Transition State Imbalance in the Ionization of Nitroaromatic Hydrocarbons: 2,2′,4,4′-Tetranitrodiphenylmethane and 2,4,4′-Trinitrodiphenylmethane in Aqueous Dimethyl Sulphoxide Solutions[1]

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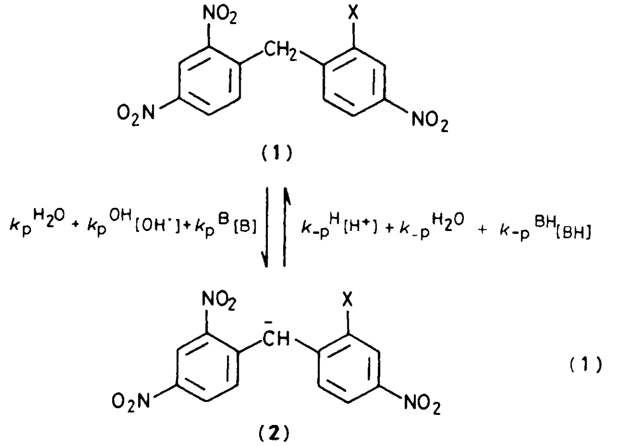
Rates of reversible proton abstraction from 2,2′,4,4′-tetranitrodiphenylmethane and 2,4,4′-trinitrodiphenylmethane by a variety of bases in 50% water–50% dimethyl sulphoxide have been measured at 25 °C. Brönsted α_{CH} and β_B values have been determined and show a charge imbalance in the transition states for these reactions, in accord with findings for similar carbon acids involving extensive charge delocalization on ionization. Intrinsic rate constants (in the Marcus sense), k_o, have been obtained for these systems, and are shown to vary considerably with choice of catalyst type. As expected, high intrinsic energy barriers for these ionizations are predicted, arising from the extensive molecular and solvent reorganization required to produce planar, delocalized carbanions. Data for the former compound have also been obtained in water, which allow a direct estimation of its $pK_a^{H_2O}$ value to be made; $pK_a^{H_2O} = 13.16$.

During the past decade, considerable information has been accumulated concerning the rates of deprotonation of carbon acids by various bases.[2] In particular, numerous studies of the deprotonation of simple nitroalkanes and of arylmethanes activated by nitro or cyano groups upon the exocyclic and/or *ortho,para* carbon atoms, employing many different solvents, have been reported.[3–16] The kinetic and thermodynamic results obtained have provided much valuable information on several important factors related to the ionization of carbon acids, *i.e.* substituent effects, solvent effects, proton tunnelling, isotopic substitution, *etc.*[2–16] However, there has recently been an increasing trend towards the discussion of structure-reactivity relationships in proton-transfer processes involving CH acids in terms of their 'intrinsic reactivities' in the Marcus sense.[2f,17–19] Such reactivities are determined from logarithmic plots of rate *versus* equilibrium data at the point at which $\Delta G^\circ = 0$. In this regard, the available data are still relatively few and more information is desirable to enable comparisons among different types of carbon acids to be made.[2f]

We have recently reported that 2,2′,4,4′-tetranitrodiphenylmethane (**1a**) exhibits appreciable kinetic and thermodynamic acidities in methanol and methanol–dimethyl sulphoxide (DMSO) mixtures.[20] We now present data for the ionization of this carbon acid and of the related 2,4,4′-trinitro analogue (**1b**) in water and/or water–DMSO mixtures. In addition, we report a complete kinetic study of the reactions shown in equation (1) in 50% H_2O–50% DMSO (v/v) at 25 °C, where $k_p^{H_2O}$, k_p^{OH}, and k_p^{B} are the rate constants for deprotonation of (**1a**) or (**1b**) by water, hydroxide ion, and any buffer base, respectively, while k_{-p}^{H}, $k_{-p}^{H_2O}$, and k_{-p}^{BH} refer to the rates of reprotonation of the corresponding carbanions (**2a**) or (**2b**) by hydronium ion, water, and any buffer acid, respectively. Our results allow the determination of the intrinsic reactivities of (**1a**) and (**1b**) in 50% H_2O–50% DMSO and provide further evidence for an imbalanced transition state in the ionization of carbon acids which yield highly delocalized carbanions.[2f,3d–f,4,12] The results presented are also compared with data for similar systems, notably those for the ionization of 4-nitro- and 2,4-dinitro-phenylacetonitriles (**3a** and **b**) to the corresponding carbanions (**4a** and **b**) in the same solvent mixture.[4b]



(1)

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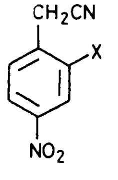

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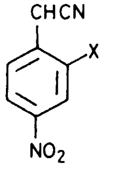

(4)

a; X = NO2
b; X = H

Results

The rates of reversible deprotonation of (**1a** and **b**) were first measured in aqueous or aqueous–DMSO tetramethylammonium hydroxide (NMe_4OH) solutions by monitoring the appearance of the absorption of the carbanions at or near $\lambda_{max.}$ 678 nm (ε 28 700 l mol^{-1} cm^{-1}) for (**2a**); 576 nm (ε 19 700 l mol^{-1} cm^{-1}) for (**2b**). All experiments were carried out under pseudo-first-order conditions with a large excess of OH^- (10^{-3}–0.2M) over the substrate concentration (*ca.* 3×10^{-5}M). Under these experimental conditions, the observed first-order rate constant,

Table 1. Rate and equilibrium constants for the reactions (**1a**) [(**1b**)] + $OH^- \rightleftharpoons$ (**2a**) [(**2b**)] + H_2O in various H_2O–DMSO mixtures at 25 °C[a]

	(**1a**) + $OH^- \rightleftharpoons$ (**2a**)				(**1b**) + $OH^- \rightleftharpoons$ (**2b**)			
% DMSO	k_p^{OH}/l mol^{-1} s^{-1}	$k_{-p}^{H_2O}$/s^{-1}	K_p^{OH}/l mol^{-1}	pK_a^{CH}	k_p^{OH}/l mol^{-1} s^{-1}	$k_{-p}^{H_2O}$/s^{-1}	K_p^{OH}/l mol^{-1}	pK_a^{CH}
0	1.056	0.152	6.95	13.16[d]				
10	1.047	0.066	15.80	12.98[d]				
20	2.77	0.015	184.4	12.13[d]	0.341	0.011	31	12.90[d]
30	4.26	0.007	608.5	11.88[d] 12.04[e]	0.465	0.010	46.5	13.06[d] 13.22[e]
40	8.65	1.8×10^{-3}	4 805	11.35[d]	0.64			
50	70,46.6[b]	5.46×10^{-4}[b]	8.53×10^{4}[b,c]	10.90[e]	2.15[b]	4.91×10^{-4}[b]	4 370[b,c]	12.19[e]
60	230				62.2			
70	1 245				502			
80	11 070				8 200			

[a] No constant ionic strength unless indicated. [b] $I = 0.5$M-NMe_4Cl. [c] K_p^{OH} spectrophotometrically determined (see text). [d] Calculated *via* equation (3) using pK values reported at 25 °C and zero ionic strength.[37] [e] Calculated *via* equation (3) using pK values determined in this work at 25 °C and I 0.5M-NMe_4Cl.

k_{obs}, for the approach to equilibrium (1) is simply given by equation (2). Plots of k_{obs} *versus* $[OH^-]$ were linear and allowed

$$k_{obs} = k_p^{OH}[OH^-] + k_{-p}^{H_2O} \qquad (2)$$

$$pK_a^{CH} = pK_s + pK_p^{OH} \qquad (3)$$

determination of the rate constants k_p^{OH} and $k_{-p}^{H_2O}$ from slopes and intercepts, respectively. In mixtures with $\geqslant 50\%$ DMSO, the intercepts were too small to allow reliable determination of $k_{-p}^{H_2O}$ and only k_p^{OH} values could be determined. The results obtained at 25 °C are summarized in Table 1, together with the values of the equilibrium constant $K_p^{OH} = k_p^{OH}/k_{-p}^{H_2O}$ for the reactions (**1a**) [(**1b**)] + $OH^- \rightleftharpoons$ (**2a**) [(**2b**)] + H_2O. Also given are the pK_a^{CH} values for the ionization of (**1a** and **b**) which were calculated through equation (3) where K_s represents the ionic product of the solvent.

Equation (1) was studied in a more detailed manner in 50% H_2O–50% DMSO using various buffers made up from carboxylic acids, phenols, and amines which were calibrated at 25 °C according to a previously reported method.[21] Dilute HCl and NMe_4OH solutions were also used. In all experiments, the ionic strength was kept constant at 0.5M with NMe_4Cl. From the observed optical density variations at $\lambda_{max.}$ of (**2a** and **b**), obtained at equilibrium as a function of pH, the half-formation of (**2a** and **b**) appears to occur at pH 10.90 and 12.19, respectively. These $pH_{\frac{1}{2}}$ values correspond to the pK_a^{CH} values in 50% H_2O–50% DMSO, for the reversible deprotonation of (**1a** and **b**) at the ionic strength indicated.

The rates of proton transfer were measured as follows. At pH < pK_a^{CH}, equilibrium (1) was approached from pH-jump experiments. These were carried out by mixing a 0.01M-NMe_4OH solution of (**2a** or **b**) with buffers or HCl solutions made up so as to attain the desired final pH. At pH > pK_a^{CH}, the equilibrium was approached in the opposite direction by mixing a neutral solution of (**1a** or **b**) with the appropriate buffer or NMe_4OH solution. In the case of (**1a**), where the equilibrium could be approached from both reactant and product sides in two buffers, *i.e.* phenol and 4-methoxyphenol, the rate data obtained in the two series of experiments for a given buffer were identical within experimental error.

In all cases, the pseudo-first-order rate constant for equilibrium approach is given by equation (4). The various rate constants of equation (4) were evaluated as follows. In HCl

$$k_{obs} = k_p^{H_2O} + k_p^{OH}[OH^-] + k_p^{B}[B] + k_{-p}^{H}[H^+] + k_{-p}^{BH}[BH] + k_{-p}^{H_2O} \qquad (4)$$

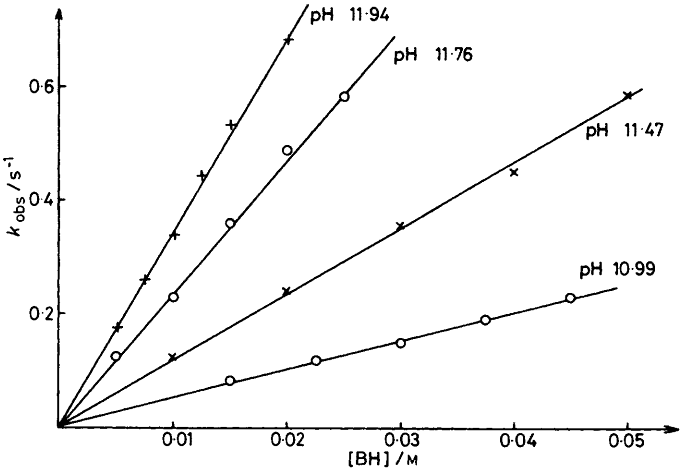

Figure 1. Effect of buffer concentration and pH on the observed rate (k_{obs}) for reaction (1) in 50% H_2O–50% DMSO (v/v) and in the case of (**1a**); BH = 4-methoxyphenol, *t* 25 °C, *I* 0.5M-NMe_4Cl

solutions, equation (4) simplifies to (5) so that k_{-p}^{H} was simply

$$k_{obs} = k_{-p}^{H}[H^+] \qquad (5)$$

obtained from a plot of k_{obs} *versus* $[H^+]$: k_{-p}^{H} 1.75×10^4 l mol^{-1} s^{-1} for (**1a**), k_{-p}^{H} 2.3×10^4 l mol^{-1} s^{-1} for (**1b**). This allows the calculation of $k_p^{H_2O} = K_a^{CH}\, k_{-p}^{H}$; $k_p^{H_2O} = 1.75 \times 10^{-7}$ and 1.15×10^{-8} s^{-1} for (**1a** and **b**), respectively. In hydroxide solutions, the rate constants were determined from the data by means of equation (2). Plots of k_{obs} *versus* $[OH^-]$ lead to $k_p^{OH} = 46.6$ l mol^{-1} s^{-1} and 2.15 l mol^{-1} s^{-1} for (**1a** and **b**), respectively. However, these plots have negligible intercepts and thus $k_{-p}^{H_2O}$ values were calculated from $k_{-p}^{H_2O} = k_p^{OH}\, K_s/K_a^{CH}$, yielding values of 3.31×10^{-4} for (**1a**) and 2.97×10^{-4} s^{-1} for (**1b**).

The k_{-p}^{BH} and k_p^{B} values were obtained from kinetic experiments conducted at three different buffer ratios, with k_{obs} being determined at 6—8 different buffer concentrations at any given pH. In buffers with pK_a < 5, equation (4) takes on the simplified form (6). Thus, the k_{-p}^{BH} rate constants were determined from the slopes of the excellent and parallel linear

$$k_{obs} = k_{-p}^{H}[H^+] + k_{-p}^{BH}[BH] \qquad (6)$$

Table 2. Rate constants for reactions (1) in 50% H_2O–50% DMSO at 25 °C[a]

			(1a) pK_a^{CH} 10.90		(1b) pK_a^{CH} 12.19	
	Buffer (acidic species)	pK_a^{BH}	k_{-p}^{BH}/l mol^{-1} s^{-1}	k_p^B/l mol^{-1} s^{-1}[c]	k_{-p}^{BH}/l mol^{-1} s^{-1}	k_p^B/l mol^{-1} s^{-1}[c]
1	H_3O^+	−1.44	1.75×10^4	7.92×10^{-9}[d]	2.3×10^4	5.36×10^{-10}[d]
2	Chloroacetic acid	3.71	2 575	1.66×10^{-4}	2 420	7.94×10^{-6}
3	Anilinium ion	3.73	3 580	2.40×10^{-4}	4 920	1.70×10^{-5}
4	Pyridinium ion	3.89	1 352	1.32×10^{-4}	1 905	9.55×10^{-6}
5	2-Chlorobenzoic acid	4.20	4 360	8.71×10^{-4}	4 130	4.17×10^{-5}
6	Formic acid	4.45	1 160	4.08×10^{-4}	1 220	2.19×10^{-5}
7	Methoxyacetic acid	4.65	884	5.01×10^{-4}	800	2.29×10^{-5}
8	γ-Picolinium ion	4.75	754	5.37×10^{-4}	1 089	3.98×10^{-5}
9	3,5-Lutidinium ion	5.01	728	9.33×10^{-4}	1 167	7.76×10^{-5}
10	Benzoic acid	5.13	1 098	1.86×10^{-3}	986	8.51×10^{-5}
11	2,6-Lutidinium ion	5.40	50.4	1.58×10^{-4}	136.2	2.19×10^{-5}
12	Acetic acid	5.78	227.5	1.74×10^{-3}	237	9.12×10^{-5}
13	2-Cyanophenol	7.97	180	0.21	202	0.012
14	Morpholinium ion	8.23	32.7	0.07	49	5.37×10^{-3}
15	4-Cyanophenol	8.45	49.1	0.174	68.1	0.012
16	2-Methoxyethylammonium ion	9.11	2.73	0.045	4.36	3.63×10^{-3}
17	2-Bromophenol	9.52	29.4	1.23	31.86	0.068
18	Butylammonium ion	9.99	1.34	0.166	1.79	0.011
19	4-Chlorophenol	10.18	11.13	2.13	10.54	0.102
20	Piperidinium ion	10.38	2.37	0.71	3.48	0.054
21	Phenol	11.21	1.62	6.05[e]	3.16	0.33
22	4-Methoxyphenol	11.47	1.20	10.87[e]	2.59	0.49
23	H_2O	17.34	1.98×10^{-5}[b]	46.6[f]	1.78×10^{-5}[b]	2.15[f]

[a] I = 0.5M-NMe_4Cl; experimental error in the rate constants k_{-p}^{BH}: ±6% or better; in pK_a^{BH} and pK_a^{CH}: ±0.05 pK unit; in the calculated rate constants k_p^B: ±15%. [b] $k_{-p}^{H_2O}/27.6$ with $k_{-p}^{H_2O}$ calculated from $k_p^{OH}K_s/K_a^{CH}$ with $pK_s = 15.83$ (see Experimental section). [c] k_p^B calculated from $k_p^B = k_{-p}^{BH}K_a^{CH}/K_a^{BH}$ unless indicated. [d] $k_p^{H_2O}/27.6$ with $k_p^{H_2O}$ calculated from $K_a^{CH}k_{-p}^{H}$. [e] Experimental k_p^B values. [f] $k_p^B = k_p^{OH}$.

plots of k_{obs} *versus* [BH] obtained at the different pH studied. For all other buffers with $pK_a^{BH} < pK_a^{CH}$, the experimental conditions chosen were such that equation (6) still applies, but the $k_{-p}^{BH}[BH]$ term is largely dominant, *i.e.* $k_{-p}^{H}[H^+] \sim 0$ in most cases. In the case of (**1a**), both the $k_{-p}^{BH}[BH]$ and $k_p^B[B]$ terms were found to contribute to k_{obs} for the phenol and 4-methoxyphenol buffers. This is illustrated in Figure 1 which shows that the slopes of the linear plots of k_{obs} *versus* [BH] are dependent on pH. Here, equation (4) reduces to (7) because the

$$k_{obs} = k_{-p}^{BH}[BH] + k_p^B[B] \qquad (7)$$

$k_p^{OH}[OH^-]$ and $k_{-p}^{H_2O}$ terms are always negligible (the plots of Figure 1 have negligible intercepts) and k_{-p}^{BH} and k_p^B were determined by a standard treatment from the data obtained at the different buffer ratios. All rate constants are summarized in Table 2, including the k_p^B values calculated from equation (8) for buffers with $pK_a^{BH} < pK_a^{CH}$. In view of the experimental errors associated with the measurements of k_{-p}^{BH}, pK_a^{CH}, and pK_a^{BH} (see Table 2), it is perhaps to be noted that the error in the calculated k_p^B rate constants may be ±15%.

$$k_p^B = k_{-p}^{BH}\frac{K_a^{CH}}{K_a^{BH}} \qquad (8)$$

Discussion

General Features.—In contrast with that of 2,4,6-trinitrotoluene (TNT), which is complicated by side reactions,[14] the ionization of 2,2′,4,4′-tetranitrodiphenylmethane (**1a**) is readily accessible in aqueous hydroxide solutions. This allows a direct measurement of a $pK_a^{H_2O}$ value of 13.16 for (**1a**) which agrees satisfactorily with the value of 13.80 previously estimated from an analysis of substituent effects on the acidity of various nitrodiphenylmethanes.[20] Assuming a similar acidity difference between (**1a**) and TNT in water as in methanol, where $pK_a^{1a} = 15.15$ and $pK_a^{TNT} = 15.60$, [14,20] one can derive a $pK_a^{H_2O}$ value of 13.61 for TNT in aqueous solution. This value is probably more reliable than that previously determined by the acidity function method in water–ethylenediamine mixtures ($pK_a^{H_2O}$ 14.45).[22]

Of interest with respect to the subsequent comparison of rates is that (**1a**) is appreciably more acidic than the trinitro analogue (**1b**); in 50% aqueous DMSO our measured pK_a value is 10.90 for (**1a**) as compared with a value of 12.19 for (**1b**). In this solvent mixture, the acidities of both (**1a** and **b**) are, however, more comparable to that of (**3b**) (pK_a 12.62 at 20 °C)[4b] than to that of (**3a**) (pK_a = 8.06 at 20 °C).[4b] This result is consistent with the general observation that the introduction of a nitro or cyano group onto the exocyclic carbon of a toluene or diarylmethane derivative has a much greater acidifying effect than does a similar introduction into the phenyl ring(s).[3,4,7,10,13]

The effect of added DMSO is to strongly increase the rate of deprotonation of (**1a** and **b**) by OH^-, k_p^{OH}, and to decrease the rate of reprotonation of the resulting carbanions (**2a** and **b**) by the solvent, $k_{-p}^{H_2O}$. The result is a marked enhancement in the thermodynamic stability of (**2a** and **b**), as evidenced by the *ca.* 2×10^4-fold increase in the equilibrium constant $K_p^{OH} = k_p^{OH}/k_{-p}^{H_2O}$ for the ionization of (**1a**) on transfer from water to 50% H_2O–50% DMSO. However, these changes in k_p^{OH}, $k_{-p}^{H_2O}$, and K_p^{OH} with increasing DMSO content of the aqueous solutions resemble those reported in other studies of similarly activated carbon acids and are explicable in the same terms as those previously discussed.[4,7,10,13,16,20]

Rate Constants for Proton Transfer.—Figures 2 and 3 show that the rate data for acid catalysis of the reprotonation of (**2a** and **b**) do not conform to a single linear Brönsted relation. In fact, several Brönsted lines may be drawn, revealing appreciable differences in the efficiency with which acid catalysts having similar pK_a values assist the proton transfers of reaction (1). A

Table 3. α_{CH} (β_{C^-}) Values for reactions (1) in 50% H_2O–50% DMSO at 25 °C[a]

	H^+	$ArNH_3^+$	Pyr, H^+	HCOOH	ArCOOH	2-NCArOH	Morph, H^+	Piper, H^+
α_{CH}	0.91	0.89	0.89	0.985	0.96	0.96	0.86	0.87
β_{C^-}	0.09	0.11	0.11	0.015	0.04	0.04	0.14	0.13

[a] Based on pK_a^{CH} = 10.90 for (**2a**) and 12.19 for (**2b**).

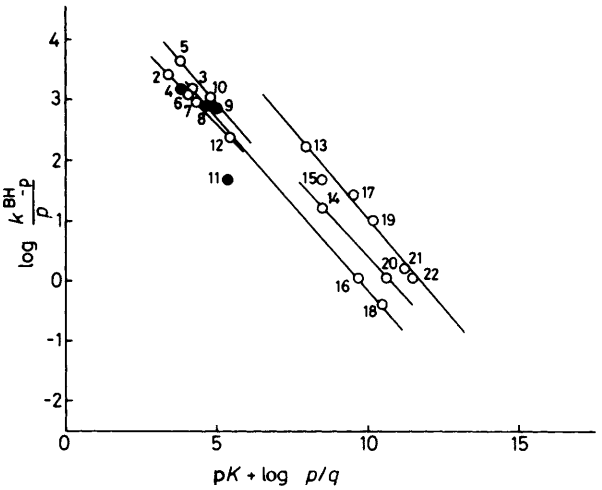

Figure 2. Statistically corrected Brönsted plots for the reprotonation of the carbanion (**2a**) by various acid catalysts in 50% H_2O–50% DMSO (v/v), *t* 25 °C, *I* 0.5M-NMe_4Cl. The numbering of the catalysts is indicated in Table 2

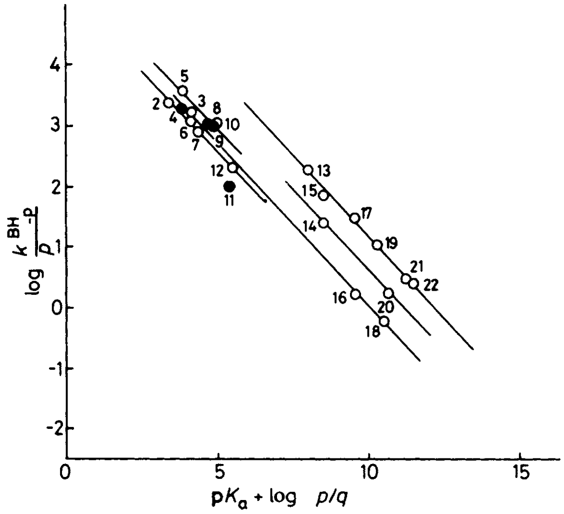

Figure 3. Statistically corrected Brönsted plots for the reprotonation of the carbanion (**2b**) by various acid catalysts in 50% H_2O–50% DMSO (v/v); *t* 25 °C, *I* 0.5M-NMe_4Cl. The numbering of the catalysts is indicated in Table 2

noteworthy feature, however, is that the Brönsted plots drawn through the points referring to each class of catalysts have essentially identical slopes. This is especially true in the case of (**2b**), as evidenced by the parallel lines in Figure 3 which provide an α_{BH} value of 0.54—0.55. A slightly wider range of α_{BH} values, ranging from 0.59 for the phenols to 0.55 for the secondary amine catalysts, is found in the case of (**2a**). In both systems, the points for water and H^+ (not shown) deviate negatively from all the lines, the deviations being in the range typical for such proton-transfer reactions.[23]

While phenols are more efficient oxygen-acid catalysts than carboxylic acids, secondary ammonium ions are better nitrogen-acid catalysts than primary ammonium ions. This latter result is a common phenomenon which is usually attributed to decreasing solvation in the order $RNH_3^+ > R_2NH_2^+$.[24—27] In the present case, it is, however, perhaps worth noting that there is no apparent difference in the behaviour of primary aliphatic amines, *i.e.* butylamine and 2-methoxyethylamine, and aromatic amines, *i.e.* aniline. On the other hand, the situation is less clearcut with tertiary amines which are usually found to be more efficient proton-transfer catalysts than primary and secondary amines.[24—27] The three unhindered pyridines used in this work, *i.e.* pyridine, γ-picoline, and 3,5-lutidine, have a relatively similar basicity making it difficult to draw a meaningful Brönsted plot.* In accord with previous findings, however, they do exhibit greater catalytic activity than primary amines. The only tertiary amine for which the observed k_{-p}^{BH} value lies well below those for other amines is 2,6-lutidine, a result undoubtedly reflecting the importance of steric hindrance in the proton-transfer reactions of equation (1) involving this molecule.[25,27]

Transition State Imbalance. Intrinsic Rate Constants.—Despite an appreciably lower basicity ($pK_a^{(2b)} - pK_a^{(2a)}$ = 1.3), the tetranitro carbanion (**2a**) is protonated by H^+, or any general acid BH, at essentially the same rate as its trinitro analogue (**2b**) in 50% H_2O–50% DMSO. This result cannot be a reflection of steric factors arising from the structural differences between (**2a**) and (**2b**). Should the presence of the second *o*-NO_2 group in (**2a**) give rise to a significant steric effect, this would reduce the protonation rates for this carbanion as compared with those for (**2b**). Furthermore, one would expect the catalytic advantage observed for the tertiary and secondary over the primary amines to be greater for the less hindered carbanion, *i.e.* (**2b**) than for the more hindered one, *i.e.* (**2a**). Inspection of Figures 2 and 3 shows that the reactivity difference between the various classes of amines is virtually identical for the two substrates, again indicating that steric effects play an insignificant role in governing the relative rates of protonation of (**2a**) and (**2b**).

The dependence of the protonation rates by a given acid upon the basicity of the carbanion is generally best appreciated by defining a Brönsted β_{C^-} value.[2f] Here, we can only obtain an order of magnitude for β_{C^-} from the ratio $\Delta\log k_{-p}^{BH}/\Delta pK_a^{CH}$. As can be seen in Table 3, the β_{C^-} values obtained for most catalysts are in the range 0—0.1. This suggests that C–H bond formation has made very little progress in the transition state. On the other hand, the α_{BH} values previously determined (Figures 2 and 3) are close to 0.5, suggesting that the proton transfer from BH to C^- is about half-complete at the transition state. These data are clearly not self-consistent, suggesting that

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* Assuming that the three points for these amines can define a reasonable Brönsted line, α_{BH} values of *ca.* 0.21 and *ca.* 0.25 are obtained which are much smaller than those found for other catalysts. Whether this situation reflects a particular behaviour of these tertiary amines or not is of course of interest but cannot be decided at this stage.

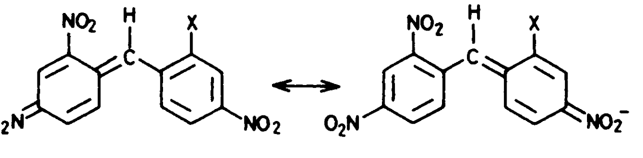
Table 4. Transition state imbalances in proton transfers

Reaction	Solvent	α_{BH}	β_{C^-}	$I = \beta_{C^-} - \alpha_{BH}$	Ref.
$ArCH_2NO_2 + R_2NH$	H_2O	0.35	−0.29	−0.64	3*b*
$ArCH_2CH(COMe)COOEt + RCOO^-$	H_2O	0.56	0.24	−0.32	12
(**1a**) [(**1b**)] + R_2NH	50% H_2O–50% DMSO	0.55	0.13	−0.42	This work
(**3a**) [(**3b**)] + R_2NH	50% H_2O–50% DMSO	0.38	0.59	0.21	4*b*

Table 5. α_{BH} (β_{B^-}) Values and intrinsic rate constants for reactions (1) in 50% H_2O–50% DMSO at 25 °C

	(**2a**)				(**2b**)			
	ArOH	RCOOH	RNH^+_3	$R_2NH_2^+$	ArOH	RCOOH	RNH_3^+	$R_2NH_2^+$
α_{BH}	0.59	0.52	0.55	0.55	0.54	0.52	0.54	0.54
β_{B^-}	0.41	0.48	0.45	0.45	0.46	0.48	0.46	0.46
log k_o	0.50	−0.60[a]	−0.65	−0.10[b]	0	−1.10[a]	−1.15	−0.55[b]

[a] Based on aliphatic carboxylic acids; based on 4-chlorobenzoic and benzoic acids: log k_o = −0.5 for (**2a**), log k_o = −0.8 for (**2b**). [b] Based on results for piperidine and morpholine.



(**5**) a; X = NO_2 (**5′**)
b; X = H

the transition states are imbalanced in the sense that C–H bond formation as 'seen' by the BH catalyst is ahead of C–H bond formation as 'felt' by the carbanion.

Transition state imbalances have been observed to be relatively common phenomena in proton transfers involving CH acids.[2f,3,4,12,28–30] The most commonly cited case is the ionization of nitroalkanes where Brönsted coefficients lie outside the normal range of 0—1.[3,31] However, appreciable imbalances have also been found in the deprotonation reactions of other carbon acids, including some arylmethane derivatives.[2f,4,12] Data for these reactions are summarized in Table 4 where the imbalance is measured by the parameter *I*, defined as $I = \beta_{C^-} - \alpha_{BH}$.

Various interpretations have been proposed to account for these imbalances[2f,3,4,28] but most of them assume that ionization proceeds *via* a transition state in which the negative charge remains relatively localized and unsolvated on the ionizable carbon atom, which possesses a significant degree of sp^3 character. The resulting carbanions have a *delocalized* negative charge, however. This, in turn, implies that the extensive structural–electronic–solvational reorganization[4b] accompanying the shift of charge to the sites where it ultimately resides lags behind the actual proton transfer to the attacking base. Conversely, this reorganization will occur ahead of the proton transfer on carbanion reprotonation.[2f]

There is no doubt that such a situation is to be expected in the systems studied in the present work. Evidence that the carbanions (**2a** and **b**) are essentially planar and have highly delocalized negative charges is provided by the values of their ^{13}C chemical shifts, *e.g.* $\delta(C_\alpha)$ = 35.0 for (**1a**) and 100.9 p.p.m. for (**2a**) in DMSO.[20] Such values clearly indicate that the bonding to the exocyclic carbons of (**2a** and **b**) is olefin-like[32] and hence that extensive molecular, *etc.* reorganization has necessarily occurred during carbanion formation. From a consideration of the well known observation that *p*-nitro groups are significantly more effective at resonance stabilization of charge than are *o*-nitro groups,[33] one can reasonably expect that the negative charges of (**2a** and **b**) lie preferably on the 4- and 4′-NO_2 groups, as visualized in structures (**5**) ⟷ (**5′**). The consequence is that the charge seen by the X substituent will appear enhanced in the transition state because it will be closer to X than it is in the carbanion, thus accounting for an imbalance with $I < 0$. A similar situation was found to prevail in the ionization of $ArCH_2NO_2$ and $ArCH_2CH(COMe)COOEt$ derivatives[3,4b,12] but the reverse was found to prevail in that of the acetonitrile derivatives (**3a** and **b**).[4b]

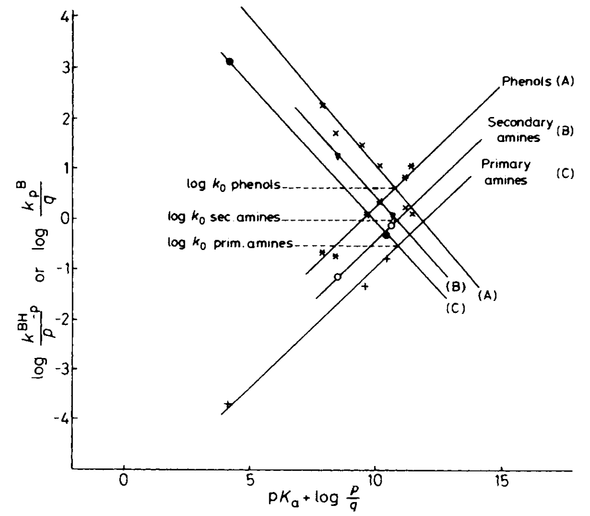


Figure 4. Variation of the intrinsic rate constant k_o of (**1a**) with the nature of the buffer

The extensive delocalization of the negative charge in (**2a** or **b**) is further emphasized from determinations of the intrinsic reactivities of the derivatives. Intrinsic reactivities may be expressed in terms of the intrinsic rate constant, k_o, of the Marcus theory,[17] defined as $k_o = k_{-p}^{BH}/p = k_p^B/q$ when $pK_a^{BH} + \log p/q - pK_a^{CH} = 0$, which can be obtained directly from the intersection of Brönsted plots such as those shown in Figure 4. It is important to note that different k_o values are obtained, depending upon the family of catalysts chosen, *i.e.* the particular Brönsted line used (Table 5). For the purpose of direct comparison of k_o values with those reported for (**3a** and **b**),[4b] *i.e.* log k_o = 2.70 and 3.70, respectively, at 20 °C also in 50% aqueous DMSO, the discussion below is restricted to our values based on the Brönsted plots for the secondary amines, morpholine and piperidine *i.e.* log k_o −0.10 and −0.55 for (**2a** and **b**), respectively, at 25 °C. Note that the difference in the temperature used in the two studies will not affect our conclusions.

As mentioned above, the k_o values for (**1a** and **b**) are 3—4 orders of magnitude lower than those for (**3a** and **b**). Since steric effects are not apparently of major importance in either system (except when crowded catalysts like 2,6-lutidine are used), this reduction is best understood in terms of the much greater structural–electronic–solvational reorganization required in the reactions of (**1a** and **b**) to give (**2a** and **b**) than in those of (**3a** and **b**) to give (**4a** and **b**). As has been discussed elsewhere,[4b] one important factor is undoubtedly enhanced solvational reorganization because of the extra nitro groups that need to be solvated in (**2a** and **b**) relative to (**4a** and **b**). Another significant factor, however, must be that charge delocalization in carbanions (**2a** and **b**) occurs over two phenyl rings, thus requiring more bond-length changes and adding greatly to the contribution of structural reorganization.* Note that the differences in k_o for (**1a** and **b**) as compared with (**3a** and **b**) correspond to differences $\Delta\Delta G_o^{\ddagger}$ in the intrinsic energy barriers of 15—20 kJ mol^{-1}, which places the $\Delta G_o^{\ddagger}$ values for (**1a** and **b**) among the highest so far measured;[2f] $\Delta G_o^{\ddagger}$ 73.5 for (**1a**), $\Delta G_o^{\ddagger}$ 76 kJ mol^{-1} for (**1b**).

It is also interesting to note that addition of an *o*-NO_2 group to (**1b**), to give (**1a**), slightly increases k_o whereas a similar addition to (**3b**), to give (**3a**), reduces k_o by a factor of 10. In this latter case, the observed reduction in k_o was expected since the additional *o*-NO_2 group considerably increases the proportion of the charge delocalized into the ring as opposed to into the nitrile group, and thus increases the energy of reorganization of the carbanion.[4b] In the case of (**1a** and **b**), the variation in k_o must have another origin. Here, the effect of the additional *o*-NO_2 group is seen to be disproportionately large on k_p^B relative to pK_a^{CH}. As pointed out by Bernasconi and Hibdon,[4b] this leads not only to an extremely low β_{C^-} value (exalted α_{CH} value) but also to an increase in k_o. A similar situation has been noted by these authors for the deprotonation by secondary amines of 1-phenylnitroethane and 1-(*p*-nitrophenyl)nitroethane where calculated log k_o values of −2.45 and −2, respectively, were derived from Bordwell's data in aqueous solution.[3b,4b]

Experimental

Materials.—2,4,4′-Trinitrodiphenylmethane and 2,2′,4,4′-tetranitrodiphenylmethane were prepared according to literature procedures and had m.p. 110 (ethanol)[34] and 182 °C (acetic acid),[35] respectively. Solvents were purified and solutions made up as described previously.[23,36] Buffers were purified commercial products.

Measurements.—Kinetic studies were made using a Durrum stopped-flow spectrophotometer, with a thermostatted cell compartment (±0.5 °C). Some slow kinetic measurements were made using a Beckman Acta III spectrophotometer.

pH Determinations in water–DMSO mixtures containing 0.5M-NMe_4Cl were carried out at 25 °C using the same procedure as that previously used at 20 °C.[21,36] The autoprotolysis constants (p*K*) of the mixtures were first determined and found to be equal to 14.83, 15.83, 18.02, and 20.17 in 30, 50, 70, and 80% DMSO, respectively. This allowed a subsequent calibration of the buffers for which the pK_a values listed in Table 2 refer to the solvent 50% H_2O–50% DMSO–0.5M-NMe_4Cl as the standard state. A Tacussel Isis 20000 electronic pH meter was used.

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