used for laser flash photolysis at NRC and elsewhere. As the beam quality and power of modern lasers improve over the next few years, it will become increasingly important to be aware of these effects if typical flash data are to be reliably interpreted. Further, two-photon processes resulting from transient excitation may play an important role in laser ablation techniques if the reactive intermediates generated can compete with the starting material for light absorption.

Benzil and its derivatives may find applications as readily available laser-specific free-radical sources. Some of these applications to vinyl polymerization are currently being explored in our laboratory.

Finally, we mentioned in earlier studies the difficulties associated with the determination of quantum yields in two-laser experiments. Work is now in progress trying to develop actinometers for two-photon, two-color processes. Preliminary data suggest that efficient chemical processes, such as that illustrated in Figure 1, may actually reflect low (<10%) quantum yields. This is likely to be the case in this system.

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An Acidity Scale, $[\mathrm{H}^+]^{h\nu}$, for Proton Quenching of Excited States

W. Brandon, A. L. Pincock, J. A. Pincock,* P. Redden, and C. Sehmbey

Department of Chemistry, Dalhousie University
Halifax, Nova Scotia, Canada B3H 4J3

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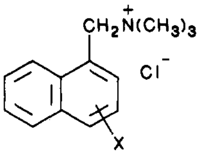
Recently, several groups have reported on photochemical reactions that occur because many functional groups have increased basicity in their excited singlet state.[1] For instance, Wan and Turro[2,3] studied the photocleavage of benzyl alcohols and the Yates Group has examined photohydrations of alkenes and alkynes.[4,5] In these cases reaction resulted from excited-state protonation which was monitored by the quenching of the substrate fluorescence. Analysis by Stern–Volmer methods and lifetimes is simple provided the quenching occurs in the region where the concentration of protons by titration is a reasonable estimate of the proton activity. At higher acidities, curved plots were observed.

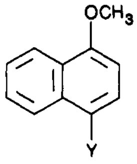
Acidity scales for ground-state equilibria and their application to acid-catalyzed reactions have been extensively studied.[6,7] Ground-state acidity scales are usually established by application of the Hammett proposal for the cancellation of indicator activity coefficient ratios. Excited-state kinetic scales are inherently different since the quantity measurable is always a ratio relative to other processes of the same excited state. Thus, the activity of the substrate excited state cancels. Moreover, these photochemical protonations are assumed to be irreversible[8] so that the activity of the protonated form can be ignored. For fluorescence quenching by protons, the Stern–Volmer relationship will be given by $I^0/I = 1 + k_q\tau[\mathrm{H}^+]^{h\nu}$ where $[\mathrm{H}^+]^{h\nu}$ is the kinetic protonating ability of the medium. Determination of these values requires an indicator whose fluorescence quenching can be measured over a range of acidities that can be anchored in the pH region. We have chosen 1-cyanonaphthalene because quenching of its fluorescence ($\phi_f = 0.37$[9]) begins at pH 1 and yet the cyano group has such a low ground-state basicity that it will remain unprotonated in quite concentrated acid solutions.

Stern–Volmer fluorescence quenching data for 1-cyanonaphthalene in 20% ethanol/80% aqueous sulfuric acid[10,11] are plotted in Figure 1 where the horizontal axis indicates titratable protons. The inset shows the linear regeion of the quenching from which the slope $k_q\tau = 0.555 \pm 0.006$ is established. On the graph, this line is then extrapolated well beyond values for titratable protons. Evaluation of $[\mathrm{H}^+]^{h\nu}$ at any given $[\mathrm{H}^+]$ involves a simple extrapolation from the quenching curve. This is shown graphically[12] for two experimental determinations of I^0/I vs. $[\mathrm{H}^+]$. Values of $[\mathrm{H}^+]$ and derived $[\mathrm{H}^+]^{h\nu}$ obtained this way are 2.44, 3.03; 2.95, 4.39; 5.30, 12.1; 6.63, 22.3; 8.58; 50.7; and 9.81, 85.1.[13] The two are identical below $[\mathrm{H}^+] = 2.0$ M. At high acidities the extrapolations required are large and the obvious concern is that they could be unreliable. However, our first test of the $[\mathrm{H}^+]^{h\nu}$ scale is successful.

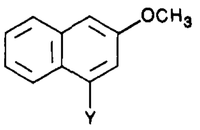
We have previously examined the effect of substituents on the photocleavage of (1-naphthylmethyl)trimethylammonium chlorides (**1**) and found that the 4-methoxy substrate gives a faster rate of heterolytic cleavage than the 3-methoxy isomer.[14] In contrast, for the proton-catalyzed cleavage of benzyl alcohols the 3-methoxy isomer reacts faster than the 4-methoxy one,[2] which is a quantitative confirmation of the "meta" effect postulated by Zimmerman in the 1960s.[15,16] To analyze the difference between the two systems, we now report on the proton fluorescence quenching of a series of 1-methoxy- (**2**–**4**) and 2-methoxynaphthalene derivatives (**5**–**7**).



1



2, Y = H
3, Y = $\mathrm{CH_3}$
4, Y = $\mathrm{CH_2OH}$



5, Y = H
6, Y = $\mathrm{CH_3}$
7, Y = $\mathrm{CH_2OH}$

Proton quenching of the fluorescence of the 1-methoxy derivatives **2**–**4** occurs in the range pH 2–0. Linear Stern–Volmer plots are obtained and the $k_q\tau$ values are reported in Table I. The quenching of the 2-methoxy derivatives occurs at higher acidities (2–10 M); the Stern–Volmer plots obtained by using titratable $[\mathrm{H}^+]$ curve upward. Attempt to evaluate the $k_q\tau$ values for **6** and **7** from the linear part of these curves at acidities lower than $[\mathrm{H}^+] = 2$ M are unreliable, as indicated by standard deviations and correlation coefficients (Table I), because the extent of quenching is small. For **5**, even this becomes impossible. Attempts to use the ground-state H_0[10] scale also failed. However, all three plots are gratifyingly linear vs. $[\mathrm{H}^+]^{h\nu}$. The calculated $k_q\tau$ values given in the table and the improved standard deviations show this to be a much more reliable method than trying to use the weak fluorescence quenching at low acidities.

The generality of this procedure for analyzing excited-state protonations awaits further testing. The simplicity of constructing a Stern–Volmer plot with 1-cyanonaphthalene as the indicator for any conditions (solvent, acid, temperature, etc.) will make this a very useful method. Such studies are in progress.

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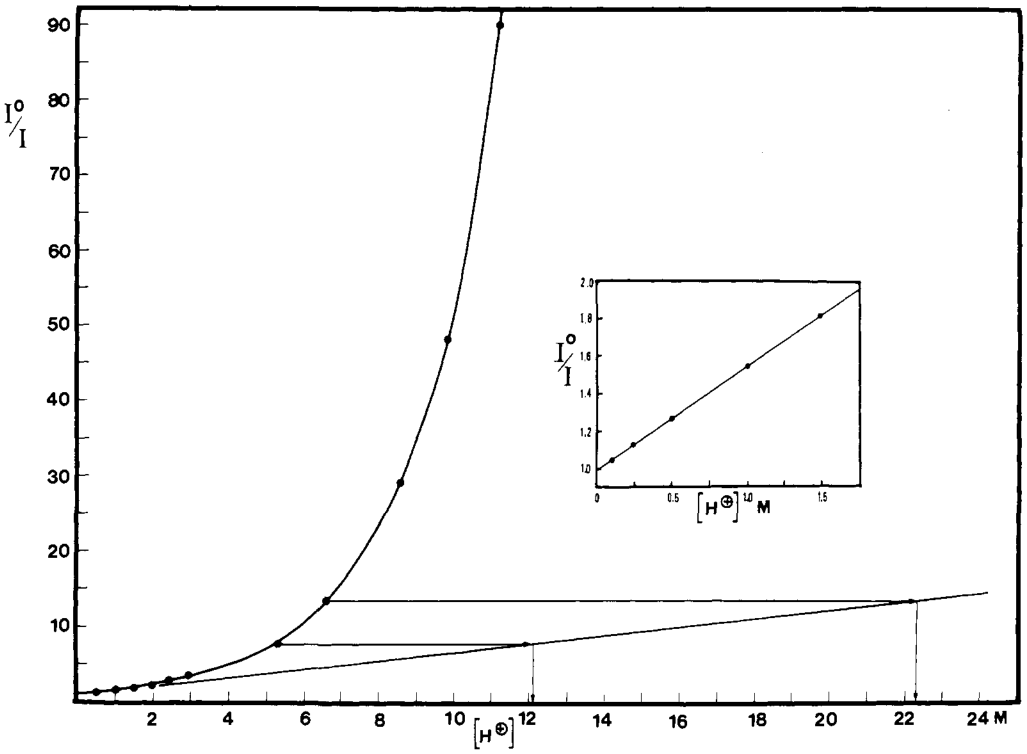

Figure 1. Stern–Volmer plot for the quenching of 1-cyanonaphthalene fluorescence vs. [H^+]. The inset shows the region of 0–1.5 M expanded.

Table I. Singlet Lifetimes and Stern–Volmer Results for the Naphthalene Derivatives **2–7**

compd	τ,[a] ns	$k_q\tau$,[b,c] M^{-1}	$10^{-9}k_q$, M^{-1} s^{-1}	$k_q\tau$,[c,d] M^{-1}	$10^{-7}k_q$, M^{-1} s^{-1}
2[e]	9.28	11.4 ± 0.2 0.9996 (8)	1.22		
3	9.88	26.0 ± 0.1 0.99995 (8)	2.63		
4	8.96	12.0 ± 0.07 0.9996 (8)	1.36		
5[f]	10.5	$\lesssim$0.1[g]	<0.01	0.072 ± 0.001 0.9991 (6)	0.68
6	14.5	0.28 ± 0.02[g] 0.98 (7)	0.019	0.292 ± 0.002 0.9998 (5)	2.0
7	9.86	0.22 ± 0.01[g] 0.98 (5)	0.017	0.216 ± 0.005 0.998 (6)	2.2

[a] By single photon counting. [b] Using [H^+] by titration. [c] Errors are standard deviation of the least-squares slope with correlation coefficient and number of points given below. [d] Using $[H^+]^{h\nu}$. [e] Values of 8.9 ns, 9.6 M^{-1}, and 1.08 × 10^9 M^{-1} s^{-1} have been reported for 20% acetonitrile/80% water.[9] [f] Values of 10 ns, <0.03 M^{-1}, and <3 × 10^6 M^{-1} s^{-1} have been reported.[9] [g] Calculated from points up to [H^+] = 2.0 M only.

Finally, some comment about the proton quenching of these substrates is required. The singlet lifetimes for the compounds allow calculations of the k_q values shown in the table. Compounds **4** and **7** are the naphthalene analogues of the benzyl alcohols studied by Wan and Turro.[2] There is clearly no meta effect. However, the reason is obvious. The 1-methoxy compounds all have similar reactivity with protons and it is well-established that the pathway for quenching of the excited state of 1-methoxynaphthalene (**2**) is via ring protonation.[9] Likely, the others are similarly quenched by protons. Since the 2-methoxy compounds are also all quenched at similar rates (about a factor of 10^2 slower than the 1-methoxy isomers) the most likely process is, again, ring protonation.[17] MO calculations[9] of the excited state of 1- and 2-methoxynaphthalene support the idea that electron density increases in the ring are greater for the 1-isomer. Clearly, substrates that have several basic centers must be examined quite carefully to determine what the k_q value obtained from fluorescence quenching means in terms of the reactivity of any given functional group. To have ascribed the k_q solely to benzylic cleavage in this case would have been wrong.

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(17) Note that 1-cyanonaphthalene and 2-cyanonaphthalene have very similar k_q values,[9] suggesting that quenching by protons occurs at nitrogen. The methoxynaphthalenes, in contrast, protonate at ring carbons. This suggests that $[H^+]^{h\nu}$ may be a fundamental property of the medium and not just a method of linearizing Stern–Volmer plots.

Acrolein Acetals as Allyl Cation Precursors in the Ionic Diels–Alder Reaction

Paul G. Gassman,* Daniel A. Singleton,[1]
James J. Wilwerding,[2] and Subhash P. Chavan

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

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Diels–Alder reactions that employ acrolein as the dienophile often give undesirable results due to the ease of polymerization of acrolein. In order to circumvent this problem, a variety of Lewis acids[3] and high pressures[4] have been employed. Even under these conditions yields are often less than 50%. Our experience with the ionic Diels–Alder reaction of allyl cations[5] suggested that acetals of acrolein[6] (**1**) should be convenient precursors of the alkoxy-substituted allyl cations **2**, which, in turn, should be ex-

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