yield* of the fluorescence of FOH on the concentrations of the additives. This adds merit to the identification of the 640 nm band in terms of the singlet and

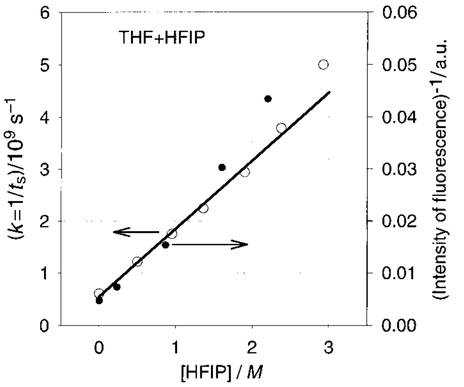


Figure 4. Stern–Volmer diagram for quenching of 9-fluorenol singlet state by HFIP in THF.

demonstrates that the singlet is quenched in a chemical reaction in which $FOH(S_1)$ probably acts as a Brönsted base. From the quenching data, the rate constant for the reaction of the singlet with these additives is obtained as $(1-3)\times 10^9\,M^{-1}s^{-1}$.

Addition of $H_2O$ into the solution of FOH in MeCN reduced the singlet lifetime from 160 ps in neat MeCN down to 50–60 ps at water contents of 1.2–2%. This is in agreement with the observations reported above and also with ref. [2]. In 80% $H_2O$/MeCN the fluorescence was weaker by one order of magnitude relative to neat MeCN.

In the case of methanol, the addition of water results in the appearance, promptly after the pulse, of an absorption band peaking at 515 nm with a concomitant decay of the singlet at 630 nm, in agreement with previous[6] observations. The 515 nm species is identified in terms of the 9-fluorenyl cation, $F^+$ (see ref's. [6, 7] and section on the 9-fluorenyl cation).

*The 9-fluorenyl radical, $F^{\bullet}$*: The 470/500 nm species mentioned above is the 9-fluorenyl radical, $F^{\bullet}$.[6, 7, 32] Absorption at 450–500 nm appears promptly after the exciting laser pulse as a shoulder on the singlet–singlet absorption band whose $\lambda_{max}$ is at ≈640 nm. After the singlet has decayed, sharp absorption bands at 470/500 nm become visible. From this one can conclude that the singlet absorption overlaps with that of the radical. When this overlap is taken into consideration, it turns out that there is a *buildup* of absorption at 500 nm (in all solvents in which the singlet was observed) on the same timescale as the singlet *decays*; this means that the radical, $F^{\bullet}$, is a product of singlet decay, or in other words, C–O bond homolysis is one of the mechanisms by which the singlet decays. Moreover, this is the case for all solvents (except for HFIP, TFE and water where no radical or singlet was detected, see section on the 9-fluorenyl cation).

This means that $F^{\bullet}$ is derived from vibrationally *relaxed* $S_1$. Evidently, vibrational relaxation, which typically takes place on the subpicosecond timescale,[33, 34] is faster than homolytic C9–O bond cleavage. After vibrational relaxation in the $S_1$ state, the energy content of FOH is 91 kcal mol$^{-1}$, as deduced from the fluorescence emission at $\lambda_{max} = 314$ nm (in MeOH). This is apparently sufficient for C–O homolysis (see also section on the 9-fluorenyl cation).

The longevity of $F^{\bullet}$ is larger than the time range of the ps spectrometer (10 ns). Therefore it was determined with our *nanosecond* laser flash-photolysis apparatus. Under these conditions, the first half-life of $F^{\bullet}$ is typically in the range 0.5–1 μs.

*The 9-fluorenyl cation, $F^+$:* In the case of HFIP, TFE, $H_2O$, and $D_2O$ the transient absorption spectrum observed differs from that in the other solvents. A sharp strong maximum at 515 nm with a shoulder at 500 nm appears after excitation with a 266 nm pulse (Figure 5a, b).

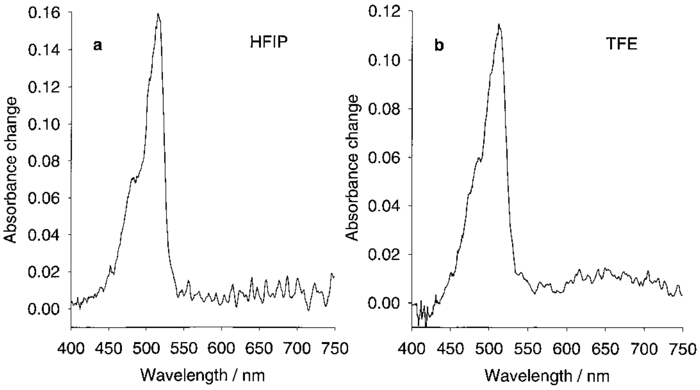


Figure 5. Absorption spectra of $F^+$ formed on photolysis of 9-fluorenol in a) HFIP and b) TFE.

The 515 nm band in HFIP was previously studied by nanosecond flash-photolysis and was identified as the fluorenyl cation $F^+$, whose lifetime in HFIP is $\tau = 30$ μs.[7] We have now studied FOH in the less acidic and more nucleophilic solvent TFE and found a significantly shorter lifetime for $F^+$, that is, $\tau = 1$ ns.[35–37]

The fluorenyl cation was also observed to be formed in $H_2O$ and $D_2O$, as shown by a strong transient at $\lambda_{max} = 515$ nm (Figure 6a). In contrast, there was *no* evidence for the fluorenyl *radical*, $F^{\bullet}$, indicating that the only photoreaction[38] in water is heterolysis.[39]

However, it was found that in $H_2O$, $D_2O$, and formamide, at very early times after the pulse, the maximum of the band assigned to $F^+$ lies not at 515 nm, but at <450 nm.[40] Subsequently, a red-shift of the band to 515 nm occurs, the kinetics of which are shown in Figure 7. This shift is assigned to the solvation of the cation $F^+$.[41–43] The spectral changes indicating the solvation of the cation were found to have the same rate in light and heavy water, that is, $4\times 10^{10}\,s^{-1}$ (Figure 7).[44] In the solvent formamide, an analogous spectral shift occurred, with a rate about twice that in water.

The lifetime of $F^+$ was measured (by its decay at 515 nm) to be 22 ps in both $H_2O$ and $D_2O$. This means that the solvent kinetic isotope effect for the decay of $F^+$ is 1.0. In water, $F^+$ will decay by production of FOH and $H^+$, a process which involves the formation of a C9–OH bond and the ultimate *cleavage* of a HO–H bond of the incoming water molecule that adds as a nucleophile to the C9 cationic site (Scheme 1).

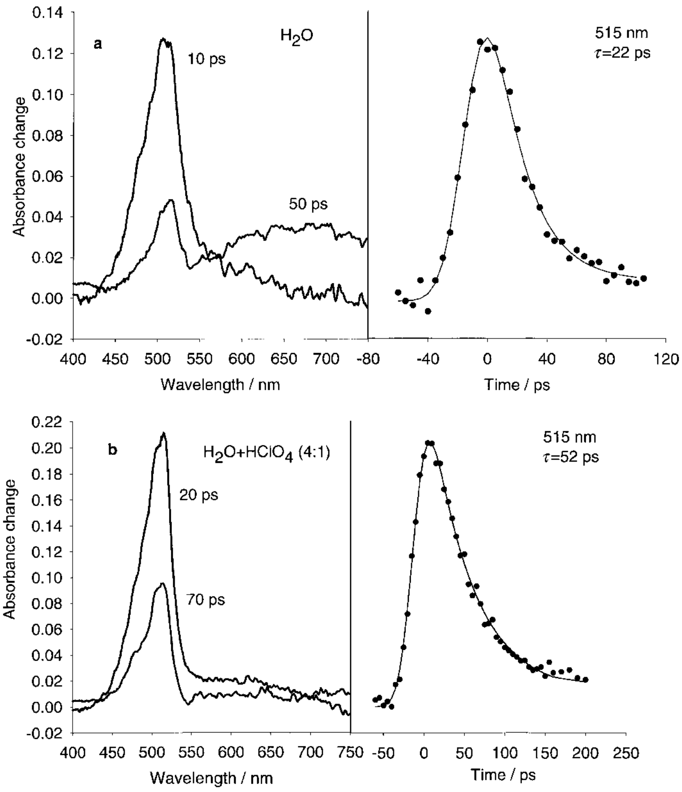


Figure 6. Transient absorption spectra and temporal behavior of the 515 nm band for 9-fluorenol in a) $H_2O$ and b) $H_2O/HClO_4$ (volume ratio 4:1).

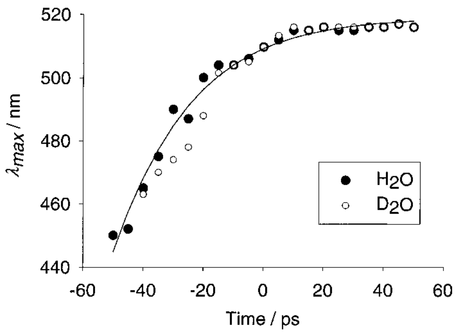
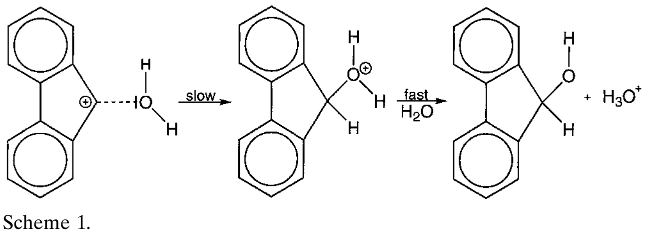


Figure 7. The temporal shift of the maximum of the $F^+$ absorption in $H_2O$ (●) and $D_2O$ (○). The fitted line is an exponential rise giving 25 ps as the reaction period.



Scheme 1.

From the absence of an O–H/D kinetic isotope effect one can conclude that in the rate determining step $C^+\cdots O$ bond formation occurs *without* concerted HO–H deprotonation.[45]

It was found that the addition of $HClO_4$ to the aqueous solution of FOH increases both the yield of $F^+$ as well as its lifetime, up to 50, 120 and 370 ps in 1:4, 1:2 and 1:1 $HClO_4/H_2O$,[46, 47] respectively (see Figures 6a/b and 8).[48]

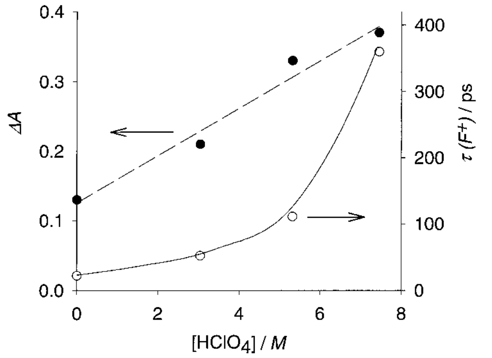
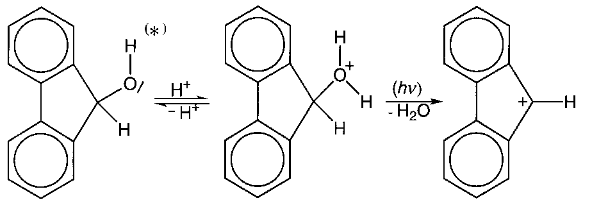


Figure 8. The effect of $HClO_4$ on the yield (ΔA) and the lifetime (τ) of $F^+$ in $H_2O$.

The increase in *lifetime* can be explained by the decreasing nucleophilicity[49] of the solvent as $[HClO_4]$ increases. The increase in *yield* may be rationalized in terms of protonation of FOH (in the ground or excited state), as shown in Scheme 2



Scheme 2.

(which is the reverse of Scheme 1, except for the electronic state of FOH). As a result of this, the bad leaving group[50] $OH^-$ ($pK_a(H_2O) = 15.7$) is converted into the good one $H_2O$ ($pK_a(H_3O^+) = -1.7$). An additional mechanistic advantage is that the formation of a contact ion pair is avoided, since $F^+$ is separated from the (distant) complementary anion by the leaving group $H_2O$.

As mentioned earlier, the formation of $F^+$ ($\lambda_{max} = 515$ nm) was also detected in aqueous methanol (1:1). Its lifetime is very short, $t = 30$ ps, in qualitative agreement with previously reported observations.[6] However, in MeOH:$H_2O$ 1:1 the 515 nm band ($F^+$) overlaps with the strong, sharp 500 nm band of $F^\bullet$ and the broad band of the singlet with maximum at 630 nm, indicating that in this solvent mixture, in contrast to the solvent $H_2O$, *both* homolysis and heterolysis occur and that the singlet has a measurable lifetime.

## Conclusions

According to the Grunwald–Winstein model, heterolytic cleavage of a covalent bond proceeds by two steps, that is, C–O bond breakage ("ionization") leading to the formation of ions with a common solvation shell ("contact ion pair"), and, subsequent separation of the ions from each other by solvation yielding "free ions" ("dissociation").[22] Both ionization and dissociation are strongly influenced by the solvent, but differently. The ion pair formation, that is, the ionization of the covalent bond, strongly depends on the ability of the solvent to function as an electron pair acceptor or donor. This

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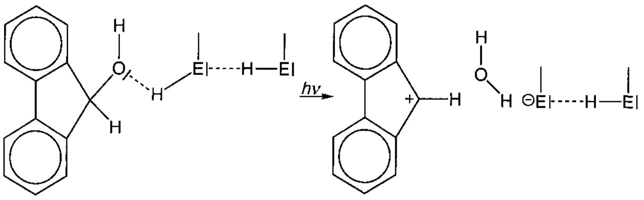
*ionizing power* of the solvent is reflected in the polarity of the solvent as expressed by the Kosower $Z$ or the Reichardt $E_T^N$ value. Thus, due to solute–solvent interaction, the "threshold" of ion pair formation (*ionization*) is lowered as a result of solvation. On the other hand, the *dissociation* of the contact ion pairs depends on the ability of the solvent to reduce the strong attraction between the ions and to separate them from each other, that is, to lead to the formation of *free* solvated ions. For this function of the solvent, its dielectric constant is important. Of all the solvents, water ($H_2O$ or $D_2O$) is the best example of both an ionizing (electron pair donor and acceptor, $E_T^N = 1.000$) and dissociating (high dielectric constant, $\varepsilon = 78.3$) medium. Among the other solvents studied formamide is highly polar *and* has a very large dielectric constant ($E_T^N = 0.799$, $\varepsilon = 111$), whereas HFIP ($E_T^N = 1.068$, $\varepsilon = 16.6$) and TFE ($E_T^N = 0.898$, $\varepsilon = 26.7$) are of very high polarity but have only moderate dielectric constants. These solvents, however, have a relatively high acidity ($pK_a(\text{HFIP}) = 9.3$, $pK_a(\text{TFE}) = 12.4$), such that protonation of FOH in the ground or excited state in a way analogous to Scheme 2 is a possibility. If this happens, the product of heterolysis is not a contact ion pair (extremely short-lived) but the "nonclassical" loose ion pair shown in Scheme 3, which is analogous to Scheme 2. Therefore, it may be their acidities which make TFE and HFIP particularly good solvents for converting FOH into $F^+$. In a more general sense, this may also be true for $H_2O$ and formamide, both of which are protic solvents.



Scheme 3. $E = O,N$.

As mentioned earlier, the solvation dynamics of the cation are reflected in the time evolution of the cation transient band (see Figure 7). In water and in formamide (solvents with high dielectric constant *and* good electron-pair donors) the shift of the absorption maximum turned out to be more pronounced[51] than in the case of HFIP or TFE, which are only poor electron-pair donors and whose $\varepsilon$ are only 16.6 and 26.7, respectively. Particularly as a result of the former property, they do not solvate the Lewis-acidic $F^+$ very well. The observed difference in spectroscopic behavior between the two categories of solvent may be related to these differences in solvation properties.

Progressing from low-polarity (e.g., the simple alcohols and ethers) to high-polarity solvents (e.g., HFIP, TFE, formamide, or $H_2O$) the C–OH bond cleavage (which proceeds *homo*lytically in the low-polarity solvents) from the excited singlet is shifted into the heterolytic direction. In order to understand this phenomenon, it is necessary to consider the thermodynamics of heterolysis in comparison with homolysis. Unfortunately, thermochemical data concerning the homo- or heterolytic C–O bond cleavage of FOH do not seem to be available in the literature. The best model for FOH we could find is *cyclo*-pentanol, for which the homo- and heterolytic (gas-phase) bond dissociation energies are 91.3 and 218 kcal mol$^{-1}$, respectively.[52] In order to relate these numbers to the aqueous phase, the hydration energies of the species involved have to be known. It is reasonable to assume that the change in hydration energies of the neutral species involved in the C–OH *homolysis* is negligible. Therefore the gas-phase value for C–OH (91.3 kcal mol$^{-1}$) can also be taken to be valid for aqueous solution. For the *heterolysis*, $F{-}OH \rightarrow F^+ + OH^-$, the problem is simplified to assigning a reasonable value to $F^+$, since that for $OH^-$ is known (–111 kcal mol$^{-1}$).[53] In lieu of an experimental value for $F^+$, this was calculated with the Born equation, taking the diameter of $F^+$ to be the same as that of $Ph_2CH$ (245 pm).[54] The result is $\Delta H_{\text{hydration}}(F^+) = -66.5$ kcal mol$^{-1}$. However, this value appears unreasonably large if compared with the –32 kcal mol$^{-1}$[55] measured for the smaller ion (diameter 215 pm) $Me_4N^+$.[56] Therefore, the –66.5 kcal mol$^{-1}$ calculated should be taken as the lower limit for $\Delta H_{\text{hydration}}$.

With these values and taking –12 kcal mol$^{-1}$ for the hydration energy of FOH (by analogy with the value for EtOH[57]), the heterolysis reaction in water $C{-}OH_{\text{hydrated}} \rightarrow C^+{}_{\text{hydrated}} + OH^-{}_{\text{hydrated}}$ turns out to be endothermic with 53–87 kcal mol$^{-1}$. In comparison, the energy of photoexcitation (with a 266 nm photon) of FOH corresponds to 107.5 kcal mol$^{-1}$, and that of the vibrationally relaxed $S_1$ of FOH (in MeOH) is 91 kcal mol$^{-1}$. These data are summarized in Figure 9.

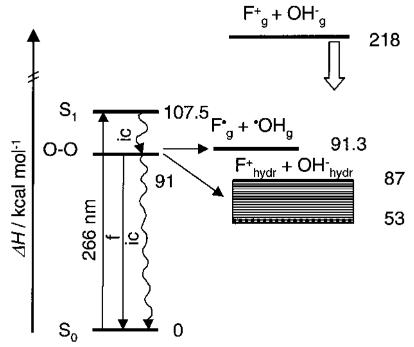


Figure 9. Excitation and bond cleavage energies.

The most important result is that, owing to hydration of the ions, heterolytic cleavage of the C–OH bond is more favorable than homolytic cleavage. However, this cannot possibly influence the *initial* way in which the C–O bond breaks, since bond breakage is typically[58] much faster (in this case, *measured* to be $\leq 10$ ps) than hydration (measured to occur within 25 ps). It is therefore suggested that it is the proton-transfer properties of the solvents HFIP, TFE, formamide, and water with respect to the (incipient) $OH^-$ leaving group which drive the C–O bond cleavage into the heterolytic direction, as symbolized in Scheme 3.[59] In contrast to hydration, proton transfer is a reaction that has the potential to be sufficiently fast ($k$ up to $10^{14}\,s^{-1}$)[60–62] to contribute in the *transition state* of the C–OH heterolysis reaction. However, from the fact that in the pure simple alcohols such as MeOH *no* heterolysis occurs, it is inferred that proton-donicity is sufficient only if it goes along with a very high polarity ($E_T^N \geq 0.8$) of the medium.

## Experimental Section

**General**: 9-Fluorenol (FOH) and fluorene were obtained from Aldrich and recrystallized from petroleum ether; 9-diazofluorene ($FlN_2$) was a gift from Prof. W. Kirmse (Bochum). 1,1,1,3,3,3-Hexafluoroisopropyl alcohol (HFIP), formamide, and 2,2,2-trifluoroethanol (TFE) were distilled under a nitrogen atmosphere to a purity of ≥ 99.8%. Dichloroethane (Acros), dichloromethane (Merck), and *N*-methylformamide (Aldrich) were spectroscopic grade and used as received. All other solvents were analytical grade from Merck. The ethers were fractionally distilled prior to use in order to remove peroxides and other impurities.

For recording fluorescence spectra a Perkin–Elmer LS-5 spectrofluorimeter was used. Fluorescence lifetimes were measured on a single photon counting apparatus with 0.8 ns time resolution.

The picosecond spectrometer was based on a mode-locked Nd:YAG laser (Continuum PY61C-10): $\lambda_{\text{fundamental}} = 1.064\,\mu$m, pulse width 20 ps, pulse repetition rate 10 Hz, pulse energy per shot 40 mJ. Radiation at $\lambda = 266$ nm (2–3 mJ per pulse) obtained by consecutive generation of the second and forth harmonics in DKDP and KDP nonlinear crystals was used for excitation.[63] The angle between the planes of polarization of the excitation and probing beams was set at 54.7° ("magic" angle) in order to eliminate any contribution to the decay kinetics of the transient absorption from rotational diffusion.[33] A white light continuum (WLC, $\lambda = 420$–$900$ nm), generated by irradiation with the 1.064 μm fundamental beam into a 25 cm quartz flow cell filled with $D_2O$, was used as a probe beam. Any remaining fundamental radiation was cut out with a dielectric-coated mirror (maximum reflectance at 1064 nm) after the cell and the WLC beam was focussed into a quartz optical fiber, which divided into two probing beams. The "lower" beam (energy $E_2$), serving as the reference beam, passed through the "virgin" solution, whereas the "upper" beam (energy $E_1$) passed through the solution volume exposed to the excitation beam. After passing through the vertically positioned quartz flow cell (dimension 2 mm in pump and 4 mm in probe direction) through which the test solution flowed (from bottom to top at 0.2 $\text{mL}\,\text{s}^{-1}$), the two probe beams were collected by quartz fibers and directed into the entrance slit of a CHROMEX 250IS spectrograph with a double diode array (Princeton Instruments) attached at the exit slit. The time delay between the pump and probe beams could be varied between 7 fs and 10 ns by a step-motor driven and computer-controlled delay line. The angle between the excitation and white light probing beams was 90°.

The transient absorption spectrum, that is, the excitation-induced change in absorbance $\Delta A$, was calculated with Equation (2):

$$\Delta A = -\log\{(E_1/E_2) \times (E_2^{o}/E_1^{o})\} \qquad (2)$$

in which $E_1$ ($E_2$) and $E_1^{o}$ ($E_2^{o}$) are the energies of the first (second) probe beams with and without pump pulse, respectively. A mechanical shutter was used to block the excitation beam during the measurements of the ratio $E_1^{o}/E_2^{o}$ ("split") of the probe beam energies. Automated performance of the setup, for example, manipulation of the delay line and the shutter, as well as the data processing, was carried out on a PC with the help of LabVIEW (National Instruments) software. After averaging 100 pulses the measurable changes of absorbance (at signal to noise level ≈2) corresponded to $\Delta A = 0.01$. The apparatus function of the setup was determined by using the $S_1 \rightarrow S_n$ absorption of *trans*-4-dimethylamino-4′-nitrostilbene in acetonitrile (in which the singlet lifetime is ≈10 ps)[64] to be 32 ps (FWHM) for $\lambda_{\text{exc}} = 266$ nm. For all measured transient kinetics, deconvolution by a nonlinear convolution/fitting process was performed,[65] by fitting the measured transients $\Delta A(t)$ with a model function $F(t) = \Sigma\alpha_i e^{-t/\tau_i}$ ($\alpha_i$ and $\tau_i$ are fitting parameters) convoluted with the system response (apparatus) function $AF(t)$: $\Delta A(t) \equiv F(t) \otimes AF(t)$.

The nanosecond flash-photolysis apparatus (KrF laser, 248 nm, 20 ns pulse width) has been described previously.[66] Absorbance of the samples was kept between 1 ns photolysis and 5 ps photolysis at the irradiated wavelength. All measurements were performed in air-saturated solutions.

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*only* photohomolysis was seen:W. M. McGowan, E. F. Hilinski *J. Am. Chem. Soc.* **1995**, *117*, 9019–9025; we have now found that also in the much more polar solvent MeCN, 9-bromofluorene undergoes photohomolysis only.

[36] In formamide, all three transients, the radical $F^{\bullet}$ (at 500 nm), the cation $F^+$ (515 nm) and $S_1$ (640 nm) were observed.

[37] The lifetime of $F^+$ in formamide is $\leq 10$ ps.

[38] A very weak broad absorption with $\lambda_{max} = 700$ nm is also observed and assigned to the hydrated electron, which forms due to two quantum ionization of 9-FOH and/or of water.

[39] This assumption is corroborated by the experimental observation that FOH is "photostable" in aqueous solution (due to reaction according to Scheme 1), as found by UV and HPLC analysis.

[40] The intensity of the 450 nm band is comparable to that at 515 nm.

[41] To our knowledge, this is the first observation of the hydration kinetics of a photochemically produced carbocation.

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[47] An increase of lifetime was also observed on addition of up to 1M $NaClO_4$

[48] Simultaneously, the (weak) 700 nm band (see ref. [38]) disappeared due to the scavenging of $e^-_{aq}$ by $H^+$ to yield $H^{\bullet}$.

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