Photochemical generation of the *N*-isopropylbenzonitrilium ion and unusually slow trapping by azide ion

Patrick H. Ruane,[a] Robert A. McClelland,*[a] A. Frank Hegarty[b] and Steen Steenken[c]

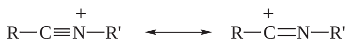
[a] *Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada*
[b] *Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland*
[c] *Max-Planck-Institut fur Strahlenchemie, D-45413 Mulheim, Germany*

Received (in Cambridge) 21st September 1998, Accepted 10th November 1998

The imidate ester 4-cyanophenyl *N*-isopropylbenzimidate undergoes efficient photoheterolysis in water producing the 4-cyanophenoxide ion and the *N*-isopropylbenzonitrilium ion. The latter is detected as a transient intermediate in flash photolysis experiments and has a relatively long lifetime ($1/k_w$) in water of 2.5 ms. The rate constants for hydroxide and azide are respectively 5.2×10^6 and 3.9×10^6 dm^3 mol^{-1} s^{-1}. This pattern is not seen with sp^2 hybridized cations, where k_{az} is normally significantly greater than k_{OH}. Further indications that azide ion is unexpectedly poor as a trap for this cation is seen in considering the $k_{az}:k_w$ value in the context of ratios directly measured for sp^2 hybridized cations. For the latter a $k_{az}:k_w$ of less than 10^5 can be taken to mean that the reaction with azide is at (or certainly very close to) the diffusion limit (*i.e.* 5–10 × 10^9 dm^3 mol^{-1} s^{-1}). The nitrilium ion **3** has $k_{az}:k_w$ equal to only 10^4 mol^{-1} dm^3 and yet its azide reaction is three orders of magnitude slower than diffusion.

Introduction

Nitrilium ions are a well established class of reactive intermediate[1–4] and can also be prepared as stable salts with weakly nucleophilic counter-ions.[5,6] Although their major resonance contributor is **1a**, their reaction with nucleophiles normally occurs at the sp-hybridized carbon center. In other words they react through form **1b**. In this sense they resemble vinyl cations and acylium ions.



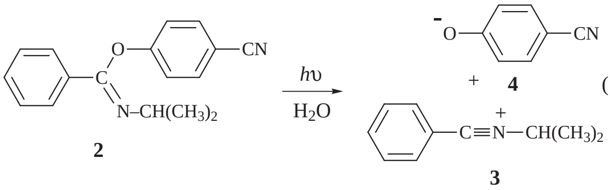
$$R-C\equiv\overset{+}{N}-R' \longleftrightarrow R-\overset{+}{C}=N-R'$$

1a **1b**

The quantitative reactivity patterns of sp^2 hybridized carbocations have been extensively investigated. Mayr and coworkers have established a general relation for the reaction with π nucleophiles in solvents such as dichloromethane and acetonitrile.[7] In aqueous and alcohol solvents, very stable carbocations have been studied extensively by Ritchie,[8] and less stable examples using the technique of laser flash photolysis (LFP)[9] or indirectly with the azide clock method.[10] Considerably less is known about the reactivity of sp-hybridized examples. There is an expectation that they may be more reactive than sp^2-hybridized examples.[11] This appears to be true for acylium ions, since the *p*-(dimethylamino)benzoyl acylium ion, despite the strongly stabilizing substituent, is estimated to have a lifetime in water of only 0.1–1 ns.[12] Vinyl cations, however, studied by LFP in solvents such as 2,2,2-trifluoroethanol (TFE) and acetonitrile, do not show a substantial difference from sp^2-hybridized analogs.[13–18] For example, the lifetime of the 4-methoxyphenylvinyl cation in TFE is very similar to that of the 4-methoxyphenethyl cation.[18]

In this paper we report a flash photolysis study of the *N*-isopropylbenzonitrilium ion **3**. This cation was formed in aqueous solutions upon irradiation of the imidate **2**, through photoheterolysis of the C–O bond. The 4-cyanophenoxide anion is a reasonable leaving group in the excited state, as suggested by some early work of Zimmerman and Somasekhara,[19] and applied in LFP studies of diarylmethyl and triarylmethyl systems.[20,21]

Despite the sp hybridized center, the nitrilium ion **3** is relatively long-lived in water. We also find that it reacts with azide ion well below the diffusion limit, so that the use of 'clock' methods for estimating rate constants for sp-hybridized cations may be questionable. In particular our results suggest that the lifetimes of imidinium ions ArN=C$^+$–NR$_2$ may be considerably longer than those calculated[11] by 'clock' methods.

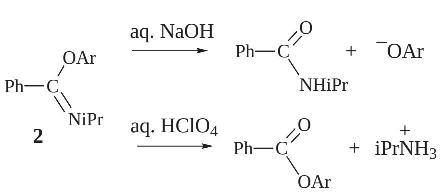


2 **4** **3** (1)

Results

Ground state hydrolysis

The imidate **2** undergoes slow hydrolysis in aqueous solutions, forming *N*-isopropylbenzamide and the 4-cyanophenoxide ion in base and 4-cyanophenyl benzoate in acid. The isopropylammonium ion is presumably also formed in the latter case.



2 (2)

The rate–pH profile (Fig. 1) shows plateau regions in acid and base with a change-over around pH 4–5.

Eqn. (3) can be fitted to the data, where k_{acid} (6.6×10^{-4} s^{-1}) is the plateau rate constant in acid, k_{base} (1.35×10^{-4} s^{-1}) is the plateau in base and K_a (2.15×10^{-5}) is the acidity constant of protonated **2**.

$$k_{obs} = (k_{acid}[H^+] + k_{base}K_a)/([H^+] + K_a) \qquad (3)$$

Experiments were also performed in dilute sodium hydroxide solutions containing small amounts of sodium azide.

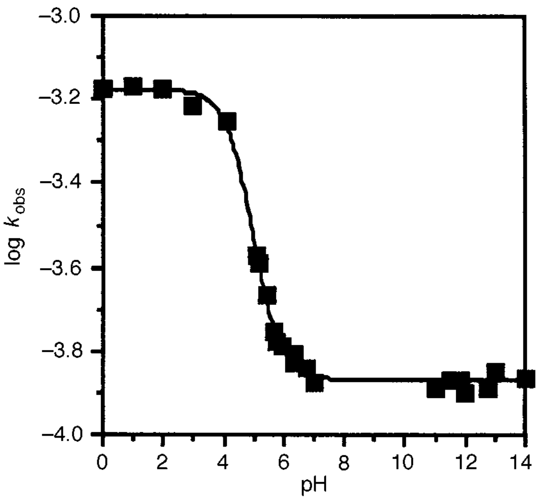


Fig. 1 Variation of log k_{obs} with pH for the hydrolysis of the imidate **2** in aqueous solution at 25 °C and ionic strength 1 mol dm^{-3} maintained with sodium perchlorate.

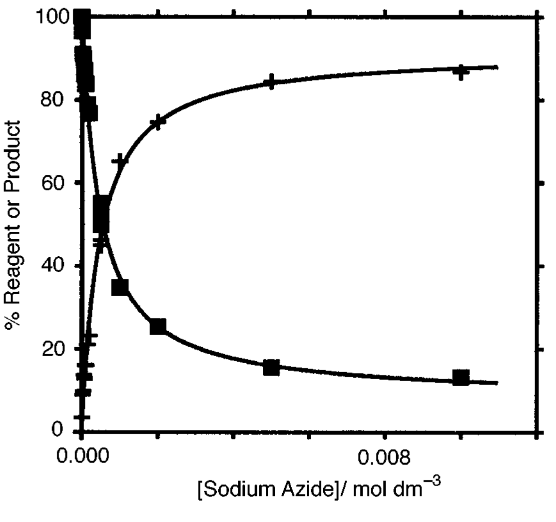
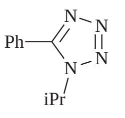


Fig. 2 Dependence on sodium azide concentration of the yield of *N*-isopropylbenzamide (squares) and tetrazole **5** (crosses) for the ground state reaction of imidate **2** in 3 × 10^{-4} mol dm^{-3} NaOH at 25 °C and ionic strength 1 mol dm^{-3} maintained with sodium perchlorate.

The observed rate constants are independent of azide concentration,† as they are of hydroxide concentration. The 4-cyanophenoxide ion continues to be formed in quantitative yield, but the tetrazole **5** is also found as a product. This forms at the expense of the *N*-isopropylbenzamide, with the relative amounts of the two depending on azide concentration as shown in Fig. 2. A feature of the data is that at high azide concentration, the yields level out at around 90% tetrazole and 10% amide.



5

Absorption spectra

Table 1 summarizes the relevant spectral information. The imidate **2** is strongly absorbing at 240–250 nm, with a spectrum that overlaps that of 4-cyanophenol. The *N*-isopropylbenzamide also overlaps with these two, as does the *N*-ethylbenzonitrilium ion, whose spectrum could be recorded in concentrated sulfuric acid. The 4-cyanophenoxide ion stands out as being different, with an absorbance centered at 270–285 nm.

Table 1 Spectral data (aqueous solutions unless otherwise specified)

Compound	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1} λ_{max}	ε/dm^3 mol^{-1} cm^{-1} at 280 nm
Imidate **2**	242	2.7 × 10^4	9.7 × 10^2
4-Cyanophenol	247	1.9 × 10^4	5.4 × 10^2
4-Cyanophenoxide	274	2.5 × 10^4	2.3 × 10^4
N-Isopropylbenzamide	226	1.0 × 10^4	1.2 × 10^2
N-Ethylbenzonitrilium[a]	244	1.2 × 10^4	2.9 × 10^3

[a] As BF_4^- salt in 85% H_2SO_4.

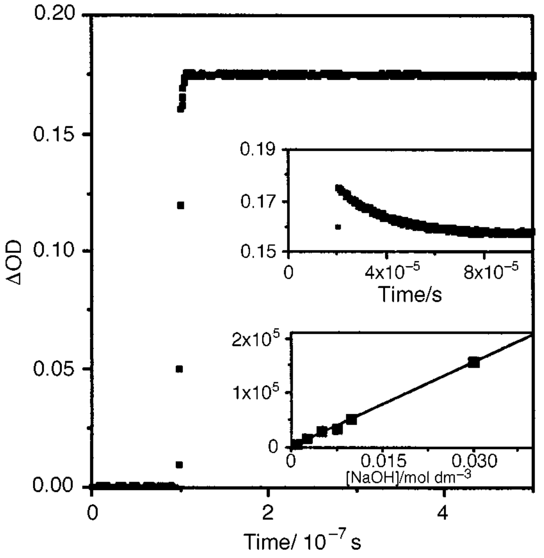


Fig. 3 Absorbance change at 280 nm following 248 nm laser excitation of the imidate **2** (5 × 10^{-4} mol dm^{-3}) in 1 × 10^{-3} mol dm^{-3} NaOH. Inset A shows the small first-order decay that is observed at longer times. Inset B shows the dependence of the first-order rate constants on the concentration of sodium hydroxide.

The flash photolysis experiments to be discussed in the next section could only be carried out with detection at wavelengths greater than 265 nm, since the strong absorbance of the precursor imidate precluded observing at lower wavelengths. The majority of the experiments were carried out with detection at 280 nm. As shown in Table 1, the imidate, amide and 4-cyanophenol are relatively weakly absorbing at this wavelength. This is true also of the nitrilium ion, although there is a shoulder in the spectrum of this species that gives it a slightly higher extinction coefficient than the other three at 280 nm.

Photochemistry

The imidate **2** (approximately 0.0001 mol dm^{-3}) was irradiated with 254 nm light in aqueous solutions of pH 5–13. The only products that are observed by HPLC are 4-cyanophenol and *N*-isopropylbenzamide. These are formed over 2–3 minutes, under conditions where there is less than 3% of the ground state hydrolysis. The chemical yield is 100%, and the quantum yield is ~20%.

Working in sodium hydroxide solutions, LFP experiments reveal a prompt formation (Fig. 3) of a large absorbance centered at 275–280 nm, whose spectrum obtained immediately after the laser pulse (not shown) closely resembles that of the 4-cyanophenoxide ion. The appearance of this species is not surprising since the ion is a product of the photolysis. The absorbance is obviously permanent in basic solutions where the phenol exists in the anionic form. There is a more weakly

---

† At lower pH (*e.g.* in phosphate buffer at pH 7), the rate constants do increase with added azide ion.

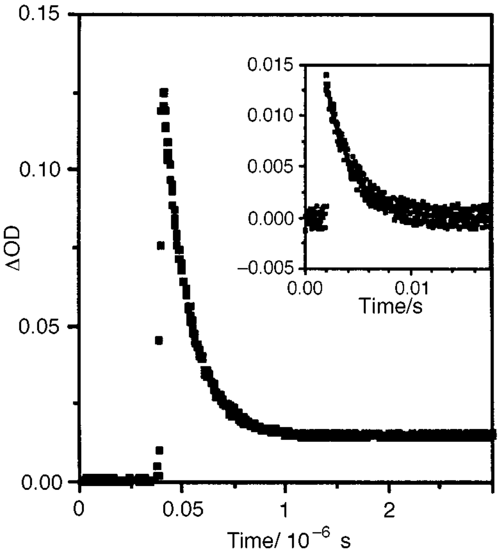


Fig. 4 Absorbance change at 280 nm following 248 nm laser excitation of imidate **2** (5 × 10^{-4} mol dm^{-3}) in 0.01 mol dm^{-3} NaH_2PO_4–0.0002 mol dm^{-3} Na_2HPO_4 (pH = 5.3). The inset shows the absorbance change at 280 nm obtained on lamp photolysis of the same solution.

absorbing transient species whose signal overlaps that of the aryl oxide. This is seen on working at longer times, and applying an offset so as to enlarge the absorbance change (Inset A to Fig. 3). This reveals a small first-order decay, with an absorbance change of about 10% of the total signal. As shown in Inset B, the rate constants for the decay depend on the concentration of sodium hydroxide, with a second-order rate constant k_{OH} of 5.2 ± 0.2 × 10^6 dm^3 mol^{-1} s^{-1} (20 °C and ionic strength = 1.0 mol dm^{-3}).

LFP experiments were also performed at pH 5–8 in phosphate buffer solutions. The prompt initial absorbance observed in base is again present, but now undergoes a rapid first-order decay (Fig. 4). The rate constants are strongly dependent on the concentration of the phosphate buffer, so much so that it is not possible to accurately extrapolate to zero buffer concentration. Experiments at different buffer ratios show the relation given in eqn. (4) with k_p = (5.7 ± 0.2) × 10^8 dm^3 mol^{-1} s^{-1} and k_d = (1.5 ±

$$k_{\text{fast decay}} = k_p[H_2PO_4^-] + k_d[HPO_4^{2-}] \qquad (4)$$

0.4) × 10^8 dm^3 mol^{-1} s^{-1} (20 °C and ionic strength = 0.01 mol dm^{-3}).

The pK_a of 4-cyanophenol is 7.95, so that, depending on the pH, there are small amounts of 4-cyanophenoxide present as a final stable product. This ion obviously gives rise to a permanent positive ΔOD at 280 nm. However, even at pH 5–5.5 where the relative amount of 4-cyanophenoxide is small, the rapid decay proceeds to a final ΔOD that is about 10–15% of the initial one (see Fig. 4). This absorbance, moreover, is not present in a spectrum recorded on a diode array spectrometer 10 seconds after laser irradiation. This led us to suspect that the transient species seen in base was still present, now considerably longer-lived since no decay could be observed even at the longest time scale of the LFP apparatus (~100 μs). Indeed, working with a lamp flash photolysis apparatus, a small first-order decay could be observed (see Inset to Fig. 4). The rate constants ($k_{\text{slow decay}}$) were independent of pH in the region pH 5–8,‡ with a rate constant k_w = (3.0 ± 0.2) × 10^2 s^{-1} at ionic strength 1.0 mol dm^{-3} and (4.0 ± 0.3) × 10^2 s^{-1} at zero ionic strength.

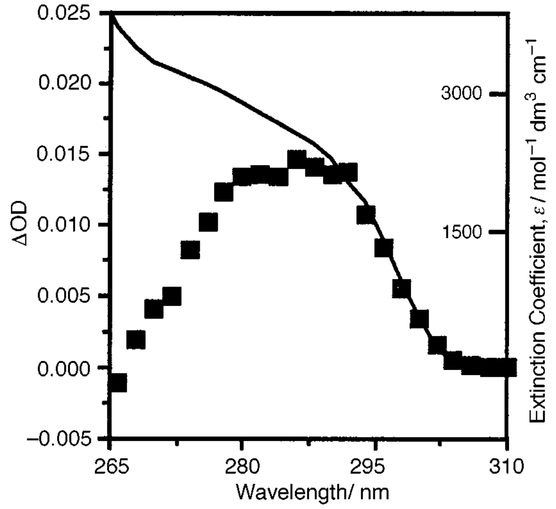


Fig. 5 The points plot the ΔOD obtained by LFP at the completion of the fast kinetic decay for the solution of Fig. 4. The line is the spectrum of *N*-ethylbenzonitrilium BF_4^- in 85% H_2SO_4, drawn so that it overlaps with the LFP spectrum at 290–300 nm.

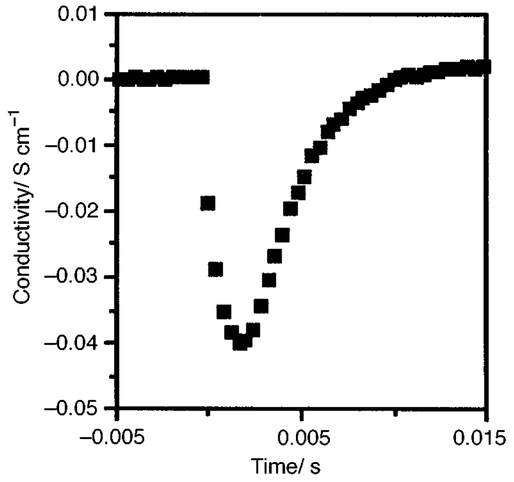


Fig. 6 Conductivity change following 248 nm laser irradiation of a solution of imidate **2** in 1 × 10^{-5} mol dm^{-3} $HClO_4$.

Sodium azide (0–400 μmol dm^{-3}) accelerated the decay in a linear fashion, with k_{az} = (3.9 ± 0.3) × 10^6 dm^3 mol^{-1} s^{-1} (20 °C and ionic strength = 1.0 mol dm^{-3}).

Fig. 5 shows the spectrum obtained using ΔOD values obtained by LFP at the end of the fast decay but before any of the slow decay, along with the spectrum of the authentic *N*-ethylbenzonitrilium ion.

Fig. 6 shows the results of an experiment involving conductivity detection, for a solution of the imidate in a very dilute perchloric acid solution. The laser flash causes a conductivity decrease, followed by an increase that returns the conductivity to its original value. The decrease does not follow good first-order behaviour. The increase on the other hand does, with k = (3.9 ± 0.1) × 10^2 s^{-1}, the same rate constant obtained for the slow absorbance change at zero ionic strength in neutral solutions.

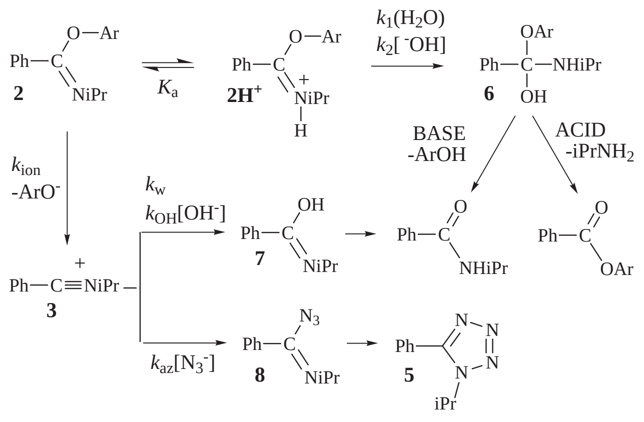
Discussion

Ground state hydrolysis

On the surface **2** is exhibiting the normal behaviour of imidate esters,[22–25] with the *N*-protonated form reacting with water or hydroxide to form a tetrahedral intermediate **6** that preferentially loses aryl oxide in base and isopropylamine in acid (see top part of Scheme 1). In terms of the rate–pH profile the

---

‡ The rate constants were also independent of the phosphate buffer concentration, provided the latter was kept below 0.01 mol dm^{-3}.



Scheme 1

plateau region in acid represents the water addition at a pH where the imidate is fully protonated. As the pH is increased and the equilibrium shifts to neutral imidate, the rate becomes first-order in H^+. The flat region at even higher pH occurs where the hydroxide addition becomes important, with the hydroxide dependency cancelled by the requirement for the protonated imidate.

The experiments with sodium azide indicate however that the situation at higher pH is more complicated. In particular, the observation of the product **5** incorporating azide with no increase in the rate constant suggests the occurrence of an S_N1 mechanism in which the nitrilium ion **3** is formed in a rate-determining ionization of **2**, prior to product-determining steps. This ion subsequently reacts with azide ion to form the adduct **8**, which would cyclize to **5**.[26] Reaction with water or hydroxide ion gives the imidic acid **7**, which tautomerizes to the amide product.§

Thus, under basic conditions there are two kinetically equivalent reactions leading to the same products, *N*-isopropylbenzamide and 4-cyanophenoxide. The kinetic expression for the entire pH region is given by eqn. (5).

$$k_{obs} = [k_1(H_2O)[H^+] + (k_2K_w/K_a + k_{ion})K_a]/([H^+] + K_a) \quad (5)$$

The constants $k_1(H_2O)$ and k_2 refer respectively to water and hydroxide addition to the protonated imidate, with K_a the acidity constant for this species. The constant k_{ion} is the rate constant for the S_N1 ionization, a process that occurs with the neutral imidate. This equation has the same form as eqn. (3), with $k_{acid} = k_1(H_2O)$, and $k_{base} = k_2K_w/K_a + k_{ion}$. Because of the kinetic ambiguity, the latter cannot be separated into the contributions from the two pathways, at least on the basis of the rate–pH profile.

Such a breakdown can however be carried out based on the products in the presence of sodium azide (Fig. 2). Eqn. (6) is the expression for the yield of the amide product.

$$\text{Percent amide} = 100f_{ion}\left(\frac{\{(k_w + k_{OH}[OH^-])/k_{az}\}}{\{(k_w + k_{OH}[OH^-])/k_{az}\} + [N_3^-]}\right) + 100(1 - f_{ion}) \quad (6)$$

In base there is an initial competition involving ionization of the neutral imidate or the pH equivalent hydroxide addition to its conjugate acid. The term $f_{ion} = k_{ion}/(k_{ion} + k_2K_w/K_a)$ is defined as the fraction that proceeds *via* the former. Amide is the only product of the tetrahedral intermediate pathway (at high pH), and this is indicated by the second term in the equation. The ionization pathway has a second competition, involving nucleophilic trapping of the nitrilium ion by water and hydroxide ion to produce amide or by azide ion to ultimately give tetrazole. This competition is reflected in the term in brackets containing the ratio $(k_w + k_{OH}[OH^-]):k_{az}$.

Table 2 Fraction of imidate reacting by S_N1 ionization, and amide: tetrazole competition for reaction of nitrilium ion in aqueous base

[NaOH]	f_{ion}	$(k_w + k_{OH}[OH^-]):k_{az}$/mol dm^{-3} Solvolysis[a]	Flash photolysis[b]
0.0003	0.92	4.6×10^{-4}	4.8×10^{-4}
0.001	0.91	1.4×10^{-3}	1.42×10^{-3}

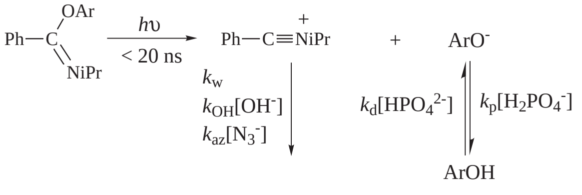
[a] Determined from ground state solvolysis by fit of eqn. (6) to experimental data. [b] Calculated from hydroxide ion concentration and absolute values of k_w, k_{OH} and k_{az} measured by flash photolysis.

Eqn. (6) was fitted to the experimental data to provide the two parameters f_{ion} and the ratio $(k_w + k_{OH}[OH^-]):k_{az}$. The results for two hydroxide concentrations are given in Table 2. It can be seen that the S_N1 ionization accounts for slightly over 90% of the reaction. Thus the pH independent rate constant at high pH can be broken down into contributions from k_{ion} of 1.26×10^{-4} s^{-1} and from k_2K_w/K_a of 9×10^{-6} s^{-1} (which means that k_2 is 1.9×10^4 dm^3 mol^{-1} s^{-1}). That the tetrahedral intermediate pathway does contribute is indicated by the yield of amide levelling off at high contributions of sodium azide (Fig. 2). Thus there must be some pathway that continues to produce amide even under conditions where trapping of the nitrilium ion by azide ion dominates over water and hydroxide trapping.

To the best of our knowledge, this is the first demonstration that an imidate ester can hydrolyze *via* an S_N1 reaction. Such an ionization is however not surprising, since imidoyl chlorides are well established to rapidly form nitrilium ions by loss of chloride ion.[3,4] The 4-cyanophenoxide is obviously not as good a leaving group. We have however previously observed that triarylmethyl 4-cyanophenoxides also undergo a slow S_N1 reaction.[21] Thus, the combination of the polar protic solvent water and a very stable cation, the nitrilium ion in the present system, can result in a situation where S_N1 ionization of the 4-cyanophenoxide can occur.

Mechanism of photochemical reaction

While the products of irradiation are obviously consistent with a relatively efficient photoheterolysis (Scheme 2), other pathways could also be considered, such as one where irradiation results in a rapid C=N hydration.[27]



Scheme 2

Consistent with the ionization mechanism however is the observation that the 4-cyanophenoxide ion is formed very rapidly, within the 20 ns laser pulse in both basic and weakly acidic solutions. In base, this ion is obviously stable and there is a large permanent positive ΔOD at 280 nm. In acid and neutral solutions, the aryloxide is protonated so that its absorbance decays.

A detailed study of this process was carried out in phosphate buffers. The rate constants [eqn. (4)] measured in such solutions

---

§ A reviewer suggested that an S_N1 reaction involving the O-protonated intermediate seems more likely. This however is not consistent with the kinetics which show unambiguously that the neutral imidate is the species reacting by this mechanism. It can also be noted that at pH 6, there is evidence that the product **5** forms by nucleophilic attack on the protonated imidate. This is characterized by the formation of this product concomitant with an increase in the rate constant.

represent an approach to equilibrium, so that there is a term $k_p[H_2PO_4^-]$ for protonation of the aryloxide and a term $k_d[HPO_4^{-2}]$ for the reverse process, the deprotonation of the 4-cyanophenol. The ratio $k_p:k_d$ should be equal to the ratio of acidity constants $K_a(H_2PO_4^-):K_a(ArOH)$, and there is good agreement — 3.8 for the former and 4.2 for the latter. It can also be seen that the rate constants are typical of a normal proton transfer that is nearly thermoneutral.[28]

Identification of nitrilium ion transient in flash photolysis experiments

The *N*-isopropylbenzonitrilium ion is obviously the other product of heterolysis. As seen with an authentic sample of the *N*-ethyl derivative, *N*-alkylbenzonitrilium ions have spectra that overlap that of the imidate **2**. Thus, attempts to observe such intermediates by flash photolysis must necessarily be carried out at wavelengths where they are less strongly absorbing. A small decay is observed in both acid and phosphate buffers at 280 nm, and there is good evidence that this represents the reactions of the nitrilium ion. (i) The absorbance change in this decay is around 10% of the signal due to the 4-cyanophenoxide. This is approximately the ratio of extinction coefficients at 280 nm (Table 1). (ii) The transient spectrum observed at pH 5–5.5 after the decay of the phenoxide should be that of the nitrilium ion. As shown in Fig. 5, this is true above 285 nm. The deviation below 285 nm occurs because the precursor imidate is beginning to absorb in these solutions so that the ΔOD measured by LFP is not just that of the nitrilium ion, but rather is the difference between the OD of this species and the imidate. (iii) The transient is quenched by the nucleophiles azide and hydroxide, as is typical of cationic intermediates. (iv) Most importantly, the trapping ratios $(k_w + k_{OH}[OH^-]):k_{az}$ calculated with the three absolute rate constants measured by flash photolysis are in excellent agreement with values obtained in the ground state solvolysis from product analysis (Table 2).

Conductivity detection

Compelling evidence for these interpretations is provided by the conductivity experiment shown in Fig. 6. The photoheterolysis produces two organic ions, so that initially there would be a small conductivity increase. This is not observed since the aryloxide is rapidly protonated by the hydronium ion present, and the removal of this highly conducting ion results in a conductivity decrease. The failure of this process to obey first-order kinetics can be attributed to the fact that a very dilute concentration of H^+ was employed in order to avoid protonation of the imidate. Thus the concentration of aryloxide produced by the laser pulse is likely to be similar to that of the H^+.

A slow conductivity increase is then observed. This represents the release of H^+ as the nitrilium ion reacts with water ($\mathbf{3} + H_2O \rightarrow \mathbf{7} + H^+$). This occurs with a rate constant k_w, and there is excellent agreement between the value obtained with conductivity detection, and the one following the absorbance decay at 280 nm. The conductivity returns to its original level, since the net result of the photolysis in this solution is the production only of neutral species (**2** + water→amide + 4-cyanophenol).

Reactivity of *N*-isopropylbenzonitrilium ion

This cation has a lifetime ($1/k$) in water alone of 2.5 ms, extending to 3.3 ms at ionic strength 1 mol dm^{-3}. By carbocation standards this is a relatively long-lived intermediate, despite the ready access of nucleophiles to the sp-hybridized carbocation center. This kinetic stability can undoubtedly be attributed to the stabilization of the cation in its nitrilium resonance contributor **1a**.

The azide-clock method converts selectivity ratios ($k_{az}:k_w$) into absolute rate constants based on the assumption that azide ion reacts at the diffusion limit.[10] A rate constant of $k_{az} = 5 \times 10^9$ dm^3 mol^{-1} s^{-1} that is typical of encounter control is taken for k_{az}. The absolute k_w is then calculated from the selectivity. The ratio $k_{az}:k_w$ for the nitrilium ion in this work is 1.3×10^4 dm^3 mol^{-1}, so that the azide-clock approach predicts a k_w of 4×10^5 s^{-1}. This is three orders of magnitude greater than the actual rate constant directly measured by flash photolysis. This obviously occurs because the reaction with azide ion is well below the diffusion limit.

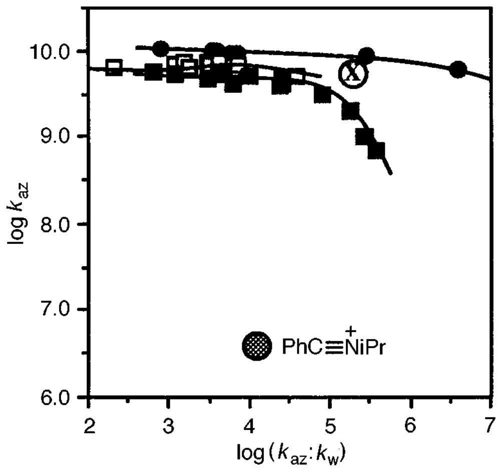


Fig. 7 Log k_{az} *versus* log ($k_{az}:k_w$) for triarylmethyl cations (closed squares, ref. 29), diarylmethyl cations (open squares, ref. 29), the xanthylium ion (**X**, ref. 30) and biarylnitrenium ions (closed circles, ref. 31).

The unusually low reactivity of azide ion with the nitrilium ion **3** is seen in the fact that it is actually slightly less reactive than hydroxide ion. This is not typical of sp^2 hybridized cations, where k_{az} is normally significantly greater than k_{OH}. The data in Fig. 7 are also relevant. This plots log k_{az} *versus* log ($k_{az}:k_w$) for various types of sp^2 hybridized carbocations — triarylmethyl cations,[29] diarylmethyl cations,[29] the xanthylium ion[30] and biarylnitrenium ions[31] (which react with azide ion as cyclohexadienyl cations[32]). Within each of these series, the more reactive ions all react with azide ion at a nearly independent rate constant. The limiting k_{az} are typical of diffusion control, falling in the range 5–10 × 10^9 dm^3 mol^{-1} s^{-1} slightly dependent on cation structure. Selectivities $k_{az}:k_w$ obviously depend on structure, but changes reflect only variations in k_w. Ultimately, for very stable cations, k_{az} becomes smaller than the diffusion limit. It can been seen however that any cation that has $k_{az}:k_w < 10^5$ (or $k_w > 10^5$ s^{-1}) has k_{az} that is close to or at the limit. On this basis, it was concluded that an experimentally measured $k_{az}:k_w$ lower than 10^5 dm^3 mol^{-1} would mean that the azide-clock approach would provide a reasonably good estimate for k_w.[9] The point for the nitrilium ion **3** in Fig. 7 shows that this is clearly not true for this system. Despite only a 10^4 azide:water ratio this cation reacts well below the diffusion limit with azide ion. We therefore caution against the application of the azide-clock method (or other clock approaches) to estimating the reactivities of sp-hybridized carbocations, until more is known about the absolute reactivities of such ions.

Experimental

N-Ethylbenzonitrilium tetrafluoroborate,[5] 1-isopropyl-5-phenyltetrazole,[26] *N*-isopropylbenzamide[33] and 4-cyanophenyl benzoate[34] were prepared by literature methods.

4-Cyanophenyl *N*-isopropylbenzimidate was prepared from the imidoyl chloride (prepared from the amide by the method of Ugi *et al.*)[35] by reacting with 1.1 equivalents of the sodium salt of 4-cyanophenol in acetonitrile for 16 hours. After removal of the solvent, water and dichloromethane were added and separated, the dichloromethane layer was dried with

$MgSO_4$ and, after filtration, the solvent removed to give a white solid that was recrystallized from petroleum ether. This compound had mp 270 °C, δ_H (200 MHz, $CDCl_3$, Me_4Si) 1.21 (6H, d), 4.02 (1H, sept), 6.97 (2H, d), 7.30–7.45 (3H, mult), 7.57 (2H, d), 7.76 (2H, mult); *m*/*z* 264 (M^+, 5%), 146 (60), 104 (100); calcd. for $C_{17}H_{16}NO_2$, 264.1262; found, 264.1251.

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. After passing through a monochromator, the signal from the photomultiplier tube was digitized and sent to a computer for analysis.

Conventional flash photolysis experiments were performed using an apparatus previously described,[36] with the sample being irradiated with a broad band flash lamp of *ca.* 100 µs duration.

Product analyses were performed with a Waters HPLC system using a C^{18} column with 2 cm^3 min^{-1} of 50 : 50 acetonitrile–water as the eluting solvent and 235 nm detection. Products were identified by comparison of retention times with those of authentic samples. The identity of the products, especially the tetrazole, was verifed by recording the NMR spectrum of a scaled-up solvolysis. Quantitative analyses were performed by determining the response factor of the standard samples at 235 nm, and correcting the peak areas of the unknown solutions.

Acknowledgements

R. A. M. acknowledges the continued financial support of the Natural Sciences and Engineering Research Council of Canada.

References

1 H. Ulrich, *The Chemistry of Imidoyl Chlorides*, Plenum, New York, 1968.
2 J. Morath and G. W. Stacey, in *The Chemistry of the Carbon-Nitrogen Double Bond*, ed. S. Patai, Wiley (Interscience), New York, 1970, ch. 8, p. 327.
3 A. F. Hegarty, J. D. Cronin and F. L. Scott, *J. Chem. Soc.*, *Perkin Trans. 2*, 1975, 429.
4 R. Ta-Shma and Z. Rappoport, *J. Am. Chem. Soc.*, 1976, **98**, 8460; 1877, **99**, 1845.
5 H. Meerwein, P. Laasch, R. Mersch and J. Spille, *Chem. Ber.*, 1956, **89**, 209.
6 S. Kabuss, *Angew. Chem.*, *Int. Ed. Engl.*, 1966, **5**, 675.
7 H. Mayr and M. Patz, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 958.
8 C. D. Ritchie, *Acc. Chem. Res.*, 1972, **5**, 348; 1986, **64**, 2239.
9 R. A. McClelland, *Tetrahedron*, 1996, **52**, 6823.
10 J. Richard, *Tetrahedron*, 1995, **51**, 1535.
11 K. N. Dalby and W. P. Jencks, *J. Am. Chem. Soc.*, 1997, **119**, 7271.
12 D. B. Song and W. P. Jencks, *J. Am. Chem. Soc.*, 1987, **109**, 3160; 1989, **111**, 8470.
13 W. Schnabel, I. Naito, T. Kitamura, S. Kobayashi and H. Taniguchi, *Tetrahedron*, 1980, **36**, 3229.
14 S. Kobayashi, T. Kitamura, H. Taniguchi and W. Schnabel, *Chem. Lett.*, 1983, 1117; 1984, 2101.
15 F. I. M. Van Ginkel, R. J. Visser, C. A. G. O. Varma and G. Lodder, *J. Photochem.*, 1985, **30**, 453.
16 S. Kobayashi, Q. Q. Zhu and W. Schnabel, *Z. Naturforsch.*, *Teil B*, 1988, **43**, 825.
17 Y. Chiang, R. Eliason, J. Jones, A. J. Kresge, K. L. Evans and R. D. Gandour, *Can. J. Chem.*, 1993, **71**, 1964.
18 F. Cozens, R. A. McClelland and S. Steenken, *Tetrahedron Lett.*, 1992, **33**, 173.
19 H. E. Zimmerman and S. Somasekhara, *J. Am. Chem. Soc.*, 1963, **85**, 922.
20 R. A. McClelland, V. M. Kanagasabapathy and S. Steenken, *J. Am. Chem. Soc.*, 1988, **110**, 6913.
21 R. A. McClelland, V. M. Kanagasabapathy, N. Banait and S. Steenken, *J. Am. Chem. Soc.*, 1989, **111**, 3966.
22 G. L. Schmir and B. A. Cunningham, *J. Am. Chem. Soc.*, 1965, **87**, 5692.
23 R. K. Chaturvedi and G. L. Schmir, *J. Am. Chem. Soc.*, 1968, **90**, 4413.
24 T. C. Pletcher, S. Koehler and E. H. Cordes, *J. Am. Chem. Soc.*, 1968, **90**, 7072.
25 T. Okuyama, T. C. Pletcher, D. J. Sahn and G. L. Schmir, *J. Am. Chem. Soc.*, 1973, **95**, 1253.
26 A. F. Hegarty, unpublished work.
27 F. Haley and K. Yates. *J. Org. Chem.*, 1987, **52**, 1817.
28 Y. Chiang, A. J. Kresge and J. F. Holzwarth, *J. Chem. Soc.*, *Chem. Commun.*, 1982, 1203.
29 R. A. McClelland, V. M. Kanagasabapathy, N. Banait and S. Steenken, *J. Am. Chem. Soc.*, 1991, **113**, 1009.
30 R. A. McClelland, N. Banait and S. Steenken, *J. Am. Chem. Soc.*, 1989, **111**, 2929.
31 D. Ren and R. A. McClelland, *Can. J. Chem.*, 1998, **76**, 78.
32 M. Novak, M. J. Kahley, E. Eiger, J. S. Helmick and H. E. Peters, *J. Am. Chem. Soc.*, 1993, **115**, 9453.
33 R. F. C. Brown and I. D. Rae, *Aus. J. Chem.*, 1964, **17**, 447.
34 A. A. Humffray and J. J. Ryan, *J. Chem. Soc.*, *B*, 1967, 468.
35 I. Ugi, F. Beck and U. Fetzer, *Chem. Ber.*, 1962, **95**, 126.
36 A. A. Allen, A. J. Kresge, N. P. Schepp and T. T. Tidwell, *Can. J. Chem.*, 1987, **65**, 1719.

Paper 8/07346E