# Comparison of the Intrinsic Reactivities of Carbon and Oxygen Nucleophiles at the 1,3,5-Trinitro-substituted Aromatic Ring

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Kinetic and equilibrium data are reported for nucleophilic attack by nitroalkane anions at unsubstituted ring positions of 1,3,5-trinitrobenzene and of 2,4,6-trinitrotoluene. The results allow the calculation for this reaction type of values for intrinsic rate coefficients, k_0, of 0.18 for $CH_2NO_2^-$ and 0.22 for $MeCHNO_2^-$. The corresponding value for the malononitrile anion, $CH(CN)_2^-$, is 2.5×10^4, and for the methoxide ion the value is 10^3. The results are discussed in terms of the electronic-structural and solvational reorganisation occurring during reaction.

There is current interest in the comparison of nucleophilic reactivity in different reaction types. These comparisons are helpfully discussed in terms of the intrinsic reactivities[1-4] of nucleophiles in the Marcus sense. Intrinsic rate constants, k_0, may be obtained by extrapolation of log k versus log K plots to $K = 1$ ($\Delta G^0 = 0$), so that thermodynamic driving forces are removed. The reaction type for which most information is available is proton transfer (protonaton of nucleophiles).[1,5,6] Increasing data are becoming available for nucleophilic additions to alkenes[1,7-9] which complement data on alkene-forming elimination reactions,[10-12] and on nucleophilic additions to carbonyl compounds.[1,13] Common features thought to affect the intrinsic reactivities of nucleophiles are the structural and solvational reorganisation which occurs during the reactions.[1]

Here we report rate measurements for the reversible attack in methanol of nitromethane anion, $CH_2NO_2^-$, and of nitroethane anion, $MeCHNO_2^-$, on 1,3,5-trinitrobenzene (TNB) and 2,4,6-trinitrotoluene (TNT) as shown in equation (1). The results

$$X = H, Me$$
$$R^1, R^2 = H, Me$$
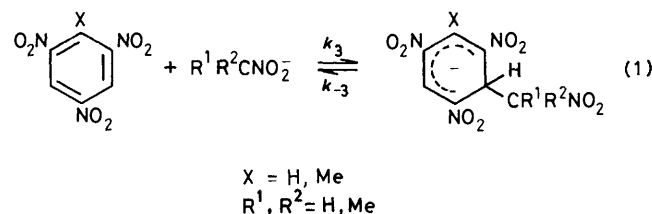
allow the calculation of the intrinsic rate coefficients for reaction of these nucleophiles at an unsubstituted position in the trinitroaromatic ring. We compare these values with those which we calculate from literature data for similar reactions of the malononitrile anion $CH(CN)_2^-$ and the methoxide ion.

Experimental

1,3,5-Trinitrobenzene was a recrystallised commercial specimen. 2,4,6-Trinitrotoluene, m.p. 82 °C (lit.,[14] 82 °C), was a gift from R.A.R.D.E., Waltham Abbey. Nitromethane, nitroethane, and malononitrile with purities > 99% were obtained from Aldrich Chem. Co. A commercial sample of 2-nitropropane was distilled under reduced pressure using a Fischer Spaltrohr column until analysis by gas chromatography indicated a purity of >99%. Solutions of sodium methoxide were prepared by dissolving clean sodium in AnalaR methanol under nitrogen. Cloudiness in the resulting solutions was removed on centrifugation. Concentrations were determined by titration with standardised acid. The AnalaR methanol used as solvent was de-gassed before use.

U.v.–visible spectra were measured with Pye–Unicam SP8-

Table 1. Equilibrium data for reaction of nitromethane[a] with sodium methoxide in methanol at 25 °C

10^2[NaOMe]/M	Absorbance, 237 nm	K_{CH}^b/l mol^{-1}
0	0.000	
0.94	0.087	22
1.89	0.146	21
4.73	0.265	23
9.50	0.345	22
18.9	0.414	23
49.5	0.473	

[a] Concentration is 5.68×10^{-5} M. [b] Calculated as $A/(0.51 - A)$ [NaOMe], where A represents absorbance.

Table 2. Equilibrium data for reaction of nitroethane with sodium methoxide in methanol at 25 °C

10^2[NaOMe]/M	Absorbance, 232 nm	K_{CH}^a/l mol^{-1}
0	0.00	
0.10	0.31	470
0.20	0.47	470
0.40	0.67	560
0.60	0.76	600
1.00	0.78	410
10.0	0.94	
20.0	0.96	

[a] Calculated as $A/(0.97 - A)$[NaOMe].

100 or Beckman Lambda 3 instruments. Kinetic measurements were made using a Hi-Tech SF 3L stopped-flow instrument. Rate coefficients were measured under first-order conditions and quoted values are the mean of at least five determinations and are precise to ± 5%.

Results and Discussion

Acidities of Nitroalkanes in Methanol.—Anions were generated from the nitroalkanes in methanol by reaction with sodium methoxide, equation (2). After equilibration, values of K_{CH}

$$R^1R^2CHNO_2 + MeO^- \underset{(1)}{\overset{K_{CH}}{\rightleftharpoons}} R^1R^2CNO_2^- \quad (2)$$
$$ (2)$$
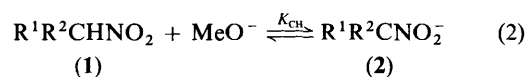
$$K_{CH} = K_a/K_m \quad (3)$$

were determined spectrophotometrically using the strong u.v. absorption of the nitroalkane anions. Data for nitromethane (1; R^1, R^2 = H) and nitroethane (1; R^1 = H, R^2 = Me) are in Tables 1 and 2 respectively. For 2-nitropropane (1; R^1,

$R^2 = Me$) virtually complete conversion into anion was achieved with a base concentration of 0.01M allowing a lower limit of 10^3 l mol^{-1} to be set for K_{CH}. The use of equation (3) together with the value[15] for methanol of pK_m 16.92 allows the calculation of the following pK_a values in methanol: (1; R^1, $R^2 = H$) 15.6, (1; $R^1 = H$, $R^2 = Me$) 14.2, (1; R^1, $R^2 = Me$) < 13.9. The corresponding values in water are 10.22, 8.60, and 7.74 respectively.[16] The increase in acidity in this series has been attributed[17,18] to the stabilising influence of methyl substituents attached to an sp^2-hybridised carbon atom.

Monitoring by u.v. of dilute solutions in methanol of the anions (2) showed them to be stable on the timescale required to examine their reactions with nitroaromatics.

Reaction of Nitroalkane Anions with TNB.—There is n.m.r. evidence for the formation in dimethyl sulphoxide of σ-adducts of structure (3) from TNB and nitroalkane anions.[19] Our results obtained in methanol containing small excesses of methoxide ions are interpreted by Scheme 1, which allows for the reaction of TNB with methoxide to produce (4). This latter reaction which is known to be very rapid on the stopped-flow timescale[20] and for which K_{OMe} has[21] the value 17 l mol^{-1} was minimised by working with [MeO$^-$] ≤ 0.01M. The major colour-forming reaction was in each case production of (3) with

(3)

(4)

Scheme 1.
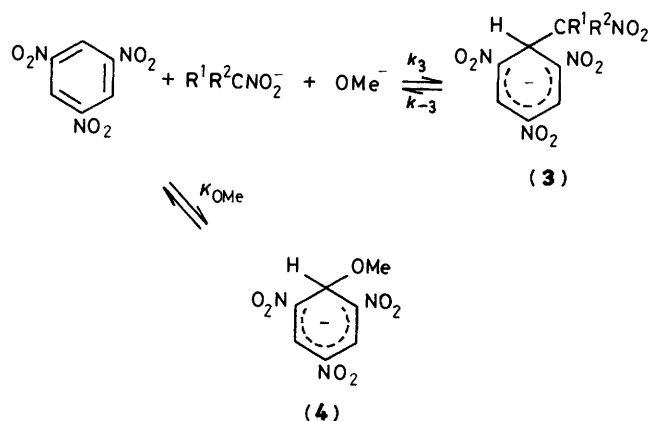
absorption maxima in methanol at 450 and 550 nm. Under first-order conditions the rate expression appropriate to this process is equation (4). In some cases a further very slow process was

$$k_{obs.} = \frac{k_3[R_1R_2CNO_2^-]}{1 + K_{OMe}[MeO^-]} + k_{-3} \qquad (4)$$

observed, but not measured, and may be attributed to di-adduct formation or to slow ionisation of the added nitroalkane group.[22]

Data for reaction with nitromethane anion are in Table 3. In this case identical kinetic results were obtained on mixing, in the stopped-flow spectrophotometer, either TNB solution with pre-equilibrated nitromethane and methoxide, or TNB plus nitromethane solution with methoxide. This indicates that for nitromethane the equilibrium of equation (2) is established rapidly compared with the reaction forming (3). The kinetic data yield values for k_3 800 l mol^{-1} s^{-1}, and k_{-3} 0.011 s^{-1} whose combination gives a value for K_3 (= k_3/k_{-3}) of 7 × 10^4 l mol^{-1} in good agreement with that obtained independently from absorbance data.

Data for reaction with nitroethane anion, in Table 4, lead to values for k_3 34 l mol^{-1} s^{-1}, k_{-3} 0.09 s^{-1}, and K_3 380 l mol^{-1}. Here measurements were made by mixing TNB solutions with pre-equilibrated nitroethane plus methoxide. Identical values for kinetic parameters were obtained with nitroethane in an excess of methoxide and with methoxide in an excess of nitroethane.

2-Nitropropane was carefully purified since the equilibrium constant for reaction of its anion with TNB has a low value so that it was necessary to avoid the presence of more reactive impurities. The rate coefficients in Table 5 are independent of the concentration of nitropropane anion showing that here equation (4) is dominated by the reverse rate coefficient and leading to a value for k_{-3} of 0.09 s^{-1}. The absorbance values give a value for K_3 of 4 l mol^{-1} leading to k_3 (= $K_3·k_{-3}$) 0.36 l mol^{-1} s^{-1}.

Reaction of Nitroalkane Anions with TNT.—There is good evidence that the major modes of 1:1 interaction of TNT with bases are σ-adduct formation at the 3-position and transfer of a side chain proton.[22–24] The possibilities for reaction with nitroalkane anions are shown in Scheme 2.

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

10^4[MeNO$_2$]$_{stoich}$/M	10^3[NaOMe]$_{stoich}^b$/M	10^5[CH$_2$NO$_2^-$]$_{eq.}^d$/M	$k_{obs.}$/s^{-1}	$k_{calc.}^e$	A(550 nm)^f	$10^4 K_3^g$/l mol^{-1}
10	0.1^c	0.20	0.013	0.013	—	—
1.0	4.0	0.81	0.017	0.017	0.0077	6.5
2.0	4.0	1.62	0.022	0.023	0.0112	6.2
3.0	4.0	2.43	0.028	0.029	0.0140	6.9
4.0	4.0	3.24	0.033	0.035	0.0150	6.4
6.0	4.0	4.86	0.045	0.046	0.0170	6.6
1.0	7.0	1.33	0.019	0.020	0.0107	6.9
2.0	7.0	2.66	0.029	0.030	0.0140	6.3
3.0	7.0	4.00	0.038	0.040	0.0160	6.4
4.0	7.0	5.32	0.047	0.048	0.0170	6.0
6.0	7.0	8.00	0.066	0.067	0.0190	7.2
1.0	10	1.8	0.022	0.023	0.0122	6.7
2.0	10	3.6	0.034	0.035	0.0149	5.6
3.0	10	5.4	0.048	0.048	0.0171	6.1
4.0	10	7.2	0.059	0.060	0.0186	7.0
6.0	10	10.8	0.088	0.085	0.0195	6.5
30	10	50	—	—	0.0223	—

[a] Concentration is 1 × 10^{-5} M. [b] Ionic strength 0.01M with NaCl. [c] p-Bromophenol buffer. [d] Equilibrium concentration, calculated with K_{CH} 22 l mol^{-1}. [e] Calculated from equation (4) with k_3 800 l mol^{-1} s^{-1}, k_{-3} 0.011 s^{-1}, and K_{OMe} 17 l mol^{-1}. [f] At completion of reaction forming (3). Measured by stopped-flow spectrophotometry in 2 mm pathlength cell. [g] Calculated as $A/(0.0223 - A)$[CH$_2$NO$_2^-$].

Table 4. Kinetic and equilibrium data for reaction of TNB^a with nitroethane anion in methanol at 25 °C

$10^4[EtNO_2]_{stoich}$/M	$10^3[NaOMe]_{stoich}$/M	$10^4[MeCHNO_2^-]_{eq}^b$/M	$k_{obs.}$/s^{-1}	$k_{calc.}^c$	$A(500$ nm$)^d$	k_3^e/l mol^{-1}
5.0	2.5	2.8	0.12	0.10	0.0041	340
5.0	3.8	3.2	0.11	0.10	0.0051	380
5.0	5.0	3.6	0.12	0.10	0.0052	360
5.0	7.5	3.9	0.10	0.10	0.0053	360
10	10	8.3	0.11	0.11	—	—
20	10	16.7	0.14	0.14	—	—
40	10	33.4	0.19	0.19	—	—
125	2.5	21	0.16	0.16	0.0198	320
150	5.0	42	0.23	0.23	0.0300	360
175	7.5	62	0.31	0.30	0.0343	350
200	10	84	0.37	0.38	0.0379	370

^{a} Concentration is 2×10^{-5} M. ^{b} Equilibrium concentration calculated with K_{CH} 500 l mol^{-1}. ^{c} Calculated from equation (4) with k_3 34 l mol^{-1} s^{-1}, k_{-3}, 0.09 s^{-1}, and K_{OMe} 17 l mol^{-1}. ^{d} Absorbance due to nitroethane adduct, measured in 2 mm cell. In some cases an additional initial absorbance due to formation of the methoxide adduct was measured. ^{e} Calculated as $A/[CH_3CHNO_2^-]$ $(0.050 - A_{slow} - A_{fast}$ due to methoxide adduct).

Table 5. Kinetic and equilibrium data for reaction of TNB^a with 2-nitropropane anion in methanol at 25 °C

		Absorbances at 450 nm^b		
$[CMe_2NO_2^-]_{eq.}$/M	$[NaOMe]_{eq.}$/M	$k_{obs.}$/s^{-1}	A_{fast}^c	A_{slow}^d	K_3^e/l mol^{-1}
---	---	---	---	---	---
0.005	0.005	0.11	0.0057	0.0017	3.7
0.010	0.005	0.09	0.0066	0.0036	4.0
0.020	0.005	0.08	0.0077	0.0070	4.1
0.030	0.005	0.08	0.0077	0.0100	4.1
0.040	0.005	0.09	0.0077	0.0140	4.4
0.020	0.010	0.09	0.012	0.0068	4.2
0.030	0.010	0.09	0.012	0.0101	4.4
0.050	0.010	0.10	0.013	0.0137	3.8

^{a} Concentration is 2×10^{-5} M. ^{b} Measured by stopped-flow spectrophotometry, 2 mm cell. ^{c} Absorbance at completion of rapid reaction, due to methoxide adduct. ^{d} Absorbance due to nitropropane-adduct. ^{e} Calculated as $A_{slow}/[CMe_2NO_2^-]$ $(0.10 - A_{slow} - A_{fast})$. This calculation uses an extinction coefficient of 2.5×10^4 l mol^{-1} cm^{-1} for adduct (3; R^1, R^2 = Me) from ref. 19, 22.

Table 6. Kinetic and equilibrium data for reaction of TNT^a with nitromethane anion in methanol at 25 °C

$[MeNO_2]_{stoich}$/M	$[NaOMe]_{stoich}$/M	$10^3[CH_2NO_2^-]_{eq.}^b$/M	$k_{obs.}$/s^{-1}	$k_{calc.}^c$	$A(450$ nm$)$	K_3^d/l mol^{-1}
0.05	0.0025	1.28	0.075	0.075	0.0037	72
0.05	0.0050	2.56	0.082	0.081	0.0074	78
0.05	0.0100	5.0	0.098	0.092	0.0117	72
0.065	0.015	8.4	0.11	0.106	0.0158	67
0.070	0.020	11	0.12	0.117	0.0187	67
0.10	0.0050	3.4	0.092	0.085	0.0080	65
0.10	0.0106	7.2	0.106	0.109	0.0150	72
0.12	0.0211	15	0.130	0.134	0.0210	61
0.13	0.0317	22	0.163	0.165	0.0250	60
0.14	0.042	30	0.200	0.200	0.0270	54
0.15	0.053	37	0.226	0.229	0.0300	58

^{a} Concentration is 1×10^{-5} M. ^{b} Equilibrium concentration calculated with K_{CH} 22 l mol^{-1}. ^{c} Calculated from equation (5) with k_3 4.3 l mol^{-1} s^{-1} and k_{-3} 0.07 s^{-1}. ^{d} Calculated as $A/(0.044 - A)[CH_2NO_2^-]$.

Table 7. Kinetic and equilibrium data for reaction of TNT^a with nitroethane anion in methanol at 25 °C

$[EtNO_2]_{stoich}$/M	$[NaOMe]_{stoich}$/M	$[MeCHNO_2^-]_{eq.}^b$/M	$k_{obs.}$/s^{-1}	$A(450$ nm$)^c$	K_3^d/l mol^{-1}
0.2	0.05	0.05	0.25	0.0028	0.66
0.2	0.10	0.10	0.26	0.0052	0.63
0.25	0.15	0.15	0.30	0.0076	0.63

^{a} Concentration is 2×10^{-5} M. ^{b} Equilibrium concentration, calculated with K_{CH} 500 l mol^{-1}. ^{c} We assume ε (450 nm) is 2.2×10^4 l mol^{-1} cm^{-1}, as found for the corresponding adduct with nitromethane. ^{d} Calculated as $A/(0.088 - A)$ [MeCHNO_2^-].

Our results show that the initial reactions with nitromethane and nitroethane anions produce species with $\lambda_{max.}$ 450 and 540 nm as expected for the adducts (5). There was no evidence in the initial stages for the production of (6) which has a distinctive visible spectrum[23] with $\lambda_{max.}$ at 370, 525, and 650 nm. Nor was

competing σ-adduct formation by reaction with methoxide ions a problem since the equilibrium constant in methanol for this process has the low value[23] of 0.07 l mol^{-1}.

Kinetic results for the initial colour-forming reaction are in Tables 6 and 7 and are interpreted by equation (5). The results

Table 8. Comparison of equilibrium and kinetic data for reactions in methanol at 25 °C

Anion	pK_a[a]	Reaction with TNB			Reaction with TNT			k_0
		K_3/l mol^{-1}	k_3/l mol^{-1} s^{-1}	k_{-3}/s^{-1}	K_3/l mol^{-1}	k_3/l mol^{-1} s^{-1}	k_{-3}/s^{-1}	
CHNO$_2^-$	15.6	7 × 10^4	800	0.011	62	4.3	0.07	0.18
MeCHNO$_2^-$	14.2	380	34	0.09	0.63	0.16	0.25	0.22
Me$_2$CNO$_2^-$	13.5[b]	4	0.36	0.09				
CH(CN)$_2^-$[c]	14.1	40	3 × 10^5	6.5 × 10^3	0.05	3.5 × 10^3	7 × 10^4	2.5 × 10^4
MeO$^-$	16.9	17[d]	7 050	305	0.07[e]	280	3 000	10^3

[a] Standard state is methanol. [b] Estimated from value in water. [c] Values for reaction with TNB from reference 25. Values for reaction with TNT were obtained by stopped-flow spectrophotometry using the methods of reference 25. [d] Values from reference 20. [e] Values from reference 23.
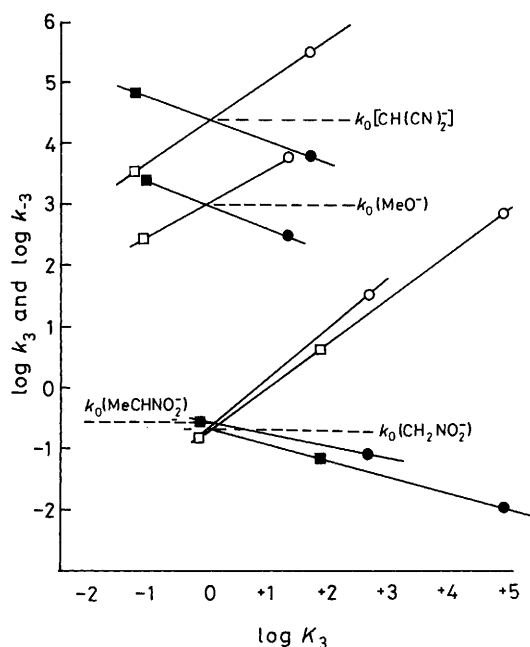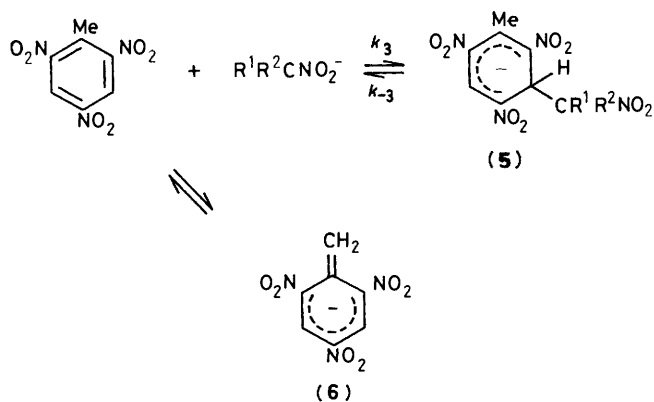

Figure 1. Reactions of nucleophiles at unsubstituted ring positions of TNB (circles) and of TNT (squares). Open symbols refer to k_3 and filled symbols to k_{-3}

Scheme 2.

$$k_{obs.} = k_3[CR_1R_2NO_2^-] + k_{-3} \qquad (5)$$

for nitromethane anion yield k_3 4.3 l mol^{-1} s^{-1}, k_{-3} 0.07 s^{-1}, and K_3 62 l mol^{-1}. The kinetics for reaction with the nitroethane
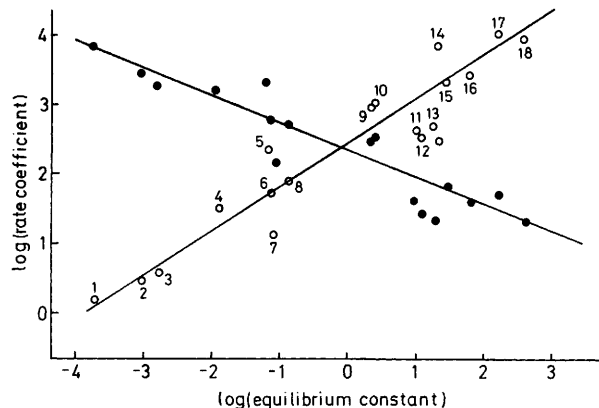

Figure 2. Logarithmic plots of rate coefficient *versus* equilibrium constant for attack of methoxide in methanol at unsubstituted ring positions of activated aromatics at 25 °C. Open circles are for forward reactions and filled circles for reverse reactions. 1. 4-Fluoro-1-methoxy-2,6-dinitrobenzene (ref. 30). 2. 4-Chloro-1-methoxy-2,6-dinitrobenzene (ref. 30). 3. 1-Methoxy-2,6-dinitro-4-trifluoromethylbenzene (ref. 30). 4. 1-Trifluoromethyl-3,5-dinitrobenzene (ref. 31). 5. 2,4,6-Trinitrotoluene (ref. 23). 6. 1-Methoxy-4-methylsulphonyl-2,6-dinitrobenzene (ref. 30). 7. 2,4-Dinitronaphthalene (ref. 32). 8. 4-Cyano-1-methoxy-2,6-dinitrobenzene (ref. 33). 9. 1-Chloro-2,4,6-trinitrobenzene (ref. 34). 10. 2,4,6-Trinitroanisole (ref. 35). 11. 1-Methoxy-3,5-dinitropyridine (ref. 36). 12. 2,4,5-Trinitronaphthalene (ref. 32). 13. N-(n-Butyl)-2,4,6-trinitroaniline (ref. 37). 14. 1,3,5-Trinitrobenzene (ref. 20). 15. 2,4,6-Trinitroaniline (ref. 37). 16. 3,5-Dinitropyridine (ref. 38). 17. 1-Methoxy-2,4-dinitro-6-trifluoromethylsulphonylbenzene (ref. 27). 18. 2,4,7-Trinitronaphthalene (ref. 32). Values in methanol have in some cases been extrapolated from literature data in methanol–dimethyl sulphoxide mixtures

anion are dominated by the reverse rate constant, giving k_{-3} 0.25 s^{-1}. Knowledge of the value of K_3 from equilibrium measurements yields k_3 (= $K_3 \cdot k_{-3}$) 0.16 s^{-1}.
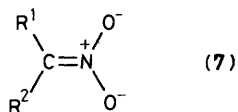
Slower reactions resulting in increased absorbance at 500 nm were observed, but not measured, and may be attributed to equilibration with (6) and/or di-adduct formation.[22–24]

Comparisons.—Rate and equilibrium data for the nitroalkane anions are collected in Table 8 where they are compared with data for the malononitrile anion and for the methoxide ion. Values of K_3 for reaction with TNB are *ca.* a thousand times higher than corresponding values for reaction with TNT reflecting the unfavourable electronic and steric effects of the methyl ring-substituent on σ-adduct formation.[23] These values of K_3, giving a measure of the carbon basicities[26] (thermodynamic affinity for carbon) of the nucleophiles, decrease in the order nitromethane > nitroethane > 2-nitropropane and this is the same order as observed for proton

basicities, as measured by pK_a values. However, the methoxide ion which has the highest proton basicity of the nucleophiles in Table 8 has relatively low carbon basicity. This is consistent with other observations[13,25,26] showing that carbon bases have considerably higher carbon basicities than oxygen bases of similar proton basicity.

The logarithmic plots of rate coefficient against equilibrium constant shown in Figure 1 allow the determination of intrinsic rate coefficients, k_0, for reaction at an unsubstituted ring position in the activated aromatic ring. They show the relatively high reactivity of the malononitrile anion and the low reactivity of the nitroalkane anions. Data for methoxide are limited in Figure 1 to reaction with TNB and TNT. However, an extended plot, Figure 2, of literature[22,27] data for reaction of methoxide in methanol at unsubstituted ring positions of ring-activated aromatics gave reasonably good straight lines with a value of k_0 of ca. 300.

These results are profitably discussed in terms of the electronic-structural reorganisation accompanying reaction and the solvent reorganisation during reaction.[1,5,7,8,28,29] In methanol the nitroalkane anions may be represented by structure (7) in which the negative charge is largely on the

$$
\begin{array}{c}
R^1 \quad\quad O^- \\
\diagdown \quad\quad \diagup \\
C = \overset{+}{N} \\
\diagup \quad\quad \diagdown \\
R^2 \quad\quad O^-
\end{array}
\quad\quad (7)
$$

oxygen atoms and is strongly solvated. Nucleophilic reaction via the carbon atom, as in equation (1), necessitates movement of charge resulting in considerable structural-electronic reorganisation with accompanying solvent reorganisation. Hence the low reactivity. On the other hand there is evidence[1,3] that in nitrile anions the negative charge is not strongly delocalised so that malononitrile anion will have more of the character of a true carbanion requiring less reorganisation during reaction and higher reactivity. The ratio of 10^5 observed here for the two types of anion reacting in methanol can be compared with ratios for reactions in water of ca. 10^8 for protonation and ca. 10^5 for addition at carbonyl carbon.[1] The methoxide ion will be strongly solvated in methanol and the intrinsic reactivity (Table 8) is considerably lower than that for the malononitrile anion reflecting the need for desolvation during bond formation at the aromatic ring. There is a marked difference here with reactivity of the methoxide ion towards protonation where desolvation is not necessary and k_0 approaches 10^{10}.

References

1 C. F. Bernasconi, Pure Appl. Chem., 1982, 54, 2335.
2 R. A. Marcus, J. Phys. Chem., 1968, 72, 891; A. O. Cohen and R. A. Marcus, ibid., p. 4249.
3 J. Hine, Adv. Phys. Org. Chem., 1977, 15, 1.
4 W. J. Albery, Annu. Rev. Phys. Chem., 1980, 31, 227.
5 C. F. Bernasconi, Tetrahedron, 1985, 41, 3219.
6 F. Terrier, J. Lelievre, A.-P. Chatrousse, and P. Farrell, J. Chem. Soc., Perkin Trans. 2, 1985, 1479.
7 C. F. Bernasconi and S. A. Hibdon, J. Am. Chem. Soc., 1983, 105, 4343.
8 C. F. Bernasconi, C. I. Murray, J. P. Fox, and D. J. Carré, J. Am. Chem. Soc., 1983, 105, 4349.
9 C. F. Bernasconi, A. Laibelman, and J. L. Zitomer, J. Am. Chem. Soc., 1985, 107, 6563, 6570.
10 C. J. M. Stirling, Acc. Chem. Res., 1979, 12, 198.
11 C. J. M. Stirling and M. Varma, J. Chem. Soc., Chem. Commun., 1981, 553.
12 D. B. Boyd, J. Org. Chem., 1985, 50, 885.
13 C. F. Bernasconi, K. A. Howard, and A. Kanavarioti, J. Am. Chem. Soc., 1984, 106, 6827.
14 A. McGookin, S. R. Swift, and E. Tittensor, J. Soc. Chem. Ind., London Trans., 1940, 59, 92.
15 C. H. Rochester and B. Rossall, J. Chem. Soc., Perkin Trans. 2, 1967, 743.
16 D. Turnbull and S. Maron, J. Am. Chem. Soc., 1943, 65, 212.
17 F. G. Bordwell, J. E. Bartmess, and J. A. Hautala, J. Org. Chem., 1978, 43, 3095; F. G. Bordwell and J. E. Bartmess, ibid., p. 3101; F. G. Bordwell, J. E. Bartmess, and J. A. Hautala, ibid., p. 3107.
18 O. A. Reutov, I. P. Beletskaya, and K. P. Butin, 'CH Acids,' Pergamon Press, Oxford, 1978.
19 C. A. Fyfe, Can. J. Chem., 1968, 46, 3047.
20 C. F. Bernasconi, J. Am. Chem. Soc., 1970, 92, 4682.
21 M. R. Crampton and H. A. Khan, J. Chem. Soc., Perkin Trans. 2, 1973, 710.
22 E. Buncel, M. R. Crampton, M. J. Strauss, and F. Terrier, 'Electron Deficient Aromatic- and Heteroaromatic-Base Interactions,' Elsevier, Amsterdam, 1984.
23 D. N. Brooke and M. R. Crampton, J. Chem. Res., 1980, (S) 340; (M) 4401.
24 C. A. Fyfe, C. D. Malkiewich, S. W. H. Damji, and A. R. Norris, J. Am. Chem. Soc., 1976, 98, 6983.
25 M. R. Crampton, T. P. Kee, and J. R. Wilcock, Can. J. Chem., 1986, 64, 1714.
26 J. Hine and R. D. Weimar, J. Am. Chem. Soc., 1965, 87, 3387.
27 F. Terrier, Chem. Rev., 1982, 82, 77.
28 W. P. Jencks, Chem. Rev., 1985, 85, 511.
29 M. J. S. Dewar and D. M. Storch, J. Chem. Soc., Chem. Commun., 1985, 94.
30 F. Terrier, F. Millot, and J. Morel, J. Org. Chem., 1976, 41, 3892.
31 F. Millot and F. Terrier, Bull. Soc. Chim. Fr., 1974, 1823.
32 W. L. Hinze, L. J. Liu, and J. H. Fendler, J. Chem. Soc., Perkin Trans. 2, 1975, 1751.
33 F. Terrier, C. A. Dearing, and R. Schaal, 'Reaction Transition States,' Gordon & Breach, London, 1973, 137.
34 L. H. Gan and A. R. Norris, Can. J. Chem., 1974, 52, 18.
35 C. F. Bernasconi, J. Am. Chem. Soc., 1971, 93, 6975.
36 F. Terrier, A. P. Chatrousse, and R. Schaal, J. Org. Chem., 1972, 37, 3010.
37 M. R. Crampton and B. Gibson, J. Chem. Soc., Perkin Trans. 2, 1980, 752.
38 F. Terrier and A. P. Chatrousse, Bull. Soc. Chim. Fr., 1972, 4549.