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The Strecker reaction: kinetic and equilibrium studies of cyanide addition to iminium ions†

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Kinetics studies are reported of the reactions of benzylidene benzylamine, **4a**, and of benzylidene allylamine, **4b**, with cyanide in aqueous buffers to give the corresponding α-aminonitriles. The results allow the calculation of values of rate and equilibrium constants for reaction of the iminium ions formed from **4a** and **4b** with cyanide ions. These values are compared with those, obtained from the hydrolysis reactions, for reaction of the iminium ions with hydroxide ions and with water. Comparison with some other iminium ions reveals that those formed from **4a** and **4b** are relatively unreactive due to the possibilities of charge delocalisation.

Introduction

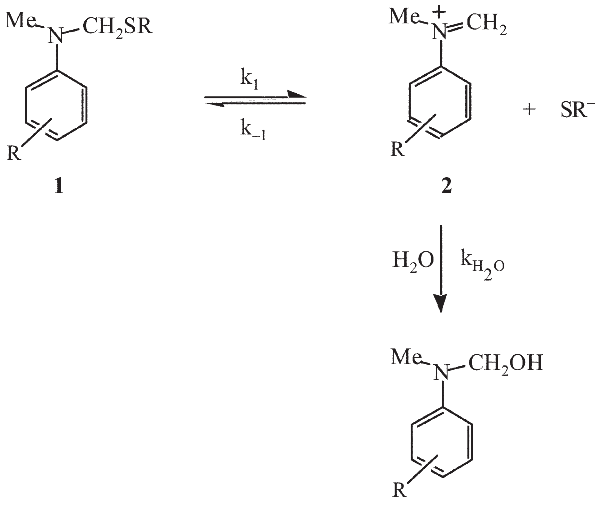
Reactions of the type shown in eqn. (1) are widely used in synthesis.

$$RNH_2 + R'CHO + HNu \rightarrow RNHCHR'Nu + H_2O \quad (1)$$

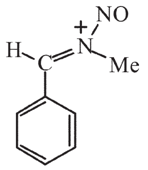
The Strecker reaction involves the use of cyanide as the nucleophile, Nu, and leads to α-aminonitriles which may be hydrolysed to give α-aminoacids.[1]

There is good evidence that in the Strecker reaction cyanide and amine initially compete for the carbonyl compound with cyanohydrin formation being favoured. The formation of α-aminonitrile follows more slowly and results from cyanide attack on an iminium ion intermediate.[2–5]

Although iminium ions are known to be reactive intermediates in many chemical and biochemical processes, including the hydrolysis of imines,[6,7] there is relatively little quantitative information available for their reactions with nucleophiles in water. Eldin and Jencks[8] investigated the hydrolysis of some ring-substituted anilinothioesters, **1**, in the presence of added thiolate ions. They assumed that the reverse reaction, k_{-1}, was diffusion controlled and obtained values of k_{H_2O} for reaction of the iminium ions, **2**, with water in the range 10^6–10^8 s^{-1} depending on the nature of R.



Similarly, high reactivity has been observed for related aliphatic iminium ions[9] and for the N-nitrosoiminium ion, **3**, where k_{H_2O} for reaction with water[10] was found to be 7×10^5 s^{-1}.



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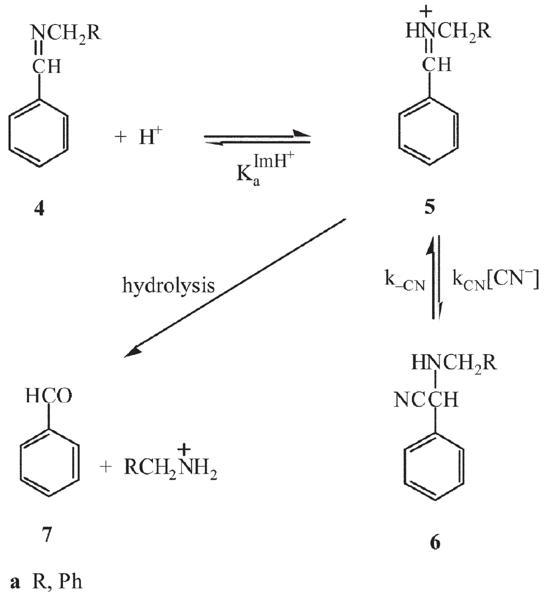
Here we report kinetic measurements for the reactions with cyanide of benzylidene benzylamine, **4a**, and benzylidene allylamine, **4b**, to give the corresponding α-aminonitriles, **6a** or **6b**, respectively, as shown in Scheme 1. Our results allow the calculation of the values of rate and equilibrium constants for reaction of the corresponding iminium ions with cyanide ions in water. In Scheme 1, k_{CN} is the rate constant for reaction of iminium ions with cyanide ions, and k_{-CN} is the rate constant for dissociation of **6**. Measurement of the hydrolysis reactions of the imines allows comparison of these values with those for reaction with hydroxide ions or water.



a R, Ph
b R, CH=CH$_2$

Scheme 1

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† Electronic supplementary information (ESI) available: derivation of eqn. (8). See http://www.rsc.org/suppdata/ob/b4/b407853e/

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Results and discussion

The imines **4a** and **4b** were prepared by reaction of benzaldehyde with the appropriate amine in acetonitrile. They show strong absorption in the UV region: λ_{max} 250 nm, $\varepsilon = 1.9 \times 10^4$ dm^3 mol^{-1} cm^{-1}. Reaction of the imines with trimethylsilyl cyanide in damp acetonitrile yielded the corresponding α-aminonitriles **6a** and **6b**. These showed no strong absorption above 220 nm. Kinetic studies of the reactions of the imines, 1×10^{-4} mol dm^{-3}, with potassium cyanide, 0.001–0.020 mol dm^{-3}, were made in aqueous buffers in the pH range 6–10. The changes with time of the UV absorbance at 250 nm were used to monitor the reactions. Two processes were observed: the faster, k_{fast}, resulted in a decrease in absorbance, while the slower, k_{slow}, gave increases in absorbance. Specimen traces measured at pH 9.01 are given in Fig. 1(a) and 1(b). The fast and slow processes accurately followed first-order kinetics, allowing the calculation of rate constants.

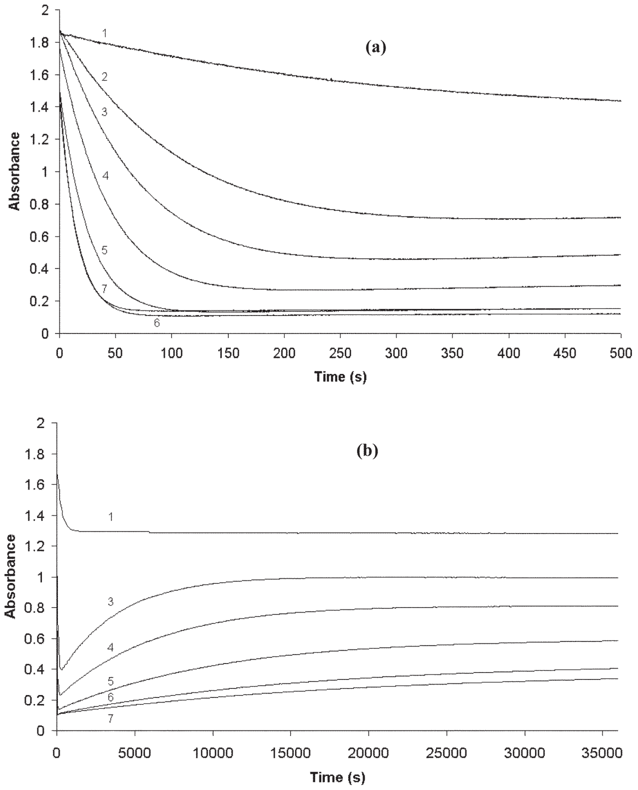


Fig. 1 Absorbance *versus* time plots for the reaction of **4a** with potassium cyanide at pH 9.01. Concentrations of KCN are: 1, 0; 2, 0.001 mol dm^{-3}; 3, 0.002 mol dm^{-3}; 4, 0.004 mol dm^{-3}; 5, 0.008 mol dm^{-3}; 6, 0.016 mol dm^{-3}; and 7, 0.020 mol dm^{-3}.

The results are interpreted in terms of Scheme 1. The faster process results in fractionation of the parent between aminonitrile formation and hydrolysis to form benzaldehyde, **7**. Compound **7** also absorbs at 250 nm, $\varepsilon = 1.5 \times 10^4$ dm^3 mol^{-1} cm^{-1}, although less strongly than **4a** or **4b**. The trace in Fig. 1(a) with no added cyanide shows that hydrolysis occurs at a measurable rate under the conditions used. Our results in Fig. 1(a) indicate that the increases in values of (Absorbance at completion) with decreasing cyanide concentration are due to benzaldehyde formation rather than to the reversibility of aminonitrile formation, *i.e.* the reverse process involving k_{-CN} is negligible here.

Hence eqn. (2) may be written,

$$\begin{aligned}\text{velocity} &= k_{fast}[\text{Imine}]_{stoich} \\ &= k_{CN}[\text{Imine H}^+][\text{CN}^-] + k_{Hyd}[\text{Imine}]_{stoich}\end{aligned} \qquad (2)$$

where k_{Hyd} is the overall rate constant for hydrolysis of the imine in both its forms, **4** and **5**, at a given pH. Here and elsewhere in this paper the subscript 'stoich' is used to represent the total, stoichiometric, concentration of a compound in all its ionisation states. The rate constants for proton transfers involved in the equilibria given in eqns. (3) and (4) are likely to be rapid.

Table 1 Variation of k_f with pH for **4a**

pH	k_f/dm^3 mol^{-1} s^{-1}	k_f(calc)^a/dm^3 mol^{-1} s^{-1}
5.94	2.8	2.8
6.40	4.7	4.8
7.28	6.6	6.8
8.55	4.9	5.7
9.01	3.5	4.1
9.85	1.1	1.1
10.40	0.50	0.40

^{a}Calculated from eqn. (7) with $k_{CN} = 6.7 \times 10^3$ dm^3 mol^{-1} s^{-1}, $\mathrm{p}K_a^{HCN} = 9.1$ and $\mathrm{p}K_a^{ImH^+} = 6.14$.

$$K_a^{HCN} = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} \qquad (3)$$

$$K_a^{ImH^+} = \frac{[\text{Im}][\text{H}^+]}{[\text{ImH}^+]} \qquad (4)$$

Hence the concentrations of iminium ions and cyanide ions may be related to the stoichiometric concentrations leading to eqn. (5).

$$k_{fast} = k_{CN}[\text{CN}^-]_{stoich}\left(\frac{[\text{H}^+]}{K_a^{ImH^+} + [\text{H}^+]}\right)\left(\frac{K_a^{HCN}}{[\text{H}^+] + K_a^{HCN}}\right) + k_{Hyd} \qquad (5)$$

At a given pH value this simplifies to eqn. (6), where k_f is given by eqn. (7).

$$k_{fast} = k_f[\text{CN}^-]_{stoich} + k_{Hyd} \qquad (6)$$

$$k_f = k_{CN}\left(\frac{[\text{H}^+]}{K_a^{ImH^+} + [\text{H}^+]}\right)\left(\frac{K_a^{HCN}}{[\text{H}^+] + K_a^{HCN}}\right) \qquad (7)$$

Values of k_f were obtained from the slopes of linear plots according to eqn. (6) of k_{fast} *versus* the stoichiometric cyanide concentration. The variation with pH is given in Table 1 for **4a** and in Fig. 2 for **4b**.

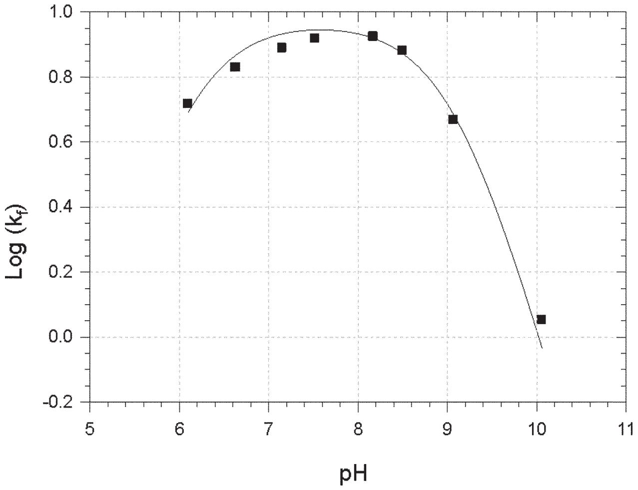


Fig. 2 Plot of $\log_{10}k_f$ *versus* pH for the reaction of **4b** with cyanide in water. The full line is calculated according to eqn. (7) with $k_{CN} = 1.04 \times 10^4$ dm^3 mol^{-1} s^{-1} and $\mathrm{p}K_a^{ImH^+} = 6.05$.

The $\mathrm{p}K_a^{HCN}$ value for hydrogen cyanide is known[11] to be 9.1, so that the two unknowns in eqn. (7) are k_{CN} and $K_a^{ImH^+}$. Experimental values for k_f for **4a** give a good fit with

Table 2 Variation of k_{slow} with cyanide concentration for **4a** in water, pH 10.4 at 25 °C

$[\mathrm{KCN}]_{\mathrm{stoich}}$	$k_{\mathrm{slow}}/10^{-4}\ \mathrm{s}^{-1}$	$k_{\mathrm{slow}}(\mathrm{calc})^{a}/10^{-4}\ \mathrm{s}^{-1}$
0.002	5.4	6.1
0.004	4.7	4.7
0.008	3.2	3.3
0.016	2.1	2.0
0.020	1.8	1.7

[a] Values calculated from eqn. (8) with $k_{-\mathrm{CN}} = 8.5 \times 10^{-4}\ \mathrm{s}^{-1}$, and with $k_{\mathrm{Hydr}} = 2.5 \times 10^{-3}\ \mathrm{s}^{-1}$ and $k_{\mathrm{f}} = 0.5\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$ which are the appropriate values at this pH.

values calculated using $k_{\mathrm{CN}} = (6.7 \pm 1) \times 10^3\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$ and $\mathrm{p}K_{\mathrm{a}}^{\mathrm{ImH}^+} = 6.14 \pm 0.1$. For **4b** the values were $k_{\mathrm{CN}} = (1.0 \pm 0.2) \times 10^4\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$ and $\mathrm{p}K_{\mathrm{a}}^{\mathrm{ImH}^+} = 6.05 \pm 0.1$. The variation in the nature of R in the remote side-chain from benzyl to allyl has little effect on the values obtained.

The plateau between pH 6.5 and 8.5 in the plot shown in Fig. 2 corresponds to the region between the pK_{a} values of the iminium ion, **5**, and hydrogen cyanide. In this region, increasing acidity increases the concentration of **5** but decreases the concentration of free cyanide ions. Decreases in value of k_{f} at pH > 9 result from decreases in the concentration of **5** when the free cyanide concentration is reaching the stoichiometric concentration. Correspondingly, decreases in k_{f} at lower pH result from decreases in the concentration of free cyanide ions when the imine is largely protonated. Hence, the results are in accord with the major reaction in the pH region 6–10 involving the attack of cyanide ions on iminium ions.

The slower process shown in Fig. 1(b) results in the decomposition to benzaldehyde. This was confirmed by isolation of the dinitrophenylhydrazone derivative of **7**. It should be noted that, in the presence of cyanide, benzaldehyde is in equilibrium with its cyanohydrin derivative[11] which does not absorb at 250 nm. The decrease in final absorbance values in Fig. 1(b) with increasing cyanide concentration reflect this equilibrium. Since the equilibration of benzaldehyde and its cyanohydrin is rapid[11] compared to formation of benzaldehyde, this process does not affect the kinetics of decomposition. Treating the iminium ions as steady-state intermediates leads to eqn. (8). The derivation is given as ESI.†

$$k_{\mathrm{slow}} = k_{-\mathrm{CN}} \frac{k_{\mathrm{Hydr}}}{k_{\mathrm{Hydr}} + k_{\mathrm{f}}[\mathrm{CN}^-]_{\mathrm{stoich}}} \tag{8}$$

The values of k_{slow} at pH 10.4 for **4a**, in Table 2, lead to a value for $k_{-\mathrm{CN}}$ of $8.5 \times 10^{-4}\ \mathrm{s}^{-1}$. Values (not shown) at pH 9.01 yield a value of $9.3 \times 10^{-4}\ \mathrm{s}^{-1}$. An alternative method for measuring $k_{-\mathrm{CN}}$ directly was by following spectrophotometrically, at 250 nm, the decomposition of **6a** in buffer solutions in the absence of cyanide. Values were found to be independent of pH in the range 6.8–10.4 and give $k_{-\mathrm{CN}} = (9.1 \pm 0.5) \times 10^{-4}\ \mathrm{s}^{-1}$. Related measurements for **4b** yield a value for $k_{-\mathrm{CN}}$ of $(5.5 \pm 0.5) \times 10^{-4}\ \mathrm{s}^{-1}$.

The hydrolysis reaction

Kinetic studies, using the change in absorbance at 250 nm, were made of the hydrolyses of the imines **4a** and **4b**, $1 \times 10^{-4}\ \mathrm{mol\ dm}^{-3}$, to give benzaldehyde and the corresponding amine. Measurements were made in the pH range 1–12 using dilute buffer solutions or solutions of hydrochloric acid, although values in the pH range 3–6 were too fast to be determined. The pH profiles for **4a** and **4b** were similar and that for **4b** is shown in Fig. 3. We did not investigate general acid/base catalysis although effects are likely to be small at the low buffer concentrations used.[7]

Following the work of Jencks and co-workers[6,7,12] the mechanism of imine hydrolysis is well understood and may be represented by the processes shown in Scheme 2. This leads[7] to eqn. (9),

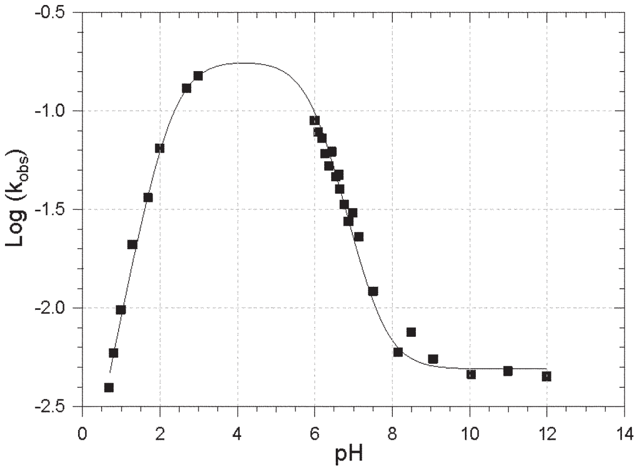
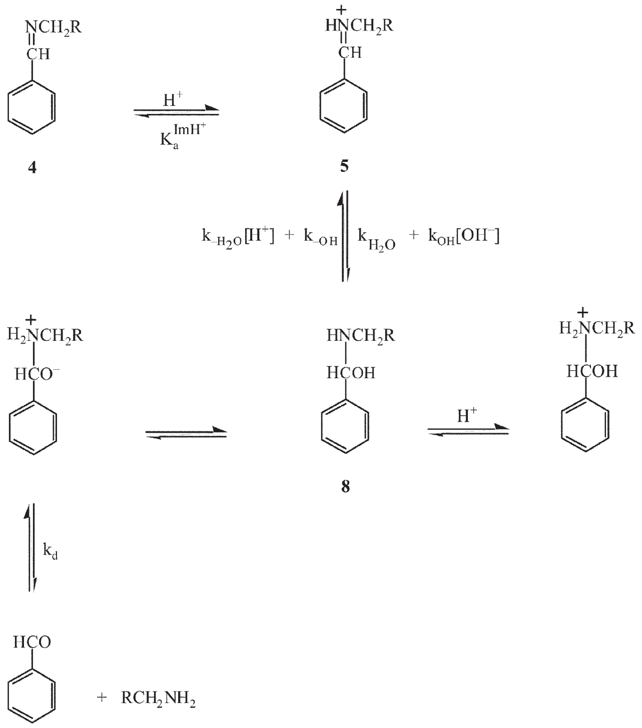


Fig. 3 pH profile for the hydrolysis of **4b**. The solid line is calculated from eqn. (9) with $k_{\mathrm{H_2O}} = 0.18\ \mathrm{s}^{-1}$, $k_{\mathrm{OH}} = 4.4 \times 10^5\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$, $\mathrm{p}K_{\mathrm{a}}^{\mathrm{ImH}^+} = 6.05$, $k_{-\mathrm{H_2O}}/k_{\mathrm{d}} = 188\ \mathrm{dm}^3\ \mathrm{mol}^{-1}$ and $k_{-\mathrm{OH}}/k_{-\mathrm{H_2O}} = 2.4 \times 10^{-8}\ \mathrm{mol\ dm}^{-3}$.

$$k_{\mathrm{obs}} = \frac{k_{\mathrm{H_2O}} + k_{\mathrm{OH}}[\mathrm{OH}^-]}{\left(1 + \dfrac{K_{\mathrm{a}}^{\mathrm{ImH}^+}}{[\mathrm{H}^+]}\right)\left(1 + \dfrac{k_{-\mathrm{H_2O}}[\mathrm{H}^+] + k_{-\mathrm{OH}}}{k_{\mathrm{d}}}\right)} \tag{9}$$

where the rate constants are defined by the processes shown in the scheme. For **4a**, values obtained are: $k_{\mathrm{H_2O}} = 0.15\ \mathrm{s}^{-1}$, $k_{\mathrm{OH}} = 2.0 \times 10^5\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$, $\mathrm{p}K_{\mathrm{a}}^{\mathrm{ImH}^+} = 6.14$, $k_{-\mathrm{H_2O}}/k_{\mathrm{d}} = 95\ \mathrm{dm}^3\ \mathrm{mol}^{-1}$ and $k_{-\mathrm{OH}}/k_{-\mathrm{H_2O}} = 1.3 \times 10^{-8}\ \mathrm{mol\ dm}^{-3}$. Values for **4b** are given in Fig. 3.



Scheme 2

The independence of k_{obs} on pH in the range 8–12 corresponds to rate-limiting attack of hydroxide on the iminium ion, **5**. The increases in value in the pH range 8–6 represent the increasing importance of reaction of **5** with water. In the pH range 1–4, decomposition of the carbinolamine intermediate **8** is rate limiting, the decreases with increasing acidity representing decreases in concentration of the reactive zwitterionic form.

Cyanohydrin formation

It is known[11] that in the presence of cyanide the hydrolysis product benzaldehyde is in equilibrium with its cyanohydrin derivative. The extent of conversion was monitored using absorbance measurements at 250 nm, where benzaldehyde absorbs strongly but the cyanohydrin shows negligible absorbance. Owing to the acid–base processes shown in Scheme 3, values of K_{obs}, defined in eqn. (10), were found to be pH-dependent. The acidity dependence is given by eqn. (11) where equilibrium constants are defined by reference to the scheme.

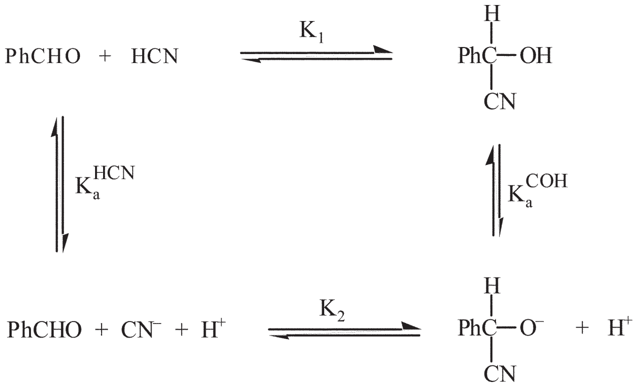
$$K_{obs} = \frac{[\text{Cyanohydrin}]_{stoich}}{[\text{Benzaldehyde}][\text{HCN}]_{stoich}} \qquad (10)$$

$$K_{obs} = K_1\left(\frac{[\text{H}^+] + K_a^{COH}}{[\text{H}^+] + K_a^{HCN}}\right) \qquad (11)$$

Measurements at pH 6.9 where $K_{obs} \approx K_1$ gave a value for K_1 of 300 ± 10 dm^3 mol^{-1}. Values of K_{obs} at pH 10.2 and 11.6 were 27 ± 3 and 7.6 ± 1 respectively. Using the known value of 9.1 for $\text{p}K_a^{HCN}$ these values lead *via* eqn. (11) to a value of $\text{p}K_a^{COH}$ of 10.75 ± 0.1. Using eqn. (12) the value for K_2 is found to be 7 ± 0.5 dm^3 mol^{-1}.

$$K_2 = K_1\frac{K_a^{COH}}{K_a^{HCN}} \qquad (12)$$

These values are close to those reported previously.[11]



Scheme 3

Comparisons

Values of rate and equilibrium constants are collected in Table 3. They show that cyanide addition to the iminium ions **5** is an extremely favourable process with values of K_{CN} ($=k_{CN}/k_{-CN}$) being *ca.* 10^7 dm^3 mol^{-1}. Changing the group R from Ph to CH=CH$_2$ has little effect on values of rate and equilibrium constants. The use of eqn. (13)

$$K_{HCN} = K_{CN}\frac{K_a^{HCN}}{K_a^{ImH^+}} \qquad (13)$$

allows the calculation of values of *ca.* 10^4 dm^3 mol^{-1} for K_{HCN}, the equilibrium constant for addition of hydrogen cyanide to the imines **4**. Knowledge of these values is important in the context of the Strecker synthesis of aminonitriles.

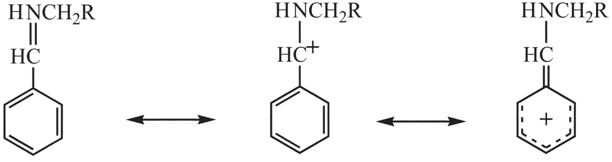
Our results show that reactivity for the iminium ions decreases in the order $\text{OH}^- > \text{CN}^- \gg \text{H}_2\text{O}$. This order of nucleophilicity reactivity is that commonly found for attack at cationic centres.[13]

Nevertheless, the iminium ions **5** are relatively unreactive when compared with some other iminium ions. Thus values for k_{H_2O} for reaction with water for **2**, 10^6–10^8 s^{-1}, and **3**, 7 × 10^5 s^{-1}, are many orders of magnitude higher than those for **5**. Also, the value of k_{H_2O} for reaction of the benzyl carbocation with water has been estimated[14] to be in excess of 10^{11} s^{-1}, although this value may be considerably reduced by electron releasing groups in the aromatic ring or in the side-chain.[15,16]

Table 3 Summary of rate and equilibrium constants

	4a	**4b**
k_{CN}/dm^3 mol^{-1} s^{-1}	6.7 × 10^3	1.0 × 10^4
k_{-CN}/s^{-1}	9.1 × 10^{-4}	5.5 × 10^{-4}
K_{CN}/dm^3 mol^{-1}	7.4 × 10^6	1.8 × 10^7
K_{HCN}/dm^3 mol^{-1}	8.1 × 10^3	1.6 × 10^4
k_{OH}/dm^3 mol^{-1} s^{-1}	2.0 × 10^5	4.4 × 10^5
k_{H_2O}/s^{-1}	0.15	0.18
$\text{p}K_a^{ImH^+}$	6.14	6.05

The ‘low’ reactivity of **5** may be understood in terms of the possibilities for charge delocalisation. As shown in Scheme 4, **5** may be regarded as carbocations stabilised both by amino groups and by a benzene ring. Similar stabilisation has been reported[17] in iminium ions generated from some aromatic enamines. The presence of the strongly electron withdrawing nitroso group at the nitrogen atom of **3** greatly enhances its reactivity relative to **5**.



Scheme 4

Experimental

The imines **4a** and **4b** were prepared by reaction of equimolar amounts of benzaldehyde and the appropriate amine in acetonitrile followed by evaporation of the solvent under reduced pressure. **4a** was also available as a commercial specimen. **4a** δ_H (400 MHz, CD$_3$CN): 4.78 (2H, s, CH$_2$), 7.3–7.8 (10H, m, ArH), 8.47 (1H, s, CH); *m*/*z* (EI) 195. **4b** δ_H (400 MHz, CD$_3$CN): 4.19 (2H, m, CH$_2$N), 5.14 (2H, dd, CH$_2$), 6.05 (1H, m, CH), 7.4–7.7 (5H, m, ArH), 8.31 (1H, s, CHN); (M + H)$^+$ *m*/*z* (CI) 146.

The *α*-aminonitriles **6a** and **6b** were prepared in solution by reaction of the appropriate imine with trimethylsilyl cyanide (1 equiv.) in damp acetonitrile. **6a** δ_H (CD$_3$CN): 2.5 (1H, m, NH), 3.84 (2H, m, CH$_2$), 4.80 (1H, d, *J* = 9.6 Hz, CH), 7.2–7.5 (10H, m, ArH). Coupling was observed between NH and hydrogens on adjacent carbon atoms. **6b** δ_H (C$_6$D$_6$): 3.05 (2H, d, CH$_2$N), 4.18 (1H, d, *J* = 9.2 Hz, CHCN), 4.98 (2H, dd, C*H*$_2$CH), 5.57 (1H, m, C*H*CH$_2$), 7.0–7.3 (5H, m, ArH); (M − H)$^+$ *m*/*z* (EI) 171.

Other materials and solvents were the purest available commercial specimens. The pH values of aqueous buffers (phosphate, borax or bicarbonate, *ca.* 0.05 mol dm^{-3}) were measured using a Jenway 3020 pH meter.

UV-vis spectra and kinetic measurements were made at 25 °C with a Perkin Elmer Lambda 2 spectrophotometer or a Shimadzu UV-2101 PC spectrophotometer. The substrate was added to the reaction mixtures as a concentrated solution in acetonitrile so that the final solvent composition was 99/1 (v/v) water–acetonitrile. Rate constants were measured under first-order conditions and are precise to ±5%. Benzaldehyde was characterised as a product of hydrolysis, in more concentrated solutions, as the 2,4-dinitrophenylhydrazone derivative, m.p. 238 °C, lit,[18] 237 °C.

Safety Cyanide is poisonous and must be treated with caution.

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