# Carbanion Reactivity; Kinetics of the Reactions of Benzyl Cyanide Anions with Aromatic Nitro-compounds

John H. Atherton,[a] Michael R. Crampton,*[b] Gaynor L. Duffield[b] and J. Andrew Stevens[b]
[a] Zeneca Fine Chemicals Manufacturing Organisation, Leeds Road, Huddersfield, UK HD2 1FF
[b] Chemistry Department, Durham University, Durham, UK DH1 3LE

Rate and equilibrium measurements are reported for the reactions in methanol of carbanions derived from 12 ring-substituted benzyl cyanides with 1,3,5-trinitrobenzene to give σ-adducts. Some data for reaction of the carbanions with 4-nitrobenzofuroxan were also measured. With increasing carbanion reactivity, rate constants approach a limit of just below $10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. Intrinsic reactivities of carbanions in σ-adduct forming reactions and in proton transfer reactions are compared.

There is current interest in the measurement of rate constants for proton transfer reactions and in the effects of molecular structure on rate constants for the dissociation of acidic species.[1–3] In the case of 'normal' acids, when the dissociating proton is bound to a strongly electronegative atom such as oxygen or nitrogen, rates are essentially diffusion controlled ($k \approx 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$) in the thermodynamically downhill direction.[4] In the reverse, thermodynamically uphill direction, rate constants are smaller by a factor of $10^{\Delta pK}$ where $\Delta pK$ is the difference in acidities of the species involved in the proton transfer. In the vicinity where $\Delta pK \approx 0$ there is a region where proton-transfer becomes partly rate-limiting and rate constants are typically $5 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$. The rate constant for the thermoneutral reaction reflects the 'intrinsic rate constant' for the process.

However marked deviations from this behaviour are typically observed for proton transfers involving carbon acids.[1–3] Here intrinsic rate constants may be several orders of magnitude lower than those expected for normal acids and the limiting rate constants are less than expected for diffusion controlled reactions. It has been convincingly argued that high intrinsic barriers are associated with lack of synchronization between bond formation and the solvent and electronic reorganization which accompanies the reaction.

The reaction of carbanions with protons is represented by eqn. (1). A related process is their reaction with electron deficient aromatics to give σ-adducts,[5,6] eqn. (2). The latter reactions result in carbon–carbon bond formation.

$$R^1R^2R^3C^- + H^+ \rightleftharpoons R^1R^2R^3CH \qquad (1)$$

$$R^1R^2R^3C^- + Ar \rightleftharpoons R^1R^2R^3C\text{-}Ar^- \qquad (2)$$
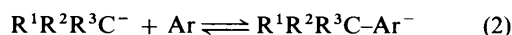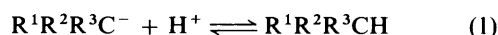
We present here the results of kinetic studies of the reactions in methanol of carbanions derived from ring-substituted benzyl cyanides with both 1,3,5-trinitrobenzene 1 and 4-nitrobenzofuroxan 2. These reactions result in the formation of the σ-adducts 3 and 4, respectively.

## Experimental

1,3,5-Trinitrobenzene and benzyl cyanide derivatives were available from previous work[7] or were commercial specimens of the highest available purity. 4-Nitrobenzofuroxan, mp 143 °C (lit.,[8] 143 °C), was prepared by nitration of benzofuroxan.[8] Solutions of sodium methoxide were prepared by



**3**

**4**
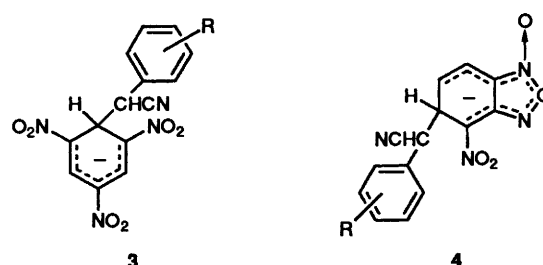
dissolving clean sodium metal in AnalaR methanol under nitrogen.

All UV–VIS spectral measurements were made at 25 °C with a Perkin-Elmer Lambda 3 or, for fast reactions, with a Hi-Tech SF-3L spectrophotometer. First-order rate coefficients were determined by following changes in absorbance at an appropriate wavelength and analysing the data using standard methods. Rate coefficients are the mean of several determinations and are precise to ± 5%.

## Results and Discussion

*Acidities of Carbon Acids in Methanol.*—Carbanions were generated from the benzyl cyanides by reaction with sodium methoxide in methanol. Values of $K_1$, defined in eqn. (3), were



$$(3)$$
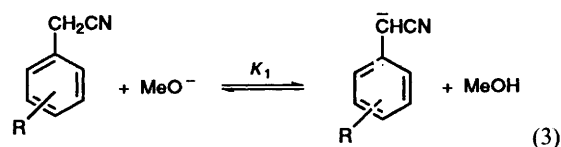
determined spectrophotometrically using the strong UV–VIS absorption of the carbanions. In all cases equilibration was rapid on the stopped-flow time-scale.

For 4-nitrobenzyl cyanide ionization occurred in dilute solutions of base where the basicity of the medium is adequately expressed by the methoxide concentration. Using eqn. (4) a

$$K_1 = \frac{[RC_6H_4CHCN^-]}{[RC_6H_4CH_2CN][MeO^-]} \qquad (4)$$

value for $K_1$ of 1.1 dm$^3$ mol$^{-1}$ was obtained in good agreement with a literature value.[9]

For less acidic benzyl cyanides sufficient ionization to allow the measurement of the ionization ratio, IR defined in eqn. (5),

**Table 1** Ionization of 3,5-bis(trifluoromethyl)benzyl cyanide in methanolic sodium methoxide

| [NaOMe]/mol dm$^{-3}$ | $H_M{}^a$ | $A$ (343 nm) | $\log_{10}$ IR$^b$ | $\log_{10} K_1{}^c$ |
|---|---|---|---|---|
| 2.20 | 18.8 | 0.095 | $-1.04$ | $-2.9$ |
| 2.40 | 19.0 | 0.150 | $-0.82$ | $-2.9$ |
| 2.60 | 19.2 | 0.270 | $-0.51$ | $-2.8$ |
| 2.80 | 19.4 | 0.358 | $-0.34$ | $-2.8$ |
| 3.00 | 19.6 | 0.408 | $-0.25$ | $-2.9$ |
| 3.20 | 19.9 | 0.640 | 0.11 | $-2.9$ |
| 3.40 | 20.1 | 0.706 | 0.22 | $-3.0$ |

$^a$ From ref. 13. Values have been calculated assuming that $H_M$ for 0.01 mol dm$^{-3}$ sodium methoxide is 14.92. $^b$ Calculated as $\log_{10}$ $A/(1.134 - A)$. $^c$ Calculated from eqn. (6).

$$IR = \frac{[RC_6H_4CHCN^-]}{[RC_6H_4CH_2CN]} \qquad (5)$$

occurred only in more basic media. Here the basicity of the medium may be expressed using the $H_M$ acidity function.[10] When values of IR could be measured in concentrated sodium methoxide solutions in methanol, eqn. (6) was used to calculate values of $K_1$.

$$\log_{10} K_1 = \log_{10} \text{IR} - \log_{10} K_{MeOH} - H_M \qquad (6)$$

The value of $K_{MeOH}$, the autoprotolysis constant of methanol[10] is $10^{-16.92}$ mol$^2$ dm$^{-6}$.

Acidity functions for methanolic sodium methoxide have been reported based on the ionization of substituted anilines[11] and also on methoxide additions to polynitrobenzenes[12] or α-cyanostilbenes.[13] Since the latter scales involve base addition they are in fact $J_M$ scales. In all these cases ionization results in the formation of negative charge which may be delocalized into an aromatic ring and the $H_M$ and $J_M$ scales closely parallel each other.[10] Since the reaction with methoxide of α-cyanostilbenes, eqn. (7), results in the formation of carbanions[13] which closely resemble those produced from ionization of benzyl cyanides it was decided to use these data to obtain values to substitute for $H_M$ in eqn. (6). An example of the calculation is given in Table 1. This leads to a value for $\log_{10} K_1$ of $-2.9$ for ionization of 3,5-bis(trifluoromethyl)benzyl cyanide, referred to a standard state in methanol. In a similar manner values of $\log_{10} K_1$ were determined for benzyl cyanides substituted as follows: 2-NO$_2$, $-0.76$; 4-CN, $-2.35$; 2,3,4,5,6-F$_5$, $-3.3$.



$$(7)$$
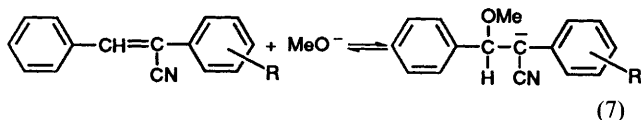
For benzyl cyanides less acidic than the pentafluoro derivative insufficient ionization occurred in methanolic sodium methoxide solutions to allow the calculation of values of $K_1$ using eqn. (6). For these compounds two approaches were used, both using the value of $\log_{10} K_1 = -2.35$ for the 4-CN derivative as an anchor point. Stewart and Kroeger[13] showed that for carbanion formation from α-cyanostilbenes, eqn. (7), a Hammett plot versus $\sigma^-$ gave a value for $\rho$ of 4.62. The similarity of carbanion formation from benzyl cyanides to this process leads us to expect a similar value for $\rho$. Making this assumption the values of $K_1$ in Table 3 were calculated. The second approach was to measure values of the ionization ratio, IR, in methanol-dimethyl sulfoxide (DMSO) mixtures containing 0.05 mol dm$^{-3}$ sodium methoxide. Increasing the DMSO content in these mixtures is known to produce
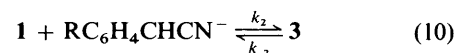
increasingly basic media[10] and use of eqn. (8) allowed the

$$\log_{10}(K_1)_{R^1} - \log_{10}(K_1)_{R^2} = \log_{10}(IR)_{R^1} - \log_{10}(IR)_{R^2} \qquad (8)$$

calculation of values of $K_1$ by a step-wise method. This method makes the reasonable assumption that in a given medium the ratio of activity coefficients for carbanion and parent is independent of the nature of the substituent, R$^1$ or R$^2$, in the benzyl cyanide. Data are in Table 2, and values of $K_1$ referred to a standard state in methanol are in Table 3. The values of $\log_{10} K_1$ calculated by the two different methods are within 0.2 units of each other giving us confidence in the values obtained.

It is perhaps worth noting that the p$K_a$ value for pentafluorobenzyl cyanide is between that of the 4-cyano and 4-trifluoromethyl derivatives. This contrasts with data for phenols where the pentafluoro-derivative is more acidic even than the 4-nitro derivative.[14] Our results however accord with previous work showing the variable resonance/inductive effects of the $C_6F_5$ substituent and in particular the relatively small effect of this grouping on the acidities of carbon acids.[15]

*Reactions with 1,3,5-Trinitrobenzene* **1**.—Kinetic measurements were made at 25 °C by mixing solutions in methanol containing **1** and substituted benzyl cyanide with sodium methoxide. Our results provide evidence for the reactions shown in eqns. (9) and (10). It is known that equilibration of **1**

$$1 + MeO^- \underset{\phantom{K_{OMe}}}{\overset{K_{OMe}}{\rightleftharpoons}} TNB\text{--}MeO^- \qquad (9)$$

$$1 + RC_6H_4CHCN^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 3 \qquad (10)$$

and its methoxide adduct is a rapid process[5,6] on the stopped-flow time-scale with an equilibrium constant,[16] $K_{OMe}$, of 17 dm$^3$ mol$^{-1}$. The amplitude of this process was minimized by working with [MeO$^-$] $\leqslant 0.01$ mol dm$^{-3}$. The major process observed was formation of adducts **3** with $\lambda_{max}$/nm 450 and 520–540 (shoulder).

Measurements were made with the concentrations of benzyl cyanide and of methoxide much greater than that of **1**. The ionic strength was maintained at 0.01 mol dm$^{-3}$ using sodium chloride as the added electrolyte. Under these conditions reactions were accurately first order and rate constants were independent of the concentration of **1** in the range $1 \times 10^{-5}$ to $1 \times 10^{-4}$ mol dm$^{-3}$. This indicates that carbanion formation, eqn. (3), is rapid and formation of adducts (3) is rate determining. Since the extent of conversion of benzyl cyanides to their carbanions is extremely low the appropriate rate expression is eqn. (11).

$$k_{obs} = \frac{k_2 K_1 [RC_6H_4CH_2CN][MeO^-]}{1 + K_{OMe}[MeO^-]} + k_{-2} \qquad (11)$$

Plots of $k_{obs}$ versus the concentration of benzyl cyanide, at constant methoxide concentration, were linear and allowed the calculation of values of $k_2 K_1$ and $k_{-2}$. Representative plots are shown in Fig. 1, and data are collected in Table 4. Combination of these values gave values for the overall equilibrium constant, $K_1 K_2$, defined in eqn. (12). Values of $K_1 K_2$ determined using

$$K_1 K_2 = \frac{k_2 K_1}{k_{-2}} = \frac{[3]}{[1][RC_6H_4CH_2CN][MeO^-]} \qquad (12)$$

equilibrium absorbances to measure the extent of conversion of **1** to **3** were in good agreement with those calculated from kinetic data.

**Table 2** Values of IR and calculation of values of $K_1$ in methanol–DMSO containing 0.05 mol dm$^{-3}$ sodium methoxide

| DMSO (%) (vol) | $\log_{10}$ IR | | | | | |
| | 4-CN | 2-CN | 4-CF$_3$ | 3-CF$_3$ | 3-Cl | 4-Cl |
|---|---|---|---|---|---|---|
| 55 | −1.11 | | | | | |
| 60 | −0.62 | −0.58 | | | | |
| 65 | −0.10 | −0.06 | | | | |
| 70 | 0.45 | 0.54 | −1.42 | −2.47 | | |
| 75 | | | −0.95 | −1.89 | −2.39 | −3.10 |
| 80 | | | −0.07 | −1.31 | −1.71 | −2.39 |
| 85 | | | 0.30 | −0.55 | −0.99 | −1.68 |
| 90 | | | 1.09 | | −0.15 | −0.87 |
| $\log_{10} K_1{}^a$ | −2.35 | −2.30 | −4.22 | −5.27 | −5.71 | −6.37 |

$^a$ Calculated using eqn. (8), taking $\log_{10} K_1 = -2.35$ for the 4-CN derivative.

**Table 3** Values of $K_1$ for ionization of benzyl cyanides in methanol

| $R^a$ | $\log_{10} K_1{}^b$ | $\log_{10} K_1{}^c$ | $\log_{10} K_1{}^d$ | $pK_a{}^e$ |
|---|---|---|---|---|
| 4-NO$_2$ | 0.04 | | | 16.9 |
| 2-NO$_2$ | −0.76 | | | 17.7 |
| 2-CN | | | −2.30 | 19.2 |
| 4-CN | −2.35 | | | 19.3 |
| 3,5-(CF$_3$)$_2$ | −2.9 | | | 19.8 |
| 2,3,4,5,6-F$_5$ | −3.3 | | | 20.2 |
| 4-CF$_3$ | | −4.06 | −4.22 | 21.0 |
| 3-CF$_3$ | | −5.08 | −5.27 | 22.1 |
| 3-Cl | | −5.40 | −5.71 | 22.4 |
| 4-Cl | | −6.19 | −6.37 | 23.2 |
| 3-MeO | | −6.60 | | 23.5 |
| H | | −7.06 | | 24.0 |
| 3-Me | | −7.46 | | 24.4 |

$^a$ Ring substituents in benzyl cyanide. $^b$ Determination in methanolic sodium methoxide. $^c$ Determination using Hammett $\rho\sigma$ plot. $^d$ Determination using methanol–DMSO mixtures (Table 2). $^e$ $pK_a = pK_1 + pK_M$.
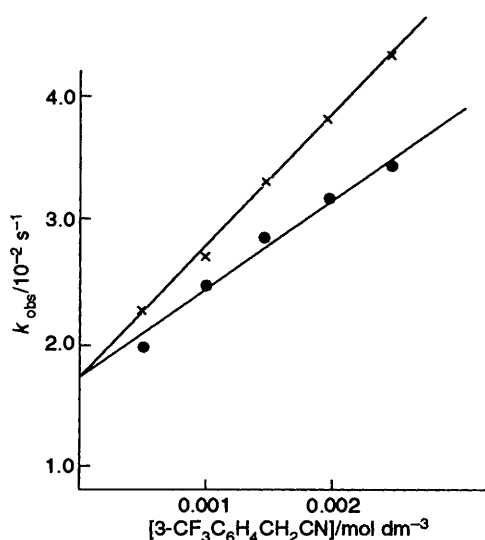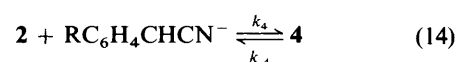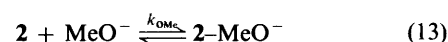


**Fig. 1** Variation of $k_{obs}$ with concentration of 3-trifluoromethylbenzyl cyanide for reaction with **1**; sodium methoxide concentrations: (●) 0.005; (×) 0.010

It is interesting that the values in Table 4 of the product $K_1 \times K_2$ are all close to $5 \times 10^4$ dm$^6$ mol$^{-2}$ and are insensitive to the nature of the ring substituent, R, in the benzyl cyanide. Hence the increases in value of $K_1$ with increasing electron withdrawal of the substituent, R, are exactly balanced by corresponding decreases in the values of $K_2$. Since ionization, eqn. (3), involves the development of a complete unit of negative

charge on the benzyl cyanide anions, the inference is that in the reaction with TNB to produce adducts (**3**) the negative charge is completely transferred from the carbanion to the trinitro-substituted aromatic ring. The slight decreases in value of $K_1K_2$ with *ortho*-substituted derivatives, R = 2-CN and 2,3,4,5,6-F$_5$ may represent a small unfavourable steric interaction in the corresponding adducts **3** resulting in decreases in values of $K_2$.

*Reaction with 4-Nitrobenzofuroxan* (**2**).—For comparison we have also measured rate constants for the reactions of some substituted benzyl cyanide anions with **2**. Since measurements were made in methanolic sodium methoxide the methoxide ions compete for **2** and there was evidence for the processes shown in eqns. (13) and (14).

$$2 + \text{MeO}^- \underset{}{\overset{k_{OMe}}{\rightleftharpoons}} 2\text{-MeO}^- \tag{13}$$

$$2 + \text{RC}_6\text{H}_4\text{CHCN}^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} 4 \tag{14}$$

It is known from $^1$H NMR measurements that reaction of **2** with methoxide alone results in the rapid formation of the 5-methoxy adduct followed by slower isomerization to the 7-methoxy adduct.[17,18] UV measurements have shown that **2** has an absorption maximum at 403 nm while the methoxy-adducts both absorb at 340 nm.[19] Kinetic studies give a value of 1950 dm$^3$ mol$^{-1}$ s$^{-1}$ for the rate constant for attack at the 5-position.[19]

We confirmed the results[19] obtained for reaction of **2** with methoxide. In the presence of benzyl cyanides we observed increases in the first order rate constant for adduct formation, measured either as a decrease in absorbance at 403 nm or as an increase in absorbance at 340 nm, which were compatible with formation of the adduct **4**. Typical data are in Table 5. We write the adduct formed as resulting from attack at the 5-position since this is likely to be the most rapid process[19] and the one to which our kinetic data apply. However it is probable that slow isomerization to give the adduct resulting from carbanion attack at the 7-position will occur.

Since under our experimental conditions the equilibrium conversion of **2** to adducts will be high, the expected rate expression is eqn. (15).

$$k_{obs} = k_{OMe}[\text{MeO}^-] + k_4K_1[\text{MeO}^-][\text{RC}_6\text{H}_4\text{CH}_2\text{CN}] \tag{15}$$

Values of the product $k_4K_1$ were obtained from the slopes of plots of $k_{obs}$ *versus* the benzyl cyanide concentration and these are collected in Table 6. Since values of $K_1$ are known, values of $k_4$ could be calculated.

Addition of benzyl cyanides (*ca.* $10^{-2}$ mol dm$^{-3}$) less acidic than the pentafluoro derivative caused no enhancement of $k_{obs}$

**Table 4** Kinetic and equilibrium data for reaction of TNB (1) with carbanions from benzyl cyanides in methanol at 25 °C

| Substituent | $k_2 K_1/\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ | $k_{-2}/\text{s}^{-1}$ | $K_1 K_2/10^4 \text{ dm}^6 \text{ mol}^{-2}$ | $\log_{10} k_2{}^a$ | $\log_{10} K_2{}^a$ |
|---|---|---|---|---|---|
| 4-NO$_2$ | $1.0 \times 10^6$ | 15 | 6.7 | 6.0 | 4.8 |
| 2-CN | $2.7 \times 10^5$ | 15 | 1.8 | 7.7 | 6.6 |
| 4-CN | $2.4 \times 10^5$ | 4.1 | 5.9 | 7.7 | 7.1 |
| 2,3,4,5,6-F$_5$ | $2.6 \times 10^5$ | 18.2 | 1.4 | 8.7 | 7.4 |
| 3,5-(CF$_3$)$_2$ | $1.4 \times 10^5$ | 2.8 | 5.0 | 8.1 | 7.6 |
| 4-CF$_3$ | $8.1 \times 10^3$ | 0.12 | 6.7 | 8.0 | 8.9 |
| 3-CF$_3$ | $1.3 \times 10^3$ | $1.7 \times 10^{-2}$ | 7.6 | 8.3 | 10.1 |
| 3-Cl | $4.7 \times 10^2$ | $1.2 \times 10^{-2}$ | 3.9 | 8.2 | 10.1 |
| 4-Cl | $2.1 \times 10^2$ | $3.4 \times 10^{-3}$ | 6.2 | 8.6 | 11.1 |
| 3-MeO | 70 | $1.1 \times 10^{-3}$ | 6.4 | 8.5 | 11.4 |
| H | 25 | $6.0 \times 10^{-4}$ | 4.2 | 8.5 | 11.7 |
| 3-Me | 19 | $4.2 \times 10^{-4}$ | 4.5 | 8.7 | 12.1 |

$^a$ Calculated using $K_1$ values derived from p$K_a$ values in Table 3.

**Table 5** Kinetic data for reaction of 2 with carbanions derived from 4-nitrobenzyl cyanide in the presence of methoxide in methanol at 25 °C

| [4-Nitrobenzyl cyanide] $10^{-4} \text{ mol dm}^{-3}$ | [NaOMe] $10^{-3} \text{ mol dm}^{-3}$ | $k_{obs}{}^a/\text{s}^{-1}$ |
|---|---|---|
| 1.0 | 3.0 | 12 |
| 2.0 | 3.0 | 22 |
| 3.0 | 3.0 | 31 |
| 4.0 | 3.0 | 41 |
| 1.0 | 5.0 | 23 |
| 2.0 | 5.0 | 37 |
| 3.0 | 5.0 | 52 |
| 4.0 | 5.0 | 67 |
| 1.0 | 7.0 | 33 |
| 2.0 | 7.0 | 52 |
| 3.0 | 7.0 | 74 |
| 4.0 | 7.0 | 92 |

$^a$ Measured both as a fading reaction at 404 nm and a forming reaction at 340 nm. Rate constants were independent of the wavelength of measurement.

**Table 6** Rate constants for reaction of substituted benzyl cyanide anions with 2 in methanol

| Substituent | $\dfrac{k_4 K_1}{10^5 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}}$ | $\dfrac{k_4}{10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$ |
|---|---|---|
| 4-NO$_2$ | 334 | 3.0 |
| 2-NO$_2$ | 93 | 5.8 |
| 4-CN | 5.4 | 14 |
| 3,5-(CF$_3$)$_2$ | 2.1 | 17 |
| 2,3,4,5,6-F$_5$ | 2.4 | 48 |

above that observed in the presence of methoxide alone. This is compatible with our analysis since it is expected, as discussed later, that values of $k_4$ will reach an upper limit of $ca.$ $10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ for the more reactive carbanions. Hence for benzyl cyanides where $K_1 < 10^{-4}$ dm$^3$ mol$^{-1}$ the condition $k_{OMe} > k_4 K_1[\text{RC}_6\text{H}_4\text{CH}_2\text{CN}]$ will apply so that the final term in eqn. (15) becomes immeasurably small. It is expected that adducts formed from 2 with all the benzyl cyanide carbanions will have greater thermodynamic stabilities than the methoxide adducts. However since the UV spectra of the two types of adduct are similar, conversion of the initially formed methoxide adducts to the more stable carbanionic adducts was not observable under our experimental conditions.

*Rate Constants for Carbon–Carbon Bond Formation.*—It is known[20] that rate constants for the carbon–carbon bond forming reactions between the enolate ions of acetone and quinolinium and acridinium cations have values in the range

$8 \times 10^5$–$4 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$. A value of $9 \times 10^5$ dm$^3$ mol$^{-1}$ s$^{-1}$ has been reported[21] for the carbon–carbon bond forming reaction of the neutral nucleophile 3,4-diaminothiophene with 4,6-dinitrobenzofuroxan. The values reported here for carbon–carbon bond formation are even higher. Fig. 2 shows a logarithmic plot of the values of the forward, $k_2$, and reverse, $k_{-2}$, rate constant for formation of adducts 3 *versus* the equilibrium constant, $K_2$. With increasing reactivity of the benzyl cyanide anions values of $k_2$ approach a limit just under $10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. These are extremely rapid reactions but are slower than expected for diffusion controlled reaction in methanol.

Also in Fig. 2 are values of $k_4$ for reaction of the benzyl cyanide anions with 2 to give 4. It was not possible here to measure values of the reverse rate constants, $k_{-4}$, or the equilibrium constants. However it is known[19] that adducts formed by nucleophilic attack on 2 have higher stabilities than corresponding adducts from 1 and it was found that for a given carbanion the value of $k_4$ was larger than $k_2$. Nevertheless the values of $k_4$ appear to approach a similar limit to the maximum found for the $k_2$ values.

The high reactivities of the benzyl cyanide anions may reflect the activation by the $\alpha$-cyano group. Thus there is evidence that the cyano-group activates mainly by inductive effects rather than resonance effects so that in the nitrile anions the negative charge is not strongly delocalized.[2,22]

There is current interest in the measurement of intrinsic rate constants, in the Marcus sense,[23] for proton transfer reactions. Bernasconi has argued that low intrinsic rate constants are associated with the lack of synchronization between bond formation (or cleavage) and the solvent- and electronic-reorganization accompanying reaction[1] (the PNS effect). By extrapolation of the plots in Fig. 2 to the point where $\log K_2 = 0$ it is possible to estimate a value for the intrinsic rate constant for the carbon–carbon bond forming reaction between the benzyl cyanide anions and 1. The value obtained for $\log k_o$ is $2.5 \pm 0.5$. In fact we have previously[7] obtained a value for $\log k_o$ of 2.3 for the reaction of 4-nitrobenzyl cyanide anions with trinitrobenzene derivatives. Our previous value for $\log k_o$ of 3.0 for reactions of the 4-cyanobenzyl cyanide anion was calculated using a p$K_a$ value of 20.5; recalculation using the current value of 19.3 gives a value for $\log_{10} k_o$ of 2.7 $\pm$ 0.5. Bernasconi[1] has shown that the effects of a remote substituent, such as R in the benzyl cyanides, on values of intrinsic rate constants is expected to be small.

It is of interest to compare, in Table 7, some values for the intrinsic rate constants for $\sigma$-adduct formation with those for proton transfer. The carbanion order is the same for the two types of reaction, reflecting variations of the PNS effect in the carbanions. However the values for $\sigma$-adduct formation are
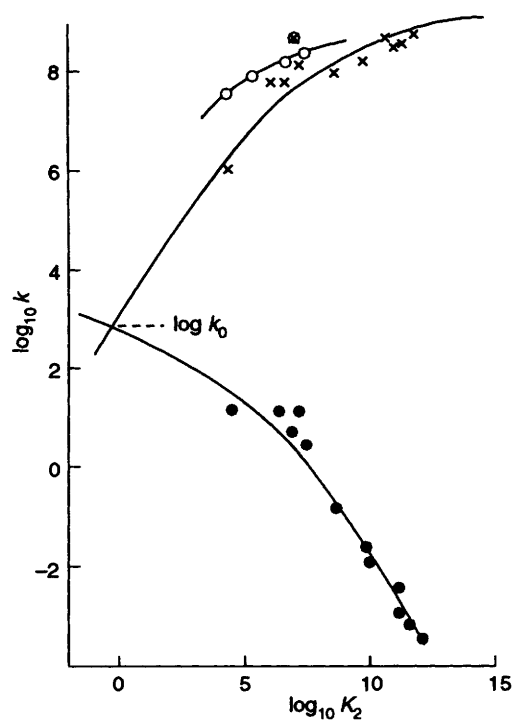
**Fig. 2** Logarithmic plots of rate coefficient *versus* equilibrium constant for reactions of benzyl cyanide anions with TNB ( × values of $k_2$ and ● values of $k_{-2}$) and with **2** (○, values of $k_4$)

**Table 7** Intrinsic rate constants ($\log_{10} k_o$) for reaction of carbanions with the trinitro-aromatic ring and for protonation

| | log $k_o$ | |
|---|---|---|
| | σ-Adduct formation | Proton transfer[b] |
| $CH(CN)_2^-$ | 4.4[a] | 7.0 |
| $CH(CN)Ph^-$ | 2.5 | 4.0 |
| $CH_2NO_2^-$ | −0.74[a] | 0.7 |

[a] Data from ref. 24. [b] Data from ref. 25.

lower than those for proton transfer. It should be noted that results for the proton transfers refer to reactions with nitrogen acids where the negative charge, in the conjugate base, is localized on the nitrogen atom. Hence the lower values obtained in reactions with the nitro-aromatics probably reflects an additional PNS effect associated with transfer of negative charge to the trinitrobenzene ring to give delocalized anions such as **3**. For related reasons it has been found [1] that intrinsic rate constants for proton transfers from carbon to carbon may be lower than those for proton transfers between carbon and nitrogen.

## References

1 C. F. Bernasconi, *Pure Appl. Chem.*, 1982, 2335; *Acc. Chem. Res.*, 1987, **20**, 301; *Adv. Phys. Org. Chem.*, 1992, **27**, 119.
2 F. Aiken, B. G. Cox and P. E. Sorensen, *J. Chem. Soc., Perkin Trans. 2*, 1993, 783.
3 F. Terrier, D. Croisat, A.-P. Chatrousse, M.-J. Pouet, J.-C. Halle and G. Jacob, *J. Org. Chem.*, 1992, **57**, 3684.
4 M. Eigen, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 1.
5 E. Buncel, M. R. Crampton, M. J. Strauss and F. Terrier, *Electron Deficient Aromatic- and Heteroaromatic-Base Interactions*, Elsevier, Amsterdam, 1984.
6 F. Terrier, *Nucleophilic Aromatic Displacement*, VCH, New York, 1991.
7 M. R. Crampton and J. A. Stevens, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1715.
8 P. Drost, *Justus Liebig Ann. Chem.*, 1899, **307**, 49; R. J. Gaughran, J. P. Picard and J. V. R. Kaufman, *J. Am. Chem. Soc.*, 1954, **76**, 2233.
9 R. A. More O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 1963, 5030.
10 C. H. Rochester, *Acidity Functions*, Academic Press, NY, 1970.
11 F. Terrier, *Ann. Chim. (Paris)*, 1969, **4**, 153.
12 F. Terrier and R. Schaal, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1966, **263**, 476.
13 R. Stewart and D. J. Kroeger, *Can. J. Chem.*, 1967, **45**, 2163; 2173.
14 A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 1961, 388.
15 O. A. Reutov, I. P. Beletskaya and K. P. Butin, *CH-Acids*, Pergamon Press, 1978, p. 57.
16 M. R. Crampton and H. A. Khan, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1710.
17 F. Terrier, F. Millot, A. P. Chatrousse, M. J. Pouet and M. P. Simonnin, *Org. Magn. Reson.*, 1976, **8**, 56.
18 E. Buncel, N. Chuaqui-Offermanns, B. K. Hunter and A. R. Norris, *Can. J. Chem.*, 1977, **55**, 2852.
19 F. Terrier, A. P. Chatrousse and F. Millot, *J. Org. Chem.*, 1980, **45**, 2666.
20 J. W. Bunting, C. Fu and J. W. Tam, *Can. J. Chem.*, 1990, **68**, 1762.
21 F. Terrier, M.-J. Pouet, E. Kizilian, J.-C. Halle, F. Outurquin and C. Paulmier, *J. Org. Chem.*, 1993, **58**, 4696.
22 W. H. Saunders and J. E. Van Verth, 12th IUPAC Conference on Physical Organic Chemistry, Padua, 1994.
23 R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891; A. O. Cohen and R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 4249.
24 J. P. Cox, M. R. Crampton and P. Wight, *J. Chem. Soc., Perkin Trans. 2*, 1988, 25.
25 C. F. Bernasconi, *Tetrahedron*, 1989, **45**, 4017.