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Solvent Effects on Intermolecular Proton Transfer: The Rates of Nitrene Protonation and Their Correlation with Swain Acity

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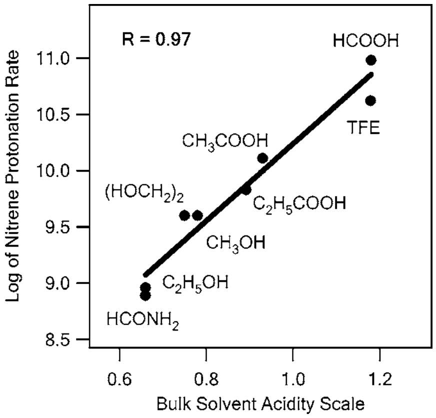
ABSTRACT



The rate of protonation of singlet 2-fluorenylnitrene was studied in eight protic solvents. The protonation rates vary between 10^{11} and 10^{9} s^{-1} and are well-correlated with Swain's acity parameters. This demonstrates that Swain acity parameters and nitrene protonation rates can be used to evaluate bulk solvent acidity.

Proton transfer is among the most elementary chemical reactions. Understanding this reaction provides fundamental mechanistic understanding important in both chemistry and biology.[1] Photoacids are very useful molecular probes and are used in photolithography.[2] Usually, a photoacid has greater acidity in its excited state than in its ground state.[3] Upon photolysis, photoacids will transfer a proton to an acceptor, in a process known as excited state proton transfer.[3] Certain proton transfer reactions can be classified as proton transfer to solvent, where the solvent acts as the proton acceptor, or as proton transfer from solvent (PTFS), where the solvent acts as the proton donor. Examples of PTFS are relatively rare.[4]

Singlet arylnitrenes are strong bases, and singlet *p*-biphenylylnitrene, for example, has a pK_b value of -2.[5] Singlet arylnitrenes are conveniently generated by light-induced decomposition of aryl azides and can be protonated to form the corresponding nitrenium ions in protic solvents (Scheme

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(2) Shirai, M.; Suyama, K.; Tsunooka, M. *Trends Photochem. Photobiol.* **1999**, *5*, 169.

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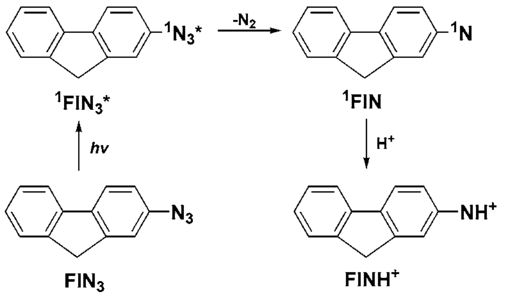
1) in competition with other reaction channels such as intersystem crossing (ISC) and ring expansion.[5–7] In addition, aryl azides are relatively stable in protic solvents,[7] providing a convenient strategy to study PTFS for strong bases. This has allowed us to study the protonation rate of singlet 2-fluorenylnitrene in a series of protic solvents with a wide range of acidity. Initially, 4-biphenylylnitrene was chosen for this study due to its favorable absorption properties, but some of the protonation rates were too slow to be accurately measured on our spectrometer. 2-Fluorenylnitrene was found to be protonated at least 2-fold faster than 4-biphenylylnitrene and thus was a good candidate to allow us to study the nitrene protonation over a wide range of solvents.

Scheme 1



Ultrafast photolysis ($\lambda_{ex} = 270$ nm) of 2-fluorenyl azide (FlN_3) in methanol produces the spectra of Figure 1. A band centered at 490 nm is formed within the instrument response (300 fs), which can be assigned to a singlet excited state of the azide ($^1FlN_3^*$), based on our previous studies.[7,8] As $^1FlN_3^*$ decays, a new band is formed, centered at 380 nm which blue shifts to 350 nm over 6 ps. The carrier of this newly formed band is assigned to singlet 2-fluorenylnitrene (^1FlN). The blue shift and band narrowing processes are typical of vibrational cooling processes (Figure 1b).[8] Subsequently, ^1FlN decays and a 450 nm band is formed, which is assigned to 2-fluorenylnitrenium ion ($FlNH^+$). This assignment is in excellent agreement with McClelland's observation of the same nitrenium ion in acetonitrile−water using nanosecond time-resolved laser flash photolysis techniques.[5] The decay of ^1FlN and the growth of $FlNH^+$ share the same time constant (250 ps) in methanol within experimental error. In methanol-OD, the time constant of the decay of ^1FlN and the growth of $FlNH^+$ lengthen to 380 ps, showing a kinetic isotope effect of 1.5. This relatively small primary isotope effect is not surprising as it is similar to values observed in the protonation of singlet aryl carbenes.[9] Ultrafast photolysis of FlN_3 in acetonitrile, a nonacidic solvent, produces the broad 490 nm band of $^1FlN_3^*$ and the 350 nm band of ^1FlN (Supporting Information, Figure S1). However, the 450 nm band was not observed in the aprotic solvent. On the basis of the known spectrum of $FlNH^+$, the absence of the 450 nm absorbing transient in acetonitrile, and the kinetic isotope effect, the assignment of the 450 nm band to $FlNH^+$ is secure.

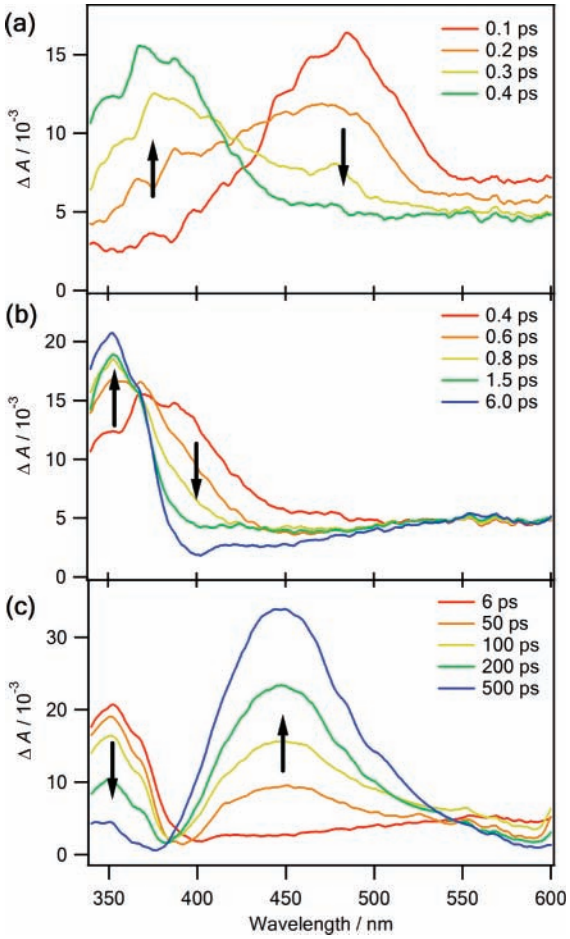


Figure 1. The transient spectra were generated by ultrafast LFP (270 nm) of 2-fluorenyl azide (FlN_3) in methanol with time windows of (a) 0.1−0.4 ps, (b) 0.4−6 ps, and (c) 6−500 ps.

The effect of solvent on the rates of nitrenium ion formation was studied in a series of protic solvents (Table 1).[10] In the eight solvents utilized in this study, the protonation time constant (τ) of ^1FlN is fastest in formic acid (10.5 ps) and slowest in formamide (1290 ps). The intersystem crossing (ISC) rate of the nitrene is 20 ns in acetonitrile. Assuming that the ISC rates in the eight solvents employed

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[10] All the solvents used are the highest grade available (>99%) and used as received. Even though small amounts of water undoubtedly are present in these experiments, the concentration of water is too low to influence the kinetics on a picosecond time scale since we do not expect strong hydrogen bonds (preassociation) between the fluorenyl azide and water.

Table 1. Solvent Parameters and the Correlations between Nitrenium Ion Formation Rates and the Swain Acity and Basity

solvent	ϵ[a]	n_D[a]	$E_T(30)$[b]	pK_a[c]	α[d]	β[d]	π^*[d]	*acity*[e]	*basity*[e]	τ/ps	log k_p	log k_{cal}[g]	log k_{cal}'[g]
$HCOOH$	51.1	1.3714	57.7		1.23	0.38	0.65	1.18	0.51	10.5	10.98	11.02	10.86
CF_3CH_2OH	27.7	1.2907	59.8	23.5	1.51	0.00	0.73	1.18[f]	0.73[f]	24	10.62		10.79
CH_3COOH	6.20	1.3720	55.2	12.6	1.12	0.45	0.64	0.93	0.13	78	10.11	10.14	10.14
C_2H_5COOH	3.44	1.3809	55.0		1.12	0.45	0.58	0.89[f]	0.60[f]	147	9.83		9.86
CH_3OH	33.0	1.3288	55.4	29.0	0.98	0.66	0.60	0.75	0.50	250	9.60	9.41	9.42
$HOCH_2CH_2OH$	41.4	1.4318	56.3		0.90	0.52	0.92	0.78	0.84	253	9.60	9.48	9.42
C_2H_5OH	25.3	1.3611	51.9	29.8	0.86	0.75	0.54	0.66	0.45	1090	8.96	9.08	9.14
$HCONH_2$	111.0	1.4472	56.6	23.5	0.71	0.48	0.97	0.66	0.99	1290	8.89	9.01	8.97

[a] The dielectric constant ϵ and the refractive index n_D are obtained from CRC Handbook of Chemistry and Physics, 87th ed. [b] The $E_T(30)$ data are in kcal·mol^{-1} and obtained from ref 11. [c] The pK_a values are measured in DMSO and obtained from Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456. [d] The α, β, and π^* data are obtained from ref 16. [e] The acity and basity data are obtained from ref 14, except where noted. [f] These data are calculated based on the correlations between the available acity and basity data and the KAT parameters.[16] Acity = 0.03 + 0.64α + 0.25π^*. Basity = 0.04 + 0.035β + 0.94π^* (exclude acetic acid). [g] The data are fitted into the equation $\log k_p = a \times acity + b \times basity + c$ by multilinear regression analysis. Log k_{cal} is the fitting for six solvents with original Swain's acity and basity: $\log k_{cal} = 3.76 \times \text{acity} - 0.13 \times \text{basity} + 6.66$; log k_{cal}' is the fitting for all eight solvents; $\log k_{cal}' = 3.34 \times \text{acity} - 0.31 \times \text{basity} + 7.07$.

in this study are similar to that in acetonitrile, we can conclude that the decay of the nitrene will be largely controlled by protonation, which is at least 20 times faster than ISC.

Simple correlations of log k_p with solvent physical properties, such as dielectric constant and refractive index, were not found (Supporting Information, Figures S2 and S3), where k_p is the apparent protonation rate constant and equals $1/\tau$. We also considered empirical solvent parameters. Dimroth's $E_T(30)$ parameters[11] provide a widely used scale to evaluate solvent polarity. In this case, however, the correlation between log k_p and $E_T(30)$ is also scattered (Supporting Information, Figure S4). A traditional Brønsted plot (log k_p versus pK_a) was also scattered (Supporting Information, Figure S5).[12] The acidity of a particular organic solute in DMSO does not correlate with the rate of nitrene protonation in the bulk organic solvent!

Kamlet, Abboud, and Taft (KAT) developed the solvatochromic solvent parameters α and β to describe solvent hydrogen bonding donor (HBD) and hydrogen bonding acceptor (HBA) abilities.[13] A better HBD solvent deprotonates more easily. Our data show a fair correlation with the α parameters (Supporting Information, Figure S6).

Subsequently, Swain et al. coined the terms *acity* and *basity* to describe a set of new parameters to measure the acid−base properties of bulk solvents, using the equation aA + bB + c, where A and B depend only on solvent and a, b, and c depend on the reaction. A refers to the anion-solvating tendency, and B refers to the cation-solvating tendency of the solvent. The authors fitted the free energy changes due to solvent using 1080 data sets for 61 solvents and 77 solvent-sensitive reactions and physicochemical properties, taken from the literature, such as reaction rate constants, equilibrium constants, product ratios, UV−vis, IR, and NMR spectra. They found that A and B can describe solvent hydrogen bond donating and accepting abilities[14] and proposed that these parameters could be used to evaluate *bulk* solvent acidity and basicity. To a first-order approximation,[15] the rate of nitrene protonation = $k_{H+}[H^+][^1FlN] = k_p[^1FlN]$, where k_{H+} is the bimolecular rate constant for the reaction between ^{1}FlN and a proton where, [H^+] and [^{1}FlN] are proton and 2-fluorenylnitrene concentration in solvent. Thus, the nitrene protonation rate k_p can, in principle, correlate with the acidity of bulk solvent, as quantified by the acity scale.

Excluding TFE and propionic acid, six of the eight solvents used in this study have known Swain acity parameters.[14] The correlation of log k_p with the six solvent acities is excellent (R = 0.99, the solid line of Figure 2). Stimulated by the similarity between the KAT and Swain's parameters, Marcus found a relationship between these two sets of solvent empirical parameters.[16] The two missing Swain parameters

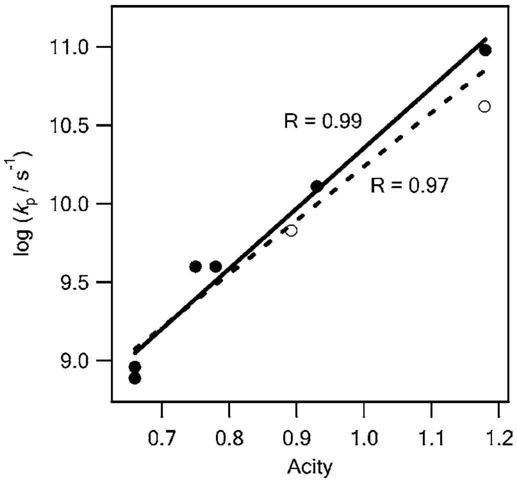

Figure 2. The correlation of log k_p with Swain's acity parameters. The acity parameters for formic acid, acetic acid, methanol, ethanol, ethylene glycol, and formamide (solid circles) are obtained from ref 14. The acity parameters for 2,2,2-trifluoroethanol and propionic acid (open circles) are calculated from KAT's parameters.[16] The dashed line is the best fit linear correlation of the data for all eight solvents of this study (R = 0.97). The solid line is the linear correlation of the data for the six solvents excluding 2,2,2-trifluoroethanol and propionic acid (R = 0.99).

of 2,2,2-trifluoroethanol and propionic acid were calculated accordingly based on Marcus relationships.[16] Including the two calculated *acity* parameters, the correlation of log k_p with solvent acities remains excellent ($R = 0.97$, the dashed line of Figure 2).

Multilinear regression analysis has been performed on these data following Swain's equation log $k_p = a \times acity + b \times basity + c$. When we consider six solvents (excluding 2,2,2-trifluoroethanol and propionic acid, Supporting Information, Figure S7) or upon consideration of all eight solvents (Supporting Information, Figure S8), a multilinear regression analysis has a large correlation coefficient. The absolute value of the fitting coefficient a is found to be more than 10 times greater than b. This demonstrates that the ability of a bulk solvent to solvate the conjugate anion produced in a proton transfer reaction is the dominant effect on nitrene protonation.

In summary, the rate of protonation of a nitrene in an organic solvent does not correlate with the acidity of the solvent when that solvent is a solute in DMSO, nor does it correlate with other simple parameters such as dielectric constant or E_T parameters. The rate protonation of singlet arylnitrenes does correlate with Swain's acity parameters. The Swain scale and the rate of nitrene protonation provide a convenient way to measure the bulk acidities of neat organic solvents.

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Supporting Information Available: Transient spectra of 2-fluorenyl azide in acetonitrile and the correlations of log k_p with solvent parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) An apparent violation is that the nitrene protonation is faster in TFE than in acetic acid. However, pK_a for acetic acid is smaller than that of TFE. This is not surprising because pK_a is a scale to measure molecular properties. It is inappropriate to use molecular properties to evaluate bulk solvent properties.

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(15) It is of course possible that the nitrene reacts with the solvent molecule directly to achieve proton transfer from solvent to solute. This proton donating ability is also correlated with acity values.

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