

***N*-Arylbenzonitrilium ions. Photochemical generation and effect of substituents in the phenyl rings on lifetimes in water and reactivity with azide ion**

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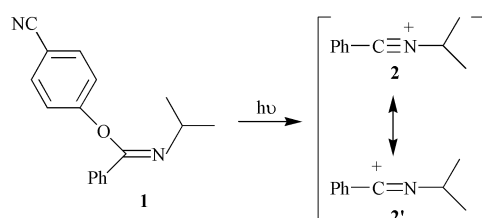
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Nitrilium ions $\text{Ar}-\text{C}\equiv\text{N}^+-\text{Ar}'$ have been studied by laser flash photolysis in aqueous solutions containing 20% acetonitrile. The cations were generated by photoheterolysis of benzimidate esters $\text{Ar}-\text{CZ}=\text{N}-\text{Ar}'$ ($\text{Z} = -\text{OC}_6\text{H}_4-4-\text{CN}$) with 4-cyanophenoxide as the photochemical leaving group. Rate constants for the reaction with water (k_w), azide ion (k_{az}) and hydroxide (k_{OH}) were measured. The cation $\text{Ph}-\text{C}\equiv\text{N}^+-\text{Ph}$ is only 50-fold shorter lived in water compared to $\text{Ph}-\text{C}\equiv\text{N}^+-text{iPr}$ (**2**); thus the effect of replacing an *N*-alkyl group with *N*-phenyl is modest. These two cations are also shown to have similar lifetimes to iminium analogs, e.g. $\text{Ph}-\text{CH}=\text{N}^+(\text{Me})-\text{Ph}$. Thus, addition of water to analogous sp and sp^2 hybridized systems occurs at a similar rate, and the increased steric access to the nitrilium nitrogen plays at most a modest role. For the series where substituents in Ar' were varied with Ar equal to phenyl, the Hammett plot for $\log k_w$ correlated with σ , with $\rho = -1.4$. For the series where Ar was varied, the data correlated much better with σ^+ , although ρ^+ was only -0.6 . This remarkably small effect of substituents in Ar contrasts with the effects seen in benzylic carbocations, but is consistent with the nitrilium structure, with most of the positive charge located on the nitrogen. Rate constant ratios $k_{\text{az}} : k_w$, including the *N*-alkylnitrilium ion **2**, are constant at $\sim 10^4$, with values of k_{az} well below the diffusion limit, even for the most reactive nitrilium ions. This is very different behaviour from that of carbocations and arylnitrenium ions of similar lifetimes in water. For these cations the rate constants k_{az} would be at or at least approaching the diffusion limit.

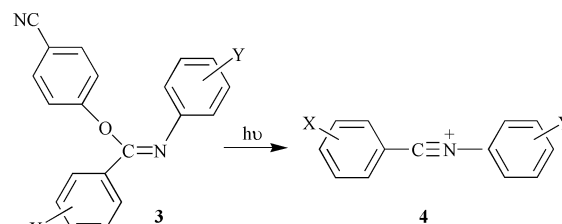
We have recently reported a flash photolysis study of the *N*-isopropylbenzonitrilium ion **2**.¹ This cation was obtained upon irradiation of the imidate ester **1**, a photoheterolysis with 4-cyanophenoxide as the leaving group (Scheme 1). This



Scheme 1

aryloxide had been employed previously in flash photolysis studies of tri- and diarylmethyl cations.^{2,3} The nitrilium ion **2** was generated in aqueous solutions and rate constants measured for its reaction with solvent (k_w), hydroxide ion (k_{OH}) and azide ion (k_{az}). By carbocation standards,⁴ the nitrilium ion **2** is relatively long-lived in water, with a lifetime ($1/k_w$) of 2.5 milliseconds. This cation reacts with nucleophiles at the carbon end of the $\text{C}\equiv\text{N}$ triple bond, i.e. via the resonance contributor **2'**. There are now extensive studies of structure–reactivity relations for carbocations such as the tri- and diarylmethyl cations where the electrophilic center is sp^2 hybridized.^{4–7} Studies of sp -hybridized examples are, however, more limited.^{8–16} One of the unusual features of the reactivity of **2** was its relatively poor quenching by azide ion. Azide is an excellent nucleophile for sp^2 -hybridized carbocations, and has seen extensive use as a clock, with the assumption that the azide–cation combination is diffusion limited.^{17,18} Such an assumption for **2** produces a lifetime that is wrong by three-orders of magnitude.

In this paper, we report a flash photolysis investigation of a series of *N*-arylbenzonitrilium ions **4** (Scheme 2), with substitu-



Scheme 2

ent variation in both aromatic rings. The cations were obtained photochemically from imidate precursors **3**, with 4-cyanophenoxide as a leaving group. One of the objectives in this study was to evaluate how substituent variation at the two ends of the nitrilium ion affect reactivity. We also anticipated that the *N*-arylnitrilium ions would be more short-lived than the *N*-alkyl derivative **2**, as did turn out to be the case. In this respect we were interested in seeing what would happen with the rate constants for azide.

Results

We start by discussing the evidence that the benzimidates, **3**, do produce nitrilium ions, **4**, and 4-cyanophenoxide upon irradiation in aqueous solutions. This takes the form of experiments with parent **3**, 4-cyanophenyl *N*-phenylbenzimidate. These experiments (as is true of all of the experiments in this paper) were conducted in 20% acetonitrile because of solubility problems in 100% aqueous solutions. The laser flash photolysis also required that the irradiation be carried out in solutions with pH greater than the $\text{p}K_a$ of 4-cyanophenol. The 4-cyanophenoxide is a product, as will be discussed below. Irradiation in more acidic solutions produces decays associated with the protonation of the 4-cyanophenoxide (as was noted previously).¹ In

the present case this interfered with the decays due to the nitrilium ion.

Fig. 1 shows spectra obtained by laser flash photolysis (LFP) of the benzimidate in a basic solution. There is immediate absorbance increase in the region 260–320 nm that occurs in the 20 ns laser pulse, and results in a spectrum with an apparent λ_{max} at 280–285 nm. This is not necessarily a true λ_{max} since the LFP apparatus only measures a difference in absorbance (ΔA), *i.e.* the absorbance after the pulse minus the absorbance of the solution before. The initial ΔA values are shown as the closed symbols in Fig. 1. This absorbance decays following good exponential kinetics, with $k = 4 \times 10^5 \text{ s}^{-1}$ for the system of Fig. 1. The decay does not go to zero, but to the absorbances indicated by the open symbols in Fig. 1.

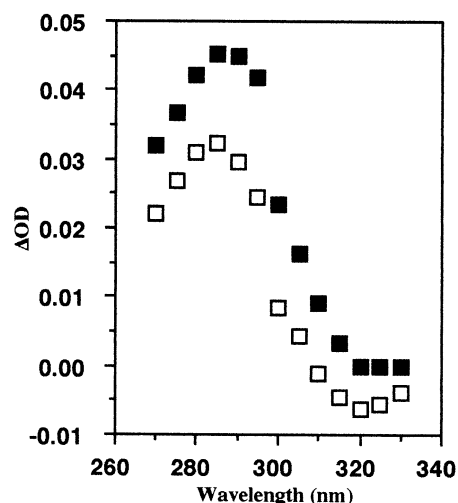


Fig. 1 Absorbance changes observed with laser flash photolysis (248 nm irradiation) of 4-cyanophenyl *N*-phenylbenzimidate ($1.5 \times 10^{-5} \text{ mol dm}^{-3}$) in $0.006 \text{ mol dm}^{-3}$ sodium hydroxide in 20% acetonitrile : 80% water. The closed squares are the readings of ΔA immediately after the laser pulse. The open squares are the readings at the completion of the exponential decay process.

The analysis of these spectra and spectral changes is complicated since all of the species—the benzimidate starting material, the nitrilium ion, and the products—have overlapping absorbances. This can be seen in Fig. 2, which depicts the optical densities obtained in an experiment where a cuvette containing

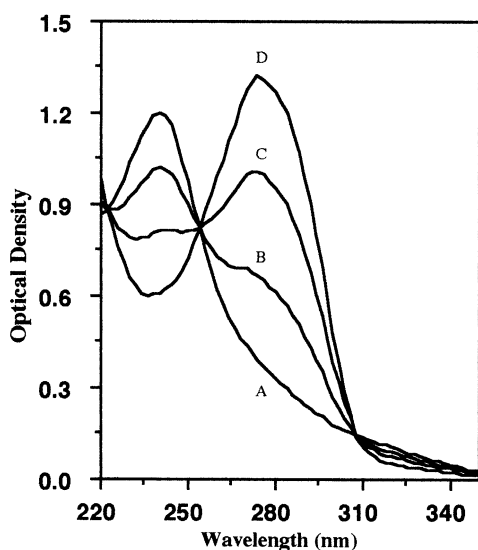


Fig. 2 Spectra (1 cm pathlength) obtained with 4-cyanophenyl *N*-phenylbenzimidate ($4.5 \times 10^{-6} \text{ mol dm}^{-3}$) in $0.002 \text{ mol dm}^{-3}$ sodium hydroxide in 20% acetonitrile : 80% water. Spectra were obtained before irradiation (A) and after 3 minutes (B), 7 minutes (C) and 16 minutes (D) irradiation at 254 nm in a Rayonet reactor. Additional irradiation produced no further change.

the benzimidate was irradiated in a Rayonet reactor, and the spectra recorded at various times. Spectrum A obtained before irradiation is that of the benzimidate. This has a λ_{max} at 240 nm, but there is tailing absorbance out past 300 nm. Upon irradiation a new peak grows with a λ_{max} of 274 nm, with isosbestic points at 224 nm and 254 nm. The λ_{max} at 274 nm corresponds to the maximum of 4-cyanophenoxide. It can be seen that the difference between curve D and curve A in Fig. 2 matches the final spectrum of Fig. 1. Our experiences with 4-cyanophenoxide as a photochemical leaving group show that the ion is generated within the 20 ns laser pulse.^{1–3} Thus, the absorbance for 4-cyanophenoxide is also present in the initial spectrum in Fig. 1. We argue that the additional absorbance present in this spectrum must be due to the other product of the photoheterolysis, the nitrilium ion.

(a) This absorbance is similar to that seen upon irradiation of compound 1, where the transient was assigned to the *N*-isopropylbenzonitrilium 2.¹ This comparison is shown in Fig. 3. The closed squares are the data for 2. As was shown in

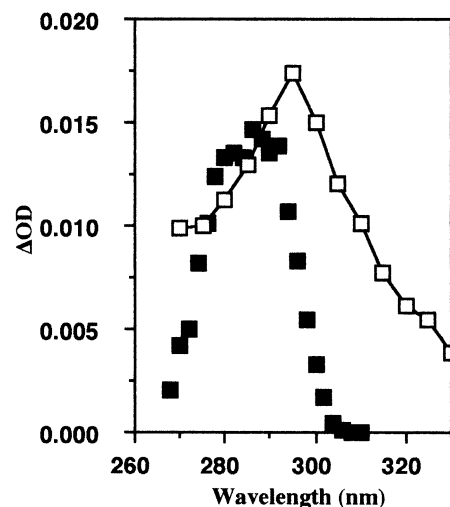


Fig. 3 Laser flash photolysis spectra of the *N*-isopropylbenzonitrilium ion (closed squares) and the *N*-phenylbenzonitrilium ion (open squares). Data for the former were obtained by irradiation of 4-cyanophenyl *N*-isopropylbenzimidate, and are the experimental points from Fig. 5 of ref. 1. The data for the latter are the differences between initial and final ΔA values in Fig. 1 of this paper.

Fig. 5 of ref. 1, the points here represent a shoulder in the overall spectrum of the nitrilium ion 2; the maximum is not real since there is overlap with other species present. The open symbols in Fig. 1 are the difference between the initial and final spectra of Fig. 1, *i.e.* with the contribution from 4-cyanophenoxide subtracted out. It can be seen that there is similarity with the ΔA values obtained for 2. There is some additional absorbance above 300 nm in the present case. This can be attributed to a contribution from the additional *N*-phenyl chromophore.

(b) HPLC analysis of the products of irradiation of 4-cyanophenyl *N*-phenylbenzimidate in 20% acetonitrile shows that there is conversion to 4-cyanophenol (or the phenoxide) and benzanilide, with no other peaks appearing. The reaction is within experimental error, quantitative even at prolonged irradiation times. As shown in Scheme 3, these are the two products expected for photoheterolysis, with the benzanilide the product of the reaction of the nitrilium ion.

(c) The spectral change from the initial to the final A values in Fig. 1 follows exponential kinetics with the same rate constant across the entire spectrum. This points to a single reactive species as being responsible. This decay is accelerated by azide ion and hydroxide ion, but not by oxygen. These are characteristics of carbocation intermediates that react with added nucleophiles,⁴ but are unaffected by O_2 .

Table 1 Substituents X and Y in *N*-(Y-aryl)-X-benzonitrilium ions and rate constants for the reactions with water, azide ion and hydroxide ion. Conditions are 20% acetonitrile, ionic strength = 0.1 mol dm⁻³ (NaClO₄), 20 °C

X	Y	$k_w \times 10^4{}^a$	$k_{az} \times 10^8{}^b$	$k_{OH} \times 10^7{}^b$
H	H	2.1	2.6	6.4
4-MeO	H	0.67	0.75	2.0
4-PhO	H	1.09	1.10	
4-Me	H	1.57	1.91	4.4
3-Me	H	1.95	2.4	
3-MeO	H	2.6	2.8	
4-Cl	H	2.4	3.2	10.0
3-Cl	H	3.2	4.5	12.0
3-CF ₃	H	4.3	4.5	
4-CF ₃	H	5.1	5.8	
H	4-MeO	1.02	1.15	4.7
H	4-PhO	1.7	1.76	
H	4-Me	1.48	2.0	6.1
H	3-Me	1.9	2.2	
H	4-Cl	5.3	5.3	10.1
H	3-Cl	7.1	7.1	14.2
H	3-CF ₃	8.9	8.1	
H	4-CF ₃	16.4	11.3	19.2

^a Units of s⁻¹. ^b Units of dm³ mol⁻¹ s⁻¹.

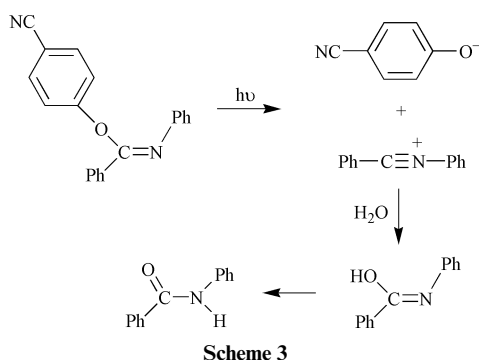


Table 1 shows the nitrilium ions studied in this work. These ions were all obtained by photolysis of a 4-cyanophenyl benzimidate precursor. Spectral changes in the region 260–320 nm similar to those of the parent system, with quenching by azide ion and hydroxide, were evidence that the ions had formed. Table 1 provides the results of the kinetic experiments. The parameter k_w is the first-order rate constant for the decay of the cation in solvent alone; k_{az} and k_{OH} are the second-order rate constants for the quenching by azide ion and hydroxide ion, obtained as the slope of plots of the observed rate constants *versus* the concentrations of the nucleophile.

Discussion

Nitrilium ion reactivity

Table 2 provides a survey of the lifetimes of relevant carbocations, iminium ions and nitrilium ions that have been measured or estimated in water. There has been a suggestion that sp²-hybridized cations should be more reactive than sp³ analogs, because of the decreased steric effect in the former.¹⁵ This is, however, not borne out in the data. The vinyl cation **10** and the carbenium analog **9** have very similar lifetimes in 2,2,2-trifluoroethanol, as noted previously.¹³ A similar conclusion can be made comparing nitrilium ions and iminium ions. The best comparison here is between the *N*-phenyliminium ion **7** and the *N*-phenylbenzonitrilium ion. While the former was not studied in water, its lifetime can be estimated, and it is only about an order of magnitude longer-lived. There is also only a small difference between the *N*-alkylnitrilium ion **2** and the iminium ion **6**, although here the analogy is not as close since

Table 2 Lifetimes of cations

Cation	$(1/k_w)/s$	$(1/k_s)/s$
4-Me ₂ NC ₆ H ₄ C ⁺ (CH ₃) ₂ (5)	$6 \times 10^{-3}{}^a$	
Ph-CH=N ⁺ (CH ₂ Ph)Bu (6)	$2-10 \times 10^{-3}{}^b$	9×10^{-5} (MeOH) ^c
Ph-C≡N-iPr (2)	$3 \times 10^{-3}{}^d$	
Ph-CH=N ⁺ (CH ₃)Ph (7)	$4-20 \times 10^{-4}{}^b$	2×10^{-5} (MeOH) ^c
Ph-C≡N-Ph (4 , X = Y = H)	$5 \times 10^{-5}{}^e$	
CH ₂ =N ⁺ (CH ₃)C ₆ H ₄ -4-Cl (8)	$3 \times 10^{-7}{}^f$	
4-MeOC ₆ H ₄ CH ⁺ -CH ₃ (9)	$\sim 3 \times 10^{-9}{}^g$	3×10^{-6} (TFE) ^h
4-MeOC ₆ H ₄ -C ⁺ =CH ₂ (10)	$\sim 7 \times 10^{-10}{}^g$	7×10^{-7} (TFE) ^h
4-Me ₂ NC ₆ H ₄ -C ⁺ =O (11)	$\sim 1 \times 10^{-10}{}^i$	

^a Ref. 16. ^b Estimated on basis of difference of 20–100 lifetimes between cations in water and methanol. Ref. 19. ^c Ref. 20. ^d Ref. 1. ^e This work. ^f Ref. 21. ^g Estimated on basis of difference of 1000 lifetimes between cations in water and TFE. ^h Ref. 13. TFE = 2,2,2-trifluoroethanol. ⁱ Ref. 11.

the latter has an electron withdrawing benzyl group on the nitrogen.

Phenyl groups are inductively electron withdrawing relative to alkyl groups. Thus, *N*-phenyl substituted nitrilium ions and iminium ions are expected to be more reactive than *N*-alkyl analogs. The data in Table 1 show that while this is the case, the effect is not large. The best comparison here is the *N*-phenylbenzonitrilium ion with the *N*-isopropyl analog **2**—a difference in lifetime of a factor of only 50.

It can also be seen that benzonitrilium ions are much longer-lived than α -phenyl substituted vinyl cations and acylium ions such as **10** and **11**. In fact the comparison in Table 2 considerably underestimates the difference, since **10** and **11** bear strong *para* π donors. Thus the analogs with just a phenyl ring will be much more reactive. This is in fact seen in the weakly nucleophilic solvent 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP). Cation **10** with the 4-methoxy substituent is 10000 times longer-lived than the unsubstituted cation PhC⁺=CH₂.¹⁶

Effects of substituents in *N*-arylbazonitrilium ions

The effects of substituents within the *N*-arylbazonitrilium ions of the present study are shown in the form of Hammett plots in Fig. 4. The data can be divided into two series, an N-series

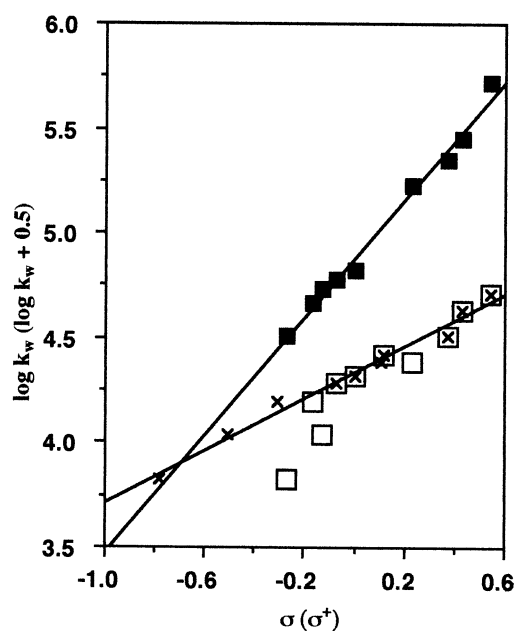


Fig. 4 Hammett plots for *N*-(Y-phenyl)-X-benzonitrilium ions. The open squares (*versus* σ) and the crosses (*versus* σ^+) represent the C-series where Y = H and the substituent X is varied. The closed squares (*versus* σ) represent the N-series where X = H and the substituent Y is varied. The 'y' axis for the C-series is $\log k_w$; the 'y' axis for the N-series is $\log k_w + 0.5$.

where the substituent Y on the *N*-aryl ring is varied with the substituent X on the *C*-aryl ring equal to hydrogen, and a C-series where the latter is varied with the former equal to hydrogen. Within both series the effect of the substituent variation is modest, particularly in comparison with other carbocations. A change from the most electron withdrawing substituent, 4-trifluoromethyl, to the best electron donor, 4-methoxy, only results in a kinetic stabilization of about one order of magnitude in both series. The N-series produces a good linear correlation (correlation coefficient = 0.989) when plotted against σ substituent constants. This correlation with σ is not surprising since the positive charge in the cation cannot be delocalized by resonance into the *N*-aryl ring (without including unfavorable zwitterionic resonance contributors). With the C-series however, a plot *versus* σ shows significant deviation in the points for the *para* π donors, especially 4-phenoxy and 4-methoxy. The σ^+ correlation is significantly improved (correlation coefficient = 0.984). Even though there must only be a small amount of positive charge at the carbon end of the C–N bond, *para* donors in the phenyl ring interact in a manner similar to that in benzylic cations.

The slopes of the correlation lines in Fig. 4 are -1.4 for the N-series *versus* σ , and -0.6 for the C-series *versus* σ^+ . This greater sensitivity to the substituent change in the *N*-aryl ring is consistent with a greater positive charge at the nitrogen. In other words, these are nitrilium ions as in resonance contributor 2 of Scheme 1, and the contribution from the vinyl cation contributor 2' is small. This conclusion is also reached when one considers the effects of substituents in other benzylic-type cations. A pertinent example are the two vinyl cations $4\text{-MeOC}_6\text{H}_4\text{C}^+=\text{CH}_2$ and $\text{C}_6\text{H}_5\text{C}^+=\text{CH}_2$ where there is a 10000-fold difference in reactivity in the solvent HFIP.¹⁶ The nitrilium ions $4\text{-MeOC}_6\text{H}_4\text{C}\equiv\text{N}^+\text{Ph}$ and $\text{C}_6\text{H}_5\text{C}\equiv\text{N}^+\text{Ph}$ show only a three-fold difference.

Azide ion

Azide ion does effectively quench the nitrilium ions of this study. However, as observed with the *N*-alkyl derivative 2 previously,¹ its reactivity is low when compared to what has been observed with other carbocations. This comparison is depicted graphically in Fig. 5 in the form of a plot of $\log k_{\text{az}}$ *versus* $\log k_{\text{w}}$. The behaviour of the carbocations and arylnitrenium ions has been commented upon previously.^{22,23} Within each series,

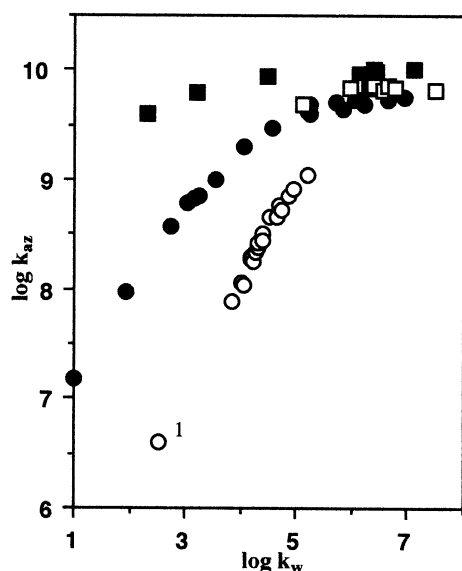


Fig. 5 Correlation of $\log k_{\text{az}}$ *versus* $\log k_{\text{w}}$ for benzonitrilium ions (open circles—this work and ref. 1 (point indicated by '1')), triarylmethyl cations (closed circles—ref. 22), diarylmethyl cations (open squares—ref. 22) and arylnitrenium ions (closed squares—ref. 23).

the more reactive derivatives react with azide with a constant rate constant that although slightly dependent on structural class lies in the range $5\text{--}10 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This behavior can be explained by the azide reaction being diffusion controlled, so that changes in structure no longer have any effect on the rate constant. This behavior is observed once these cations have a solvent rate constant of $\sim 10^5 \text{ s}^{-1}$. In other words cations of these series with lifetimes of 10 microseconds or less in water react with azide ion with a rate constant that is, at the very least, close to the diffusion limit.

This behavior is certainly not seen for the benzonitrilium ions. The *N*-aryl derivatives studied in the present work have lifetimes of 10–100 microseconds, and although the rate constants for azide ion are large, they are still 1–2 orders of magnitude smaller than the values associated with diffusion control. Fig. 6 depicts this in a different perspective, through a

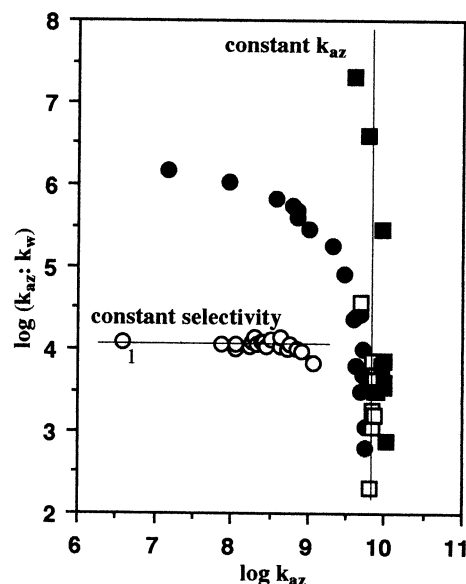


Fig. 6 Correlation of azide : water selectivity with azide reactivity. Symbols have the same meaning as in Fig. 5.

logarithmic plot of azide : water selectivity *versus* the rate constant for azide. As originally suggested by Ta-Shma and Rappoport,²⁴ the simple interpretation of this figure is that there are two separate behaviors with a short region representing the changeover from one to the other. For most of the tri- and diarylmethyl carbocations and the arylnitrenium ions, k_{az} is effectively constant because the reaction has reached diffusion control. A change in structure that increases reactivity has no effect on k_{az} , but it does increase k_{w} . This means that the selectivity $k_{\text{az}} : k_{\text{w}}$ decreases, so that a plot of $\log k_{\text{az}} : k_{\text{w}}$ *versus* $\log k_{\text{az}}$ is essentially a vertical line. The other extreme is shown by the data for the nitrilium ions, where the plot is essentially a horizontal line. In this series a change in structure that increases reactivity has essentially the same effect on k_{az} as it does on k_{w} , and the ratio $k_{\text{az}} : k_{\text{w}}$ is constant. This is true within the series of *N*-arylnitrenium ions, and also if the point for the *N*-isopropyl derivative is included. Constant selectivity with changing reactivity is a feature of highly stabilized carbocations, as observed by Ritchie.^{25,26} The nitrilium ions, although they are reactive towards water, are still in a constant selectivity region, at least so far as the azide : water ratio is concerned. The start of the changeover to diffusion control in azide is just apparent from the slight downward deviation of the points with the highest k_{az} .

Fig. 6 shows that the $k_{\text{az}} : k_{\text{w}}$ ratio in the constant selectivity region must vary over a wide range with cation structure. For the nitrilium ions this ratio is about 10^4 and for the triarylmethyl cations $2\text{--}4 \times 10^6$. The arylnitrenium ions are just starting

Table 3 Melting points and HRMS data for 4-cyanophenyl *N*-(*Y*-phenyl)-*X*-benzimidates

X	Y	Mp/°C	Formula	HRMS calc.	HRMS obs.
H	H	95–96	C ₂₀ H ₁₄ N ₂ O	298.1106	298.1113
4-MeO	H	119–120	C ₂₁ H ₁₆ N ₂ O ₂	328.1212	328.1211
4-PhO	H	179–181	C ₂₆ H ₁₈ N ₂ O ₂	390.1368	390.1355
4-Me	H	132–134	C ₂₁ H ₁₆ N ₂ O	312.1263	312.1268
3-Me	H	64–65	C ₂₁ H ₁₆ N ₂ O	312.1263	312.1268
3-MeO	H	91–93	C ₂₁ H ₁₆ N ₂ O ₂	328.1212	328.1220
4-Cl	H	125–126	C ₂₀ H ₁₃ ClN ₂ O	332.0716	332.0722
3-Cl	H	97–98	C ₂₀ H ₁₃ ClN ₂ O	332.0716	332.0718
3-CF ₃	H	82–83	C ₂₁ H ₁₃ F ₃ N ₂ O	366.0980	366.0991
4-CF ₃	H	110–111	C ₂₁ H ₁₃ F ₃ N ₂ O	366.0980	366.0974
H	4-MeO	71–72	C ₂₁ H ₁₆ N ₂ O ₂	328.1212	328.1201
H	4-PhO	156–157	C ₂₆ H ₁₈ N ₂ O ₂	390.1368	390.1351
H	4-Me	76–77	C ₂₁ H ₁₆ N ₂ O	312.1263	312.1256
H	3-Me	81–82	C ₂₁ H ₁₆ N ₂ O	312.1263	312.1266
H	4-Cl	105–106	C ₂₀ H ₁₃ ClN ₂ O	332.0716	332.0716
H	3-Cl	77–79	C ₂₀ H ₁₃ ClN ₂ O	332.0716	332.0711
H	3-CF ₃	41–42	C ₂₁ H ₁₃ F ₃ N ₂ O	366.0980	366.0995
H	4-CF ₃	96–97	C ₂₁ H ₁₃ F ₃ N ₂ O	366.0980	366.0985

to show the changeover to constant selectivity; it appears as if the constant selectivity ratio will be around 10^8 . There are also literature data for 9-arylxanthenylium ions that show constant $k_{az} : k_w$ of 10^7 .²⁷ There is no obvious reason for these differences. They cannot be related to a steric effect, since the nitrilium carbon is likely to be the most accessible with the triarylmethyl carbon the least, and the other two in between. One consequence of these differences relates to the practice of employing $k_{az} : k_w$ ratios determined from competition experiments to calculate absolute k_w values based on the assumption of diffusion control in azide ion. Whether this assumption is true will be very dependent on the class of cation. A $k_{az} : k_w$ ratio of 10^4 for an arylxanthenylium ion or a triarylmethyl cation does indeed represent a situation where the azide reaction is diffusion controlled. The same ratio for a nitrilium ion does not; in fact this is the ratio of the constant selectivity region.

Hydroxide ion

While the azide : water ratio is constant this is not true for the hydroxide : water or hydroxide : azide ratios. This is shown in Fig. 7 in the form of a plot of $\log k_{OH}$ versus $\log k_{az}$. This plot is

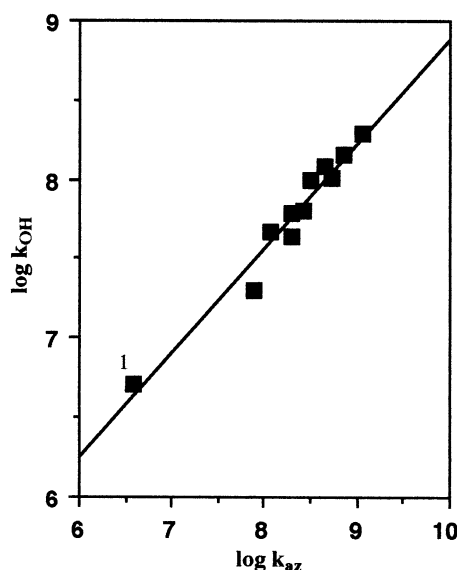


Fig. 7 Correlation of $\log k_{OH}$ and $\log k_{az}$ for benzonitrilium ions. The point marked '1' refers to the *N*-isopropyl cation **2**, data from ref. 1.

reasonably linear, but the slope is only 0.65. Thus the rate constant for hydroxide ion does not increase as rapidly as that for k_{az} (or k_w). Hydroxide ion is strongly hydrated in water. It is

therefore possible that as the cation becomes more reactive, the hydroxide reaction does not respond to the same extent because this reaction is partially limited by the need to desolvate the nucleophile before bond formation. This was observed previously for amines reacting with diarylmethyl cations in water.²⁸ For the more reactive cations desolvation of the amine was clearly a very important component of the reactivity and the rate constant for the amine showed little increase with increased cation reactivity.

Experimental

Laser flash photolysis experiments involved *ca.* 20 ns pulses at 248 nm (60–120 mJ per pulse) from a Lumonics excimer laser (KrF emission), a pulsed xenon lamp providing monitoring light. The sample was placed in a $4 \times 1 \times 1$ cm cuvette, irradiated with the laser on the 4×1 face, and monitored perpendicularly so that the path length was 4 cm. The cuvette was replaced with a fresh solution after each irradiation. After passing through a monochromator, the signal from the photomultiplier tube was digitized and sent to a computer for analysis.

The spectra in Fig. 1 were constructed point-by-point by irradiating solutions of the same concentration at varying wavelengths over a short period of time to ensure constant laser power. Kinetic experiments were performed at a monitoring wavelength of 290 nm. The ΔA -time data were fitted to the exponential equation. In general good fits were obtained, with rate constants from replicate experiments agreeing to $\pm 5\%$. The quenching experiments with azide ion were carried out by measuring the observed rate constant in 3–4 solutions of sodium azide over a concentration range 0–0.003 mol dm⁻³. With hydroxide ion concentrations of 0–0.02 were employed. Plots of $k(\text{obs})$ versus $[\text{NaN}_3]$ and $[\text{NaOH}]$ were linear, with values of k_{az} and k_{OH} being obtained as the linear regression slope.

Product analyses following the irradiation of 4-cyanophenyl *N*-phenylbenzimidate were performed with a Waters HPLC system using a C18 column with 2 cm³ min⁻¹ of 50 : 50 acetonitrile : pH 4.5 0.05 mol dm⁻³ acetate buffer as the eluting solvent and 240 nm detection. The products 4-cyanophenol and benzanilide were identified by comparison of retention times with those of authentic samples. Quantitative analyses were performed by determining the response factor at 240 nm, and correcting the peak areas of the unknown solutions.

4-Cyanophenyl *N*-(*Y*-aryl)-*X*-benzimidates **3** were prepared as follows. An appropriately substituted benzanilide (50 mmol), prepared by reaction of an *X*-substituted benzoyl chloride with a *Y*-substituted aniline, was treated in dry benzene (100 cm³) with phosphorus pentachloride (52.5 mmol).²⁹ After refluxing

for two hours, the volatiles, benzene and phosphorus oxychloride, were removed *in vacuo* to give the *N*-(*Y*-aryl)-*X*-benzimidoyl chloride as an oil or low-melting solid that was used directly in the next step. The sodium salt of 4-cyanophenol was prepared by adding a sodium hydride (65 mmol) to a stirred solution under argon of 4-cyanophenol (60 mmol) dissolved in dry THF (100 cm³). The imidoyl chloride was taken up in a minimum amount of dry THF, and this solution added to the phenoxide suspension. The mixture was refluxed under argon overnight. After cooling, water (100 cm³) was added. The THF layer was washed twice with cold 0.1 mol dm⁻³ NaOH (100 cm³) and once with water (100 cm³), followed by drying over magnesium sulfate, filtration and removal of the solvent. This left a solid that in most cases was purified by recrystallization from ethanol or ethanol : water. In a few cases, a preliminary purification using silica gel column chromatography was necessary.

Table 3 lists melting points and high resolution mass spectral data obtained for the solids. The low resolution mass spectra (electron impact) were characterized by a small peak corresponding to the molecular ion, with a large peak at *M* – 118 corresponding to the nitrilium ion derived by loss of the 4-cyanophenoxide radical. The ¹H NMR and ¹³C NMR spectra, while consistent with the structures, were complex because of the large number of overlapping signals in the aromatic region. In addition, both spectra showed broadened resonances. This suggests that there were two isomers about the C=N bond present in the CDCl₃ solution, and that these were undergoing slow conformational equilibration on the NMR time scale.

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