Intrinsic Reactivities of Some Carbanions in σ-Adduct Forming Reactions

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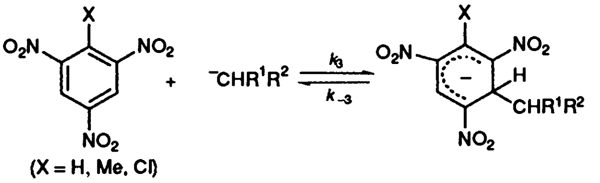
Kinetic and equilibrium data are reported for nucleophilic attack in methanol at unsubstituted ring-positions of 1,3,5-trinitrobenzene, 2,4,6-trinitrotoluene and 1-chloro-2,4,6-trinitrobenzene by carbanions derived from dimethyl malonate, ethyl cyanoacetate and 4-nitro-, 4-cyano- and 2-cyanobenzyl cyanides. The results are used to determine intrinsic reactivities for the carbanions in these σ-adduct forming reactions and are discussed in terms of the electronic and solvent reorganisation occurring during reaction.

The reactions of nucleophiles with ring-activated aromatic compounds may result in the formation of relatively stable anionic σ-adducts.[1] Measurement of the rate coefficients and equilibrium constants for these reactions allows the comparison, respectively, of the nucleophilicities and basicities of the nucleophiles for reaction at a carbon centre. Much data is now available for such reactions involving nucleophiles reacting *via* oxygen and sulphur.[1–3] However, data for reactions with carbanionic nucleophiles is limited to some derivatives of malonic acid[4–6] and to some nitroalkane anions.[7]

We report here kinetic and equilibrium data for the reactions (Scheme 1) of a series of carbanions at unsubstituted ring-positions of 1-substituted-2,4,6-trinitrobenzenes in methanol as the solvent. The results are used to calculate the intrinsic rate constants, in the Marcus sense,[8] of the nucleophiles in these σ-adduct forming reactions. There is current interest in comparing the intrinsic reactivities of nucleophiles in different reaction types[9–11] and data are available for proton transfer reactions (protonation of nucleophiles) and for nucleophilic additions to alkenes.[12] Bernasconi has argued[10] convincingly that high intrinsic barriers are associated with lack of synchronisation between bond formation and the solvent and electronic reorganisation which occurs during reaction.



Scheme 1

Experimental

1,3,5-Trinitrobenzene and 1-chloro-2,4,6-trinitrobenzene were recrystallised commercial specimens. 2,4,6-Trinitrotoluene, m.p. 82 °C (lit.,[13] 82 °C) was a gift from RARDE, Waltham Abbey. Ethyl cyanoacetate, dimethyl malonate, 4-nitrobenzyl cyanide and 2-cyanobenzyl cyanide were commercial specimens of the highest available purity. 4-Cyanobenzyl cyanide was prepared by reaction of 4-cyanobenzyl bromide with 1.1 equiv. of potassium cyanide in ethanol–water at 60 °C; on pouring the reaction mixture into ice–water a solid precipitated which was recrystallised from methanol to give pale yellow needles m.p. 100 °C (lit.,[14] 100 °C). Solutions of sodium methoxide were prepared by dissolving clean sodium metal in AnalaR methanol under nitrogen.

All UV–VIS spectral measurements were made at 25 °C with Perkin-Elmer Lambda 3 or Philips PU 8725 instruments 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%.

The subscripts for rate and equilibrium constants refer to the ring-position at which attack occurs in 1-substituted-2,4,6-trinitrobenzenes. Thus, k_3 and k_{-3} are the rate constants for forward and reverse reaction at the 3-position. For ease of comparison of data, reaction at an unsubstituted position of trinitrobenzene (TNB) are also referred to using k_3, k_{-3} and K_3.

Results and Discussion

Acidities of Carbon Acids in Methanol.—Carbanions were generated from the carbon acids by reaction with sodium methoxide. Values of K_{CH}, defined in eqn. (1), were determined

$$\underset{\mathbf{1}}{CH_2R^1R^2} + MeO^- \xrightleftharpoons{K_{CH}} {}^-CHR^1R^2 \qquad (1)$$

spectrophotometrically using the strong UV absorption of the carbanions. Dimethyl malonate, ethyl cyanoacetate and 4-nitrobenzyl cyanide were sufficiently acidic for measurements to be made in methanol. However, for the cyanobenzyl cyanides it was necessary to use methanol–dimethyl sulphoxide mixtures to achieve appreciable ionisation. Here, values of K_{CH} in methanol were obtained by extrapolating data measured in mixed solvents using an acidity function approach.[15] The use of eqn. (2) together with the value[16] for methanol, $pK_M = 16.92$,

$$K_{CH} = K_a/K_M \qquad (2)$$

allowed the calculation of pK_a values for the carbon acids in methanol. Data are presented in Table 1.

Reactions with 1,3,5-Trinitrobenzene (TNB).—Kinetic measurements were made in methanol at 25 °C using stopped-flow spectrophotometry. Because of the relative instability of the carbanions, solutions containing TNB and the carbon acid were mixed in the spectrometer with sodium methoxide in methanol. All measurements were made at ionic strength 0.01 mol dm^{-3} with sodium chloride as the added electrolyte. The results provide evidence for the processes shown in Scheme 2. Formation of the methoxide adduct, **4**, was observed as a very rapid colour-forming reaction. The equilibrium constant, K_{OMe}, has a value[17] of 17 dm^3 mol^{-1}, so that the amplitude of this process was minimised by working with $[MeO^-] \leqslant 0.01$ mol dm^{-3}. With each carbanion used the major process resulted in

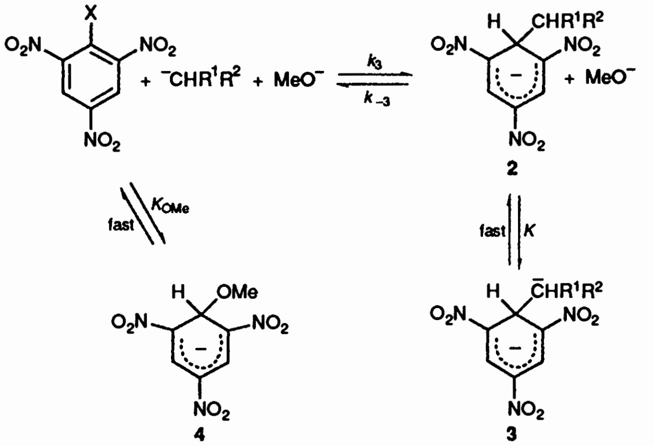
Table 1 Acidities of carbon acids in methanol

$^-CHR^1R^2$	λ_{max}/nm	$10^{-4}\ \varepsilon$/dm^3 mol^{-1} cm^{-1}	K_{CH}/dm^3 mol^{-1}	pK_a
$R^1 = R^2 = CO_2Me$	258	2.5	0.45	17.27
$R^1 = CN, R^2 = CO_2Et$	245	1.6	24	15.53
$R^1 = H, R^2 = 4\text{-}NO_2C_6H_4$	520	3.0	1.2	16.85
$R^1 = H, R^2 = 4\text{-}CNC_6H_4$	390	3.6	2.5×10^{-4}	20.52
$R^1 = H, R^2 = 2\text{-}CNC_6H_4$	340	1.8	3.5×10^{-4}	20.38

Table 2 Kinetic and equilibrium data for reaction of TNB[a] with dimethyl malonate anion in methanol at 25 °C

$[CH_2R^1R^2]_{stoich}$/ mol dm^{-3}	[NaOMe]$_{stoich}$/ 10^{-3} mol dm^{-3}	$[^-CHR^1R^2]$/ 10^{-5} mol dm^{-3} [b]	k_{obs}/s^{-1} [c]	k_{calc}/s^{-1} [d]	A_{550} (2, 4) [e,f]	A (4) [e,g]	K_{obs}/ 10^2 dm^3 mol^{-1} [h]
0.0025	5.0	0.56	25	25	0.10	0.04	98
0.0050	5.0	1.12	27	27	0.16	0.04	104
0.0100	5.0	2.23	30	29	0.23	0.03	93
0.0200	5.0	4.45	35	34	0.40	0.03	105
0.0400	5.0	8.82	45	44	0.62	0.02	119
0.0500	5.0	10.98	50	48	0.64	0.02	103
0.0050	10.0	2.23	29	29	0.25	0.06	91
0.0100	10.0	4.46	34	33	0.40	0.05	99
0.0200	10.0	8.88	41	42	0.57	0.04	96
0.0300	10.0	13.26	50	51	0.67	0.03	93
0.0400	10.0	17.61	60	60	0.80	0.02	114
0.0500	10.0	21.91	69	69	0.93	—	—
0.0600	10.0	26.18	79	78	0.95	—	—
0.300	10.0	120	—	—	1.19	—	—
0.400	10.0	150	—	—	1.19	—	—

[a] [TNB] is in the range 1×10^{-5} mol dm^{-3} to 1×10^{-4} mol dm^{-3}. All measurements at $I = 0.01$ mol dm^{-3} with sodium chloride. [b] Concentration of dimethylmalonate anion, calculated with $K_{CH} = 0.45$ dm^3 mol^{-1}. [c] Identical values were obtained at 460 nm and at 550 nm. [d] Calculated from eqn. (3) with $k_3 = 2.4 \times 10^5$ dm^3 mol^{-1} s^{-1}, $k_{-3} = 24$ s^{-1}, $K_{OMe} = 17$ dm^3 mol^{-1}, and $K = 0$ dm^3 mol^{-1}. [e] Absorbances normalised to a pathlength of 1 cm and [TNB] 1×10^{-4} mol dm^{-3}. [f] Equilibrium absorbance due to adducts **2** and **4**. [g] Equilibrium absorbance due to adduct **4**. [h] Calculated as $[A\,(2,4) - A(4)]/\{[1.19 - A\,(2,4)]\,[^-CHR^1R^2]\}$.



Scheme 2

the formation of adduct **2** with λ_{max} = 450–460 nm, and 520 nm (shoulder). For the more acidic carbon acids there was evidence for rapid equilibration of **2** with the dianion **3**. We saw no spectroscopic evidence for the formation or intermediacy of radical species during reaction of the carbanions with TNB or the other nitro compounds used.

Measurements were made with the concentrations of carbon acid and of methoxide much greater than that of TNB. Under these conditions reactions were accurately first order and measured rate coefficients were independent of the TNB concentration in the range 1×10^{-5} to 1×10^{-4} mol dm^{-3}. This indicates that carbanion formation, eqn. (1), is rapid and formation of the carbanionic adduct **2** is rate determining. The appropriate rate expression is given as eqn. (3).

$$k_{obs} = \frac{k_3[^-CHR^1R^2]}{1 + K_{OMe}[MeO^-]} + \frac{k_{-3}}{1 + K[MeO^-]} \qquad (3)$$

Data for reaction with dimethyl malonate anion are in Table 2. Plots of k_{obs} *vs.* $\{[^-CHR^1R^2]/(1 + K_{OMe}[MeO^-])\}$ have slopes and intercepts which are independent of the methoxide concentration and give values for k_3 of 2.4×10^5 dm^3 mol^{-1} s^{-1} and k_{-3} of 24 s^{-1}. The independence of the intercepts on base concentration indicates that K, the equilibrium constant for the formation of **3** has a value < 10 dm^3 mol^{-1}. This is in accord with the relatively weak acidity of dimethyl malonate, and hence of **2**. The invariance of K_{obs} on methoxide concentration similarly indicates a low value for K [eqn. (4)]. The value for K_3 of 1×10^4 dm^3 mol^{-1} obtained from the absorbance data is in good agreement with that obtained from the combination of k_3 and k_{-3} values. At the low values of dimethyl malonate anions used here, there was no evidence for formation of a diadduct.[4]

$$K_{obs} = K_3(1 + K[MeO^-]) \qquad (4)$$

The results for reaction with the ethyl cyanoacetate anion are in Table 3, and indicate substantial ionisation of the adduct **2** to give **3**. This is in accord with the higher acidity expected for this adduct. Kinetic and equilibrium data are in accord with values of $k_3 = 9.3 \times 10^4$ dm^3 mol^{-1} s^{-1}, $k_{-3} = 40$ s^{-1} and 230 dm^3 mol^{-1}.

The anion of 4- nitrobenzyl cyanide absorbs strongly in the visible region and at 450 nm the extinction coefficient is 2.0×10^4 dm^3 mol^{-1} cm^{-1}. In order to determine values of K_{obs} it was necessary to subtract absorbances due to the carbanion from the total absorbance. The error associated with the values of K_{obs} is therefore large. Rate coefficients could be determined accurately, and plots according to eqn.

Table 3 Kinetic and equilibrium data for reaction of TNB[a] with ethyl cyanoacetate anion in methanol at 25 °C

$[^{-}CHR^1R^2]$/ 10^{-4} mol dm^{-3} [b]	[MeO$^-$]/ 10^{-3} mol dm^{-3} [b]	k_{obs}/s^{-1}	k_{calc}/s^{-1} [c]	$A(2,3,4)$ [d,e]	$A(4)$ [d,f]	K_{obs}/ 10^2 dm^3 mol^{-1} [g]	K_{calc}/ 10^2 dm^3 mol^{-1} [h]
0.28	2.47	29	28	—	—	—	—
0.55	2.44	31	31	—	—	—	—
1.09	2.39	38	36	0.67	0.05	37	39
0.53	4.95	24	23	0.62	0.10	63	49
1.05	4.89	28	28	0.74	0.09	42	49
1.56	4.84	32	33	1.02	0.07	50	49
3.98	4.60	53	54	1.41	0.05	42	49
7.42	4.53	83	84	1.64	0.03	38	47
0.39	9.96	16	15	0.59	0.18	64	70
0.96	9.90	20	20	0.97	0.14	69	70
1.43	9.86	24	24	1.17	0.12	70	70
3.75	9.62	42	42	1.53	0.07	57	70
10.60	8.94	99	99	1.95	0.03	68	70
16.67	8.33	141	149	—		—	—

[a] [TNB] in the range 1×10^{-5} mol dm^{-3} to 1×10^{-4} mol dm^{-3}. All measurements at $I = 0.010$ mol dm^{-3} with sodium chloride. [b] Equilibrium concentrations, calculated with $K_{CH} = 24$ dm^3 mol^{-1}. [c] Calculated from eqn. (3) with $k_3 = 9.3 \times 10^4$ dm^3 mol^{-1} s^{-1}, $k_{-3} = 40$ s^{-1}, $K_{OMe} = 17$ dm^3 mol^{-1} and $K = 230$ dm^3 mol^{-1}. [d] Absorbances at 450 nm, normalised to a pathlength of 1 cm and [TNB] 1×10^{-4} mol dm^{-3}. [e] Equilibrium absorbance due to adducts **2**, **3** and **4**. [f] Equilibrium absorbance due to adduct **4**. [g] Calculated as $[A(2,3,4) - A(4)]/\{[2.22 - A(2,,3,4)][^{-}CHR^1R^2]\}$. [h] Calculated from eqn. (4) with $K_3 = 2.3 \times 10^3$ and $K = 230$ dm^3 mol^{-1}.

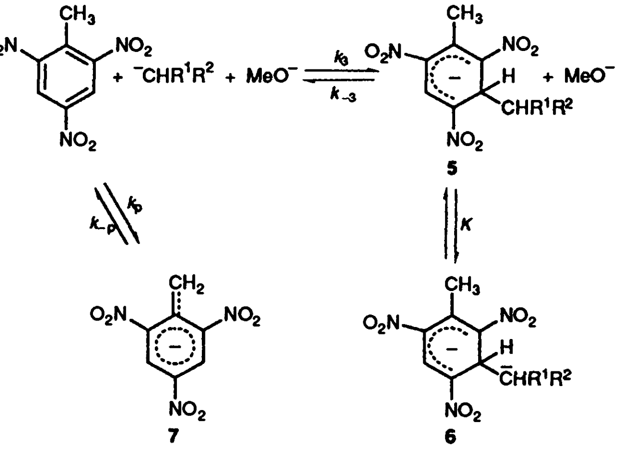
(3) of k_{obs} *vs.* $[^{-}CHR^1R^2]/(1 + K_{OMe}[MeO^-])$, obtained at constant methoxide concentration, were linear with slope, k_3, of 9.6×10^5 dm^3 mol^{-1} s^{-1}. From the variation with sodium methoxide concentration of the values of the intercepts it was possible to calculate values for $k_{-3} = 18$ s^{-1} and $K = 40$ dm^3 mol^{-1}. Data are in Table 8.*

For 4-cyano- and 2-cyanobenzyl cyanides the values of K_{CH} in methanol are low (Table 1) and the concentrations of carbanions may be accurately calculated as K_{CH}[NaOMe]-$[R^1R^2CH_2]$. Here there was no evidence for ionisation of the adducts **2** to give **3**. Slopes and intercepts of plots of $\{[R^1R^2CH][NaOMe]/(1 + K_{OMe}[NaOMe])\}$ were independent of methoxide concentration and allowed the calculation of values for the 4-cyano derivative of $k_3 = 8.8 \times 10^8$ dm^3 mol^{-1} s^1 and $k_{-3} = 4.1$ s^{-1}, and for the 2-cyano derivative $k_3 = 7.7 \times 10^8$ dm^3 mol^{-1} s^{-1} and $k_{-3} = 15$ s^{-1}. Values of K_3 calculated from absorbance data were in good agreement with those calculated by combination of rate coefficients. Data are in Tables 9 and 10.*

Reactions with 2,4,6-*Trinitrotoluene* (*TNT*).—In agreement with previous work in related systems[18,19] our results provide evidence for the processes shown in Scheme 3. Carbanion attack at the 3-position to give **5** was seen as a rapid process giving adducts with $\lambda_{max} = 450$–460 nm. Formation of trinitrobenzyl anion **7** was a much slower process resulting in a characteristic visible spectrum with $\lambda_{max} = 320$, 525 and 650 nm. The direct addition of methoxide at the 3-position of TNT is known[18] to have an equilibrium constant with the low value of 0.07 dm^3 mol^{-1} so that this process was unimportant at the base concentrations used. The rate expression for the equilibration of TNT and adducts **5** and **6** is eqn. (5). Rate and

$$k_{obs} = k_3[^{-}CHR^1R^2] + \frac{k_{-3}}{1 + K[MeO^-]} \qquad (5)$$

equilibrium data for reaction with the anion of 4-cyanobenzyl cyanide are in Table 4, and data for the remaining four carbanions are available in Tables 11–14.* Values of K_3 were found to be smaller than for reaction with TNB and the reverse rate coefficient, k_{-3}, dominated eqn. (5) so that measured rate coefficients showed little variation with carbanion concentration.



Scheme 3

Reactions with 1-*Chloro*-2,4,6-*trinitrobenzene* (*ClTNB*).—There is now considerable evidence[1–6] that nucleophilic attack at unsubstituted positions of picryl chloride is faster than at the chloro-substituted positions. Rate and absorbance data are interpreted in terms of Scheme 4. We also observed competitive attack by methoxide on the substrate. Reaction with methoxide at the 3-position was seen as a very rapid process, but since the equilibrium constant has the value[20] of 2.6 dm^3 mol^{-1} this had very low amplitude. Methoxide attack at the 1-position resulted in the slow formation of 2,4,6-trinitroanisole which, in the presence of methoxide, was present as the 1,1-dimethoxy adduct with $\lambda_{max} = 414$ nm and 490 nm (sh).

We are concerned here primarily with carbanion attack at the 3-position and data for reaction with the ethyl cyanoacetate anion are in Table 5, while data involving other carbanions are available in Tables 15–18.* In the case of the ethyl cyanoacetate anion, kinetic and equilibrium data for attack at the 3-position accord well with eqns. (5) and (4) respectively, with values of $k_3 = 9300$ dm^3 mol^{-1} s^{-1}, $k_{-3} = 30$ s^{-1} and $K = 600$ dm^3 mol^{-1}. Attack at the 1-position was seen as a slow colour-forming reaction at 480 nm, and rate coefficients accord well

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* Tables 8–18 are available as a supplementary publication, Sup. No. 56851 (14 pp.). For details of the supplementary publications scheme see 'Instructions for Authors' *J. Chem. Soc., Perkin Trans. 2*, 1991, issue 1.

Table 4 Kinetic and equilibrium data for reaction of TNT with the anion of 4-cyanobenzyl cyanide[a] in methanol at 25 °C

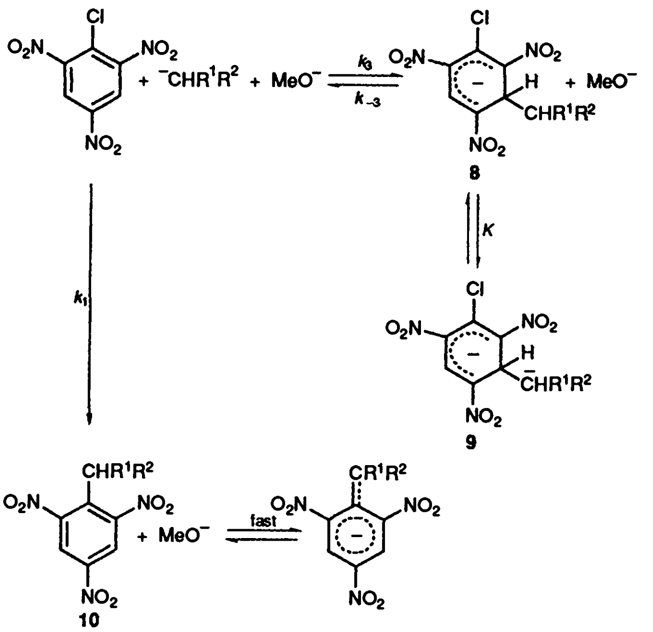
[NaOMe]/10^{-3} mol dm^{-3}	[CH$_2$R^{1}R^2]/10^{-3} mol dm^{-3}	$10^3 A_{450}$[b]	K_3K_{CH}[c]/dm^6 mol^{-2}	k_{obs}/s^{-1}[d]
5	6	10.9	174	20
5	8	13.1	157	21
5	12	18.9	151	21
5	16	24.2	146	22
10	4	14.6	175	16
10	8	28.0	169	18
10	12	48.8	198	20

[a] I = 0.01 mol dm^{-3} with NaCl. [b] Absorbance measured by stopped-flow spectrophotometry. Normalised to a pathlength of 1 cm and [TNT] 1 × 10^{-4} mol dm^{-3}. [c] Calculated as $A_{450}/(2.1 - A_{450})$[CH$_2$R^{1}R^2][NaOMe]. Using the known value of K_{CH}, we calculate $K_3 = 6.4 \times 10^5$ dm^3 mol^{-1}. [d] Corresponds to k_{-3}. Hence k_3 (equal to $k_{-3}K_3$) has the value 1.3 × 10^7 dm^3 mol^{-1} s^{-1}.

Table 5 Kinetic and equilibrium data for reaction of ClTNB with ethyl cyanoacetate ions[a] in methanol at 25 °C

[$^-$CHR^{1}R^2]/ 10^{-4} mol dm^{-3}	[NaOMe]/ 10^{-3} mol dm^{-3}	k_{obs}/s^{-1}	k_{calc}/s^{-1}[b]	A_{500}[c]	K_{obs}/ 10^2 dm^3 mol^{-1}[d]	K_{calc}/ 10^2 dm^3 mol^{-1}[e]	k_{slow}/s^{-1}[f]	k_{calc}/s^{-1}[g]
1.91	9.8	6.3	6.1	0.41	21	21	—	—
3.75	9.6	9.0	7.9	0.70	25	21	—	—
13.0	8.7	17.0	16.9	—	—	—	0.10	0.11
16.7	8.3	21.3	20.5	1.10	19	19	0.12	0.12
23.3	7.7	27.4	27.0	1.18	19	17	0.14	0.13
29.1	7.1	34.0	33.0	1.20	16	16	0.15	0.15
13.0	6.2	20.0	18.4	0.91	13	15	0.13	0.13
18.0	5.7	22.0	23.6	0.98	12	14	0.15	0.15
0.53	4.9	7.3	8.0	0.092	13	12	—	—
2.1	4.8	9.1	9.7	0.31	13	12	0.06	0.05
4.0	4.6	11.1	11.7	0.48	12	12	0.08	0.08
9.0	4.1	17.9	17.0	0.69	10	11	0.12	0.13
15.3	3.5	23.0	24.0	0.90	11	10	0.22	0.18
1.1	2.4	14.2	13.3	0.103	7	8	—	—
3.9	2.1	17.4	16.8	0.26	6	7	—	—
0.67	1.9	14.6	14.5	0.053	6	7	—	—
90	31	—	—	1.45	—	—	—	—

[a] I = 0.01 mol dm^{-3} with NaCl. [b] Calculated from eqn. (5) with k_3 = 9300 dm^3 mol^{-1} s^{-1}, k_{-3} = 30 s^{-1} and K = 600 dm^3 mol^{-1}. [c] Absorbance (500 nm) at completion of adduct-forming reaction after subtraction of equilibrium absorbance due to 3-methoxy adduct. Normalised to cell of 1 cm pathlength and [ClTNB] = 1 × 10^{-4} mol dm^{-3}. [d] Calculated as $A/(1.45 - A)$[$^-$CHR^{1}R^2]. [e] Calculated from eqn. (4) with K_3 = 310 dm^3 mol^{-1} and K = 600 dm^3 mol^{-1}. [f] Formation of **10** measured as a colour-forming reaction at 480 nm. [g] Calculated from eqn. (6) with k_1 = 290 dm^3 mol^{-1} s^{-1}, K_3 310 dm^3 mol^{-1} and K = 600 dm^3 mol^{-1}.



Scheme 4

with those expected from eqn. (6), with k_1 = 290 dm^3 mol^{-1} s^{-1}. Thus attack at the 1-position is *ca.* 30 times slower than at the 3-position.[1–6] Data are summarised in Table 6.

$$k_{\text{slow}} \frac{k_1[^-\text{CHR}^1\text{R}^2]}{1 + K_3[^-\text{CHR}^1\text{R}^2](1 + K[\text{MeO}^-])} \qquad (6)$$

Comparisons.—All data are summarised in Table 6. Values of K_3 for reaction of carbanions with TNT are between 300 and 800 times smaller than those for the corresponding reaction with TNB. This can be ascribed[18] partially to the polar effect of the methyl group, but mainly to the disruption of the planarity of the nitro-groups at the 2- and 6-positions of TNT which will reduce the electron-withdrawing capability of these groups. Values of K_3 for ClTNB are between three and seven times smaller than corresponding values for TNB. Here the polar effect of the chloro-substituent which will tend to increase values of K_3 is more than outweighed by the steric effect resulting in loss of conjugation of the nitro-grounds with the ring. Changes with substrate of values of the rate coefficient k_3 are much larger than corresponding changes of k_{-3} and this may indicate a product-like transition state resembling the σ-adduct, where bond-formation is well advanced.

Values of log K_3 give a measure of the carbon basicities of the carbanions while pK_a values of the carbon acids measure the corresponding proton basicities [eqn. (7)]. A plot of these

$$\text{H}^+ + \text{R}^1\text{R}^2\text{CH}^- \xrightleftharpoons{K_a^{-1}} \text{R}^1\text{R}^2\text{CH}_2 \qquad (7)$$

quantities, including some literature data is shown in Fig. 1. There is some scatter but the slope is close to unity. The

Table 6 Summary of kinetic and equilibrium data for reactions in methanol at 25 °C

Carbanion $R^1R^2CH^-$						
R^1	R^2	Reaction	k_3/dm^3 mol^{-1} s^{-1}	k_{-3}/s^{-1}	K_3/dm^3 mol^{-1}	K/dm^3 mol^{-1}
CO_2Me	CO_2Me	TNB	2.4×10^5	24	1.0×10^4	<10
		TNT	1.95×10^3	65	30	<10
		ClTNB	2.17×10^4	6.3	3.4×10^3	<10
CN	CO_2Et	TNB	9.3×10^4	40	2.3×10^3	230
		TNT	4.8×10^2	160	3	(100)
		ClTNB	9.3×10^3	30	310	600
CN	$4\text{-}NO_2C_6H_4$	TNB	9.6×10^5	18	5.3×10^4	40
		TNT	1.4×10^4	65	210	30
		ClTNB	1.75×10^5	17	1.0×10^4	40
CN	$4\text{-}CNC_6H_4$	TNB	8.8×10^8	4.1	2.1×10^8	—
		TNT	1.3×10^7	21	6.2×10^5	—
		ClTNB	1.3×10^8	3.8	3.4×10^7	—
CN	$2\text{-}CNC_6H_4$	TNB	7.7×10^8	15	5.1×10^7	—
		TNT	7.6×10^6	53	1.4×10^5	—
		ClTNB	8.6×10^7	12.1	7×10^6	—

Table 7 Intrinsic rate constants (log k_0) for reaction of carbanions with the trinitro-aromatic ring and for protonation

	log k_0	
$^-CHR^1R^2$	σ-Adduct formation	Proton transfer[a]
$R^1 = R^2 = CN$	4.4[b]	7.0
$R^1 = CN; R^2 = 4\text{-}CNC_6H_4$	3.0	—
$R^1 = CN; R^2 = 2\text{-}CNC_6H_4$	3.0	—
$R^1 = CN; R^2 = CO_2Et$	2.4	—
$R^1 = CN; R^2 = 4\text{-}NO_2C_6H_4$	2.3	3.95
$R^1 = R^2 = CO_2Me$	2.0	—
$R^1 = Me; R^2 = NO_2$	−0.65[b]	—
$R^1 = H; R^2 = NO_2$	−0.74[b]	0.73

[a] Data from ref. 12. [b] Data from ref. 7.

reactions differ in that on protonation the charge on the carbanion is neutralised while the σ-adduct formed in Scheme 1 still carries a negative charge. The unit slope of Fig. 1 may be taken to indicate that in the σ-adduct the negative charge resides in the trinitrobenzene moiety, and there is independent evidence[21] that the $C_6H_3(NO_2)_3^-$ entity, although negatively charged, may be electron withdrawing relative to hydrogen.

It is of interest to compare the reactivities of the carbanions in terms of their intrinsic rate constants for reaction at an unsubstituted position of the trinitro-substituted benzene ring. Values of log k_0 were obtained from the intersection of plots of log k_3 and log k_{-3} *vs.* log K_3. A typical plot is shown in Fig. 2 and results are collected in Table 7, where they are compared with data for proton transfer from the carbon acids in aqueous dimethyl sulphoxide. Important factors in determining intrinsic reactivities are thought to be the degrees of electronic and solvent reorganisation accompanying reaction.[9–12] When large changes in these factors occur and when they are not synchronised with bond formation (or cleavage) the intrinsic rate constants are low. Values in Table 7 indicate that intrinsic rate constants tend to decrease with increasing resonance stabilisation of the carbanions. Thus, decreases in intrinsic reactivity are found in changing the ring-substituent in benzyl cyanide from a cyano- to a nitro-group, and also on changing the group attached to the carbon centre from cyano to alkoxycarbonyl to nitro. There is evidence[9,22] that in nitrile anions the negative charge is not strongly delocalised so that they have more of the character of true carbanions requiring less reorganisation during reaction. Solvation will also be important, and in methanol the strong solvation of oxyanions will result in increasing stabilisation in the series **11** < **12** < **13**.

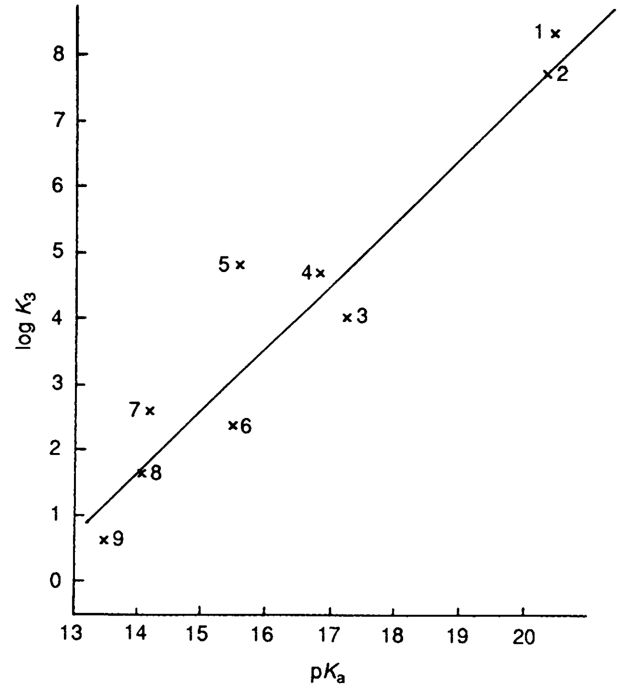
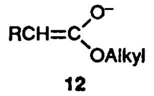


Fig. 1 Plot of log K_3 *vs.* pK_a for reaction of carbanions with TNB. Carbanions are derived from: 1, 4-cyanobenzyl cyanide; 2, 2-cyanobenzyl cyanide; 3, dimethyl malonate; 4, 4-nitrobenzyl cyanide; 5, nitromethane (ref. 7); 6, ethyl cyanoacetate; 7, nitroethane (ref. 7); 8, malononitrile (ref. 6); and 9, 2-nitropropane (ref. 7). Line is drawn with slope = 1.0.

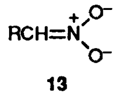
$RCH{=}CN^-$

11



$RCH{=}C(O^-)OAlkyl$

12



$RCH{=}\overset{+}{N}(O^-)O^-$

13

However, the factors of electronic and solvent reorganisation will only be important in decreasing reactivity if they are out of

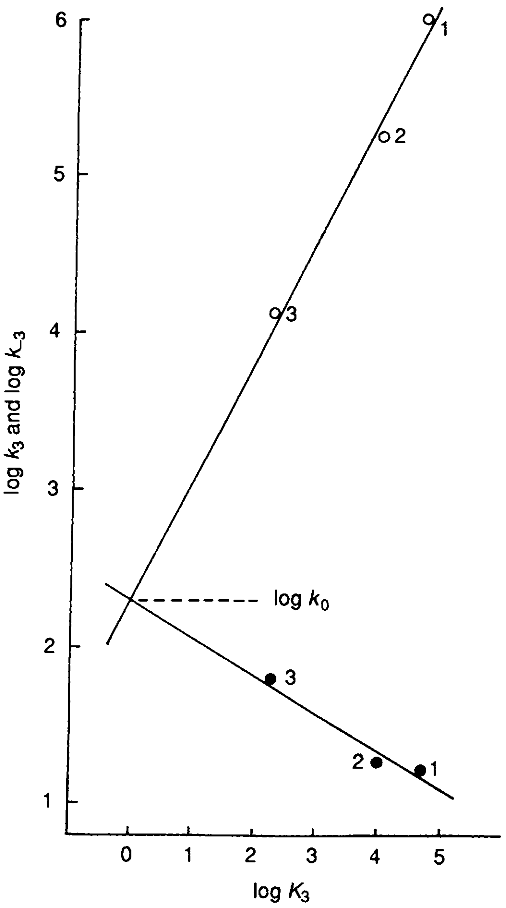


Fig. 2 Reaction of the 4-nitrobenzyl cyanide anion at unsubstituted ring positions of: 1, TNB; 2, ClTNB; and 3, TNT. Open symbols ○ refer to k_3 and filled symbols ● to k_{-3}.

step with bond formation. Our results provide evidence for a product-like transition state in the σ-adduct forming reactions so that electron reorganisation and desolvation of the anion will precede bond formation. In terms of the reverse reaction, *i.e.* dissociation of σ-adduct, there will be an early transition state in which bond breaking precedes the electron re-organisation and solvation in the carbanion. Comparison, in Table 7, with intrinsic rate constants for ionisation of the carbon acids shows a remarkably similar trend in values indicating that similar factors pertain to both reaction types.

Acknowledgements

We thank the SERC for a research studentship (J. A. S.).

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Paper 1/03146E
Received 25*th June* 1991
Accepted 17*th July* 1991