The Effect of Nitro Substitution upon Diphenylmethane Reactivity

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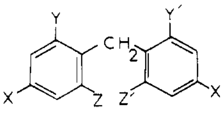
Rate and equilibrium data for the reversible deprotonation of 2,2′,4,4′,6,6′-hexanitro- and 2,2′,4,4′,6-pentanitrodiphenylmethanes (**1a** and **1b**) by hydroxide ion and various carboxylate and phenoxide ions have been measured in 50% aqueous DMSO at 25 °C. The equilibrium acidities of **1a** and **1b** (pK_a^{CH}) are much higher than anticipated from the acidifying effect measured for *o*-nitro substitution in comparing similar data for 2,2′,4,4′-tetranitro-, 2,4,4′-trinitro- and 4,4′-dinitrodiphenylmethanes (**1c**, **1d**, and **1e**, respectively). This result is attributed to steric factors. These are known to prevent a mutual coplanarity of the two phenyl rings in diphenylmethyl anions like those deriving from **1a** and **1b** (**C-1a** and **C-1b**) which possess more than two *o*-nitro groups. **1a** and **1b** would thus behave as α-(2,4,6-trinitrophenyl)- and α-(2,4-dinitrophenyl)-substituted 2,4,6-trinitrotoluenes rather than polynitrodiphenylmethanes, both compounds giving rise to a carbanion which must be viewed as having a sp²-hybridized exocyclic carbon conjugated with only one aromatic picryl ring. The intrinsic reactivities of **1a** and **1b**, as determined from the Brønsted plots for carboxylate and phenoxide ion reactions, are found to be low and of the same order as those measured for **1c** and **1d**, despite the fact that those latter compounds give essentially planar carbanions with a highly delocalized negative charge. This suggests that the lesser contribution of the charge dispersion to the stabilization of **C-1a** and **C-1b** is approximately balanced by an enhanced solvational demand of the nitro groups in the conjugated picryl ring.

Introduction

In connection with our continuing interest in the relationship between the intrinsic reactivities of carbon acids and the need for skeleton–electronic–solvational reorganization in forming strongly resonance stabilized carbanions,[1,2] we have become interested in a kinetic and thermodynamic study of the ionization of polynitrodiphenylmethanes.[3,4] In a previous investigation, we found that the reactions of 2,4,4′-trinitrodiphenylmethane (**1d**) and 2,2′,4,4′-tetranitrodiphenylmethane (**1c**) with a variety of carboxylate, phenoxide, and amine bases in 50% water–50% Me_2SO exhibit intrinsic energy barriers which are among the highest so far measured for ionization of carbon acids.[1] These results were consistent with planar structures of the resulting carbanions **C-1c** and **C-1d**, implying extensive delocalization of the negative charge over the two phenyl rings, as shown in resonance structures A–D. The ionization of **1c** and **1d** was also found to involve strongly imbalanced transition states, with a negative value of the imbalance I, as defined by $I = \beta_B - \alpha_{CH}$ where β_B and α_{CH} are, respectively, the Brønsted coefficients for variation of deprotonation rate with pK_as of base (carboxylate and phenoxide ions; $\beta_{RCOO^-} = 0.48$ for **1c** and **1d**; $\beta_{ArO^-} = 0.41$ for **1c** and 0.46 for **1d**) and pK_as of carbon acid ($\alpha_{CH} = 0.985$ and 0.96 for deprotonation of **1c** and **1d** by formate and 2-cyanophenoxide ions, respectively).[2] This suggested that the negative charge lies preferably on the 4- and/or 4′-nitro groups in **C-1c** and **C-1d** (resonance structures A and B), in agreement with the well-known observation that *p*-nitro groups are significantly more effective at resonance stabilization than *o*-nitro groups.[5]



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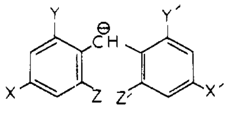
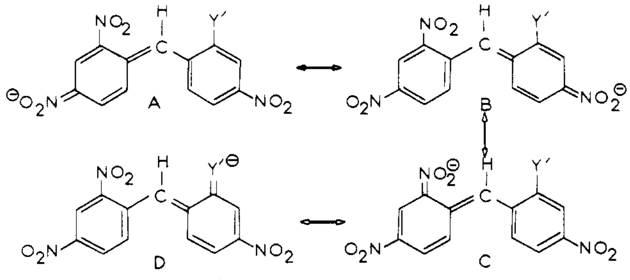


C-1

(a) $X = X' = Y = Y' = Z = Z' = NO_2$
(b) $X = X' = Y = Y' = Z = NO_2$, $Z' = H$
(c) $X = X' = Y = Y' = NO_2$, $Z = Z' = H$
(d) $X = X' = Y = NO_2$, $Y' = Z = Z' = H$
(e) $X = X' = NO_2$, $Y = Y' = Z = Z' = H$
(f) $X = NO_2$, $X' = Y = Y' = Z = Z' = H$
(g) $X = X' = Y = Y' = Z = Z' = H$



A,B,C : Y′=NO2,H D : Y′=NO2

Recently, a thorough structural study of the series of *o*- and *p*-nitro-substituted diphenylmethyl carbanions **C-1a–f** by NMR and UV–visible spectroscopy has been carried out.[6] This study has supported the view that the two aromatic rings of mono-*o*-nitro- and di-*o*-nitro-substituted diphenylmethyl carbanions are coplanar, or nearly so, thus confirming that the negative charge can be highly dispersed over the two phenyl rings in **C-1c** and **C-1d**. In contrast, this study showed clearly that no mutual coplanarity of the two phenyl rings can be achieved in the carbanions **C-1b** and **C-1a** of 2,2′,4,4′,6-penta- and 2,2′,4,4′,6,6′-hexanitrodiphenylmethanes (**1b** and **1a**) which have three and four *o*-nitro groups, respectively. Hence, the delocalization of the negative charge in **C-1b** and **C-1a** can occur in only one of the two activated phenyl rings at a given time (resonance structures E–J).[6] This behavior, together with the idea that the accumulation of *o*-nitro groups in the precursors might also result in steric hindrance to proton abstraction by bases, made it of interest to extend our

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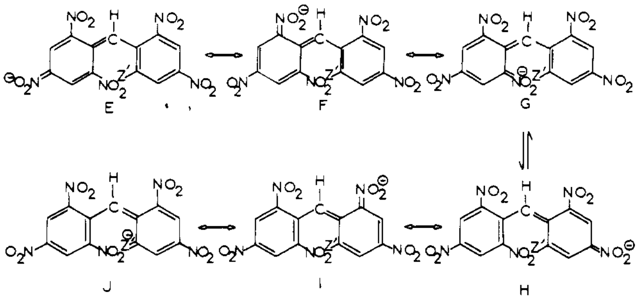
kinetic and thermodynamic investigations to the ionization of **1a** and **1b**. In this paper, we report a study of the reversible deprotonation of **1a** and **1b** by carboxylate, phenoxide, and hydroxide ions under similar conditions to those used for **1c** and **1d**. Comparison of the results for **1a** and **1b** with those for **1c** and **1d** shows both interesting similarities and differences, the latter being consistent with our spectroscopic work.[6]



Results

Rates and pK_a^{CH} values for the reversible deprotonation of **1a** and **1b** were measured in 50% H_2O–50% DMSO (v/v) by monitoring spectrophotometrically the appearance or disappearance of the absorption of the conjugated carbanions **C-1a** and **C-1b** at or near λ_{max}: 575 nm (ϵ 19 300 L mol^{-1} cm^{-1}) for **C-1a**; 550 nm (ϵ 26 700 L mol^{-1} cm^{-1}) for **C-1b**. Experiments were carried out using various buffer solutions made up from carboxylic acids and phenols. Use of amine buffers was precluded by the high ability of a 2,4,6-trinitro-substituted phenyl ring to undergo fast addition of the amine reagent at an unsubstituted ring carbon to form relatively stable σ-adducts.[5,7,8] Dilute NMe_4OH and HCl solutions were also used. In all cases, the ionic strength was kept constant at 0.5 M with NMe_4Cl. Under most conditions, the reactions studied can be represented by eq 1 where BH and B refer to buffer acid and base species, respectively.

$$1 \underset{k_{-p}^{H_2O} + k_{-p}^{H}[H^+] + k_{-p}^{BH}[BH]}{\overset{k_p^{H_2O} + k_p^{OH}[OH^-] + k_p^{B}[B]}{\rightleftharpoons}} \mathbf{C\text{-}1} \qquad (1)$$

The pK_a^{CH} values of **1a** and **1b** were first determined from the observed optical density variations at λ_{max} of **C-1a** and **C-1b** obtained at equilibrium as a function of pH. The half-formation of **C-1a** and **C-1b** occurred at pH 5.01 and 7.68, respectively. These $pH_{1/2}$ values correspond to the pK_a^{CH} values for the ionization of **1a** and **1b** at $I = 0.5$ M.

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 freshly prepared 0.01 M NMe_4OH solution of **C-1a** or **C-1b** with carboxylic acid 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 **1b** with the appropriate phenol buffer or NMe_4OH solution. In the case of a few carboxylic acid or phenol solutions, e.g. acetic acid for **1a** and 2-cyanophenol for **1b**, where the equilibrium could be approached from both reactant and product sides, the rate data obtained in the two series of experiments for a given buffer were identical within experimental error. In all instances, the rates were determined under pseudo-first-order conditions with a large excess of the buffer, base, and acid reagent over the substrate concentration ($\approx 3 \times 10^{-5}$ M). Under these experimental conditions, the observed rate constant, k_{obsd}, for the approach to equilibrium is given by eq 2.

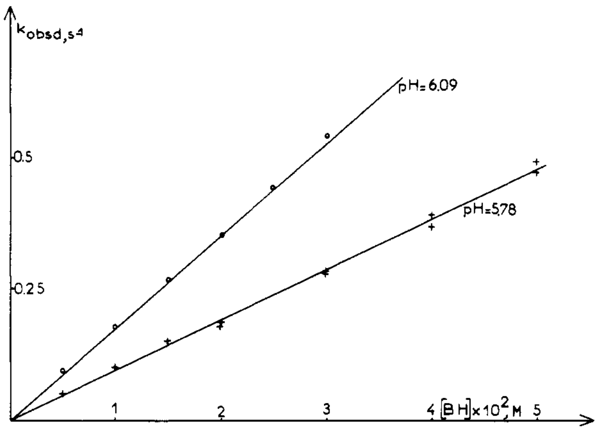


Figure 1. Effect of buffer concentration and pH on the observed rate constant (k_{obsd}) for the deprotonation of **1a** in 50% H_2O–50% DMSO (v/v): BH = CH_3COOH, $t = 25$ °C, $I = 0.5$ M NMe_4Cl.

$$k_{obsd} = k_p^{H_2O} + k_p^{OH}[OH^-] + k_p^{B}[B] + k_{-p}^{H_2O} + k_{-p}^{H}[H^+] + k_{-p}^{BH}[BH] \qquad (2)$$

The evaluation of the various rate constants of eq 2 was made as follows. In dilute NMe_4OH solutions, eq 2 simplifies to 3 so that k_p^{OH} was simply obtained from plots

$$k_{obsd} = k_p^{OH}[OH^-] + k_{-p}^{H_2O} \qquad (3)$$

of k_{obsd} vs $[OH^-]$ which were linear; $k_p^{OH} = 26\,000$ L mol^{-1} s^{-1} for **1a**; $k_p^{OH} = 675$ L mol^{-1} s^{-1} for **1b**. However, these plots showed negligible intercepts and thus we calculated the $k_{-p}^{H_2O}$ values from $k_{-p}^{H_2O} = k_p^{OH}K_s/K_a^{CH}$ where K_s is the autoprotolysis constant of the 50% H_2O–50% DMSO mixture containing 0.5 M NMe_4Cl ($pK_s = 15.83$ at 25 °C).[3] This afforded: $k_{-p}^{H_2O} = 3.93 \times 10^{-7}$ s^{-1} for **1a**; $k_{-p}^{H_2O} = 4.78 \times 10^{-6}$ s^{-1} for **1b**. In HCl solutions, eq 2 simplifies to 4. Hence, k_{-p}^{H} was obtained from a plot of k_{obsd} versus $[H^+]$: $k_{-p}^{H} = 138$ L mol^{-1} s^{-1} for **1a**; $k_{-p}^{H} = 318$ L mol^{-1} s^{-1} for **1b**. This allowed the calculation of $k_p^{H_2O}$ from $k_p^{H_2O} = K_a^{CH}k_{-p}^{H}$: $k_p^{H_2O} = 1.34 \times 10^{-3}$ s^{-1} for **1a**; $k_p^{H_2O} = 6.6 \times 10^{-6}$ s^{-1} for **1b**.

$$k_{obsd} = k_{-p}^{H}[H^+] + k_p^{H_2O} \qquad (4)$$

The k_{-p}^{BH} and k_p^{B} values were obtained from kinetic experiments conducted at three different buffer ratios with k_{obsd} being determined at 6–8 different buffer concentrations at any given pH. In carboxylic acid buffers which have pK_a values in the range 3.71–5.78, eq 2 reduces to 5.

$$k_{obsd} = k_{-p}^{H}[H^+] + k_{-p}^{BH}[BH] + k_p^{B}[B] + k_p^{H_2O} \qquad (5)$$

In the case of **1b** ($pK_a^{CH} = 7.68$), the $k_p^{B}[B]$ and $k_p^{H_2O}$ terms were essentially negligible and the k_{-p}^{BH} rate constants were readily determined from the slopes of the excellent and parallel linear plots of k_{obsd} vs [BH] obtained at different pH with a given buffer. In the case of **1a** ($pK_a^{CH} = 5.01$), $k_p^{H_2O}$ is negligible but both the $k_p^{B}[B]$ and $k_{-p}^{BH}[BH]$ terms contributed to k_{obsd}. This is illustrated in Figure 1 which shows that the slopes of the linear plots of k_{obsd} vs [BH] were pH dependent in agreement with rearrangement of eq 5 to 6. The k_{-p}^{BH} and k_p^{B} values were thus determined from a standard treatment of the data obtained at the different buffer ratios. At pH < 4, all buffer plots according to eq 5 or 6 showed appreciable

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Table I. Rate Constants for the Ionization of 2,4,4′-Trinitro-, 2,2′,4,4′-Tetranitro-, 2,2′,4,4′,6-Pentanitro-, and 2,2′,4,4′,6,6′-Hexanitrodiphenylmethanes in 50% H_2O–50% DMSO[a]

			1a ($pK_a^{CH} = 5.01$)		**1b** ($pK_a^{CH} = 7.68$)		**1c** ($pK_a^{CH} = 10.90$)[b]		**1d** ($pK_a^{CH} = 12.19$)[b]	
entry	buffer (acidic species BH)	pK_a^{BH}	k_p^B, $M^{-1}\,s^{-1}$	k_{-p}^{BH}, $M^{-1}\,s^{-1}$	k_p^B, $M^{-1}\,s^{-1}$	k_{-p}^{BH}, $M^{-1}\,s^{-1}$	k_p^B, $M^{-1}\,s^{-1}$	k_{-p}^{BH}, $M^{-1}\,s^{-1}$	k_p^B, $M^{-1}\,s^{-1}$	k_{-p}^{BH}, $M^{-1}\,s^{-1}$
1	H_3O^+	−1.44	4.87×10^{-5}	138	2.41×10^{-7}	318	7.92×10^{-9}	17500	5.36×10^{-10}	23000
2	chloroacetic acid	3.71	1.07	21.4	3.34×10^{-3}	31.2	1.66×10^{-4}	2575	7.94×10^{-6}	2420
3	2-chlorobenzoic acid	4.20	5.73	31.5	1.43×10^{-2}	43.2	8.71×10^{-4}	4360	4.17×10^{-5}	4130
4	formic acid	4.45	2.23	7.47	7.70×10^{-3}	13.1	4.08×10^{-4}	1160	2.19×10^{-5}	1220
5	methoxyacetic acid	4.65	2.74	6.18	1.01×10^{-2}	10.8	5.01×10^{-4}	884	2.20×10^{-5}	800
6	benzoic acid	5.13	16.1	10.1	3.57×10^{-2}	12.7	1.86×10^{-3}	1098	8.51×10^{-5}	986
7	acetic acid	5.78	8.23	1.37	3.45×10^{-2}	2.74	1.74×10^{-3}	227.5	9.12×10^{-5}	237
8	2,6-dichlorophenol	7.40	400	1.63						
9	2-cyanophenol	7.97	665	0.73	2.42	1.22	0.21	180	0.012	202
10	4-cyanophenol	8.45	510	0.19	1.94	0.38	0.17	49.1	0.012	68.1
11	2-bromophenol	9.52	1970	6.1×10^{-2}	8.36	0.12	1.23	29.4	0.068	31.86
12	4-chlorophenol	10.18	3840	2.6×10^{-2}	23.4	7.40×10^{-2}	213	11.13	0.102	10.54
13	phenol	11.21	6400	4.04×10^{-3}	39.6	1.17×10^{-2}	6.05	1.62	0.33	3.16
14	4-methoxyphenol	11.47	9880	3.43×10^{-3}	73.4	1.19×10^{-2}	10.87	1.20	0.49	2.59
15	H_2O	17.34	2.60×10^{4}[d]	1.43×10^{-8}[c]	675[d]	1.73×10^{-7}[c]	46.6[d]	1.98×10^{-5}[c]	2.15[d]	1.78×10^{-5}[c]

[a] $I = 0.5$ M NMe_4Cl, $t = 25$ °C; experimental error in the rate constants: ±6% or better; in pK_a^{BH} and pK_a^{CH}: ±0.05 pK unit; in the calculated rate constants: ±15%. [b] Data from ref 3. [c] $k_p^{H_2O}/27.6$ with $k_p^{H_2O}$ calculated from $K_a^{CH}k_{-p}^{H}$. [d] $k_p^B = k_p^{OH}$. [e] $k_{-p}^{H_2O}/27.6$ with $k_{-p}^{H_2O}$ calculated from $k_p^{OH}K_s/K_a^{CH}$ with $pK_s = 15.83$ (see ref 3).

Table II. Rate and Equilibrium Constants for the Reactions 1 + $OH^- \Leftrightarrow$ C-1 in 50% H_2O–50% DMSO at 25 °C

	diphenylmethane (no. of NO_2 groups)						
	1a[a] (6)	**1b**[a] (5)	**1c**[b] (4)	**1d**[b] (3)	**1e**[c] (2)	**1f**[d] (1)	**1g**[e] (0)
k_p^{OH}, 1 $mol^{-1}\,s^{-1}$	26000	675	46.6	2.15	0.09	≈0.003	–
$k_{-p}^{H_2O}$, s^{-1}	3.93×10^{-7}	4.78×10^{-6}	5.46×10^{-4}	4.91×10^{-4}	0.01	≈50	–
pK_a	5.01	7.68	10.90	12.19	14.94	≈20	≈32
ΔpK_a[f]		2.67	3.22	1.29	2.75	≈5	≈12

[a] This work. [b] Reference 3; $I = 0.5$ M NMe_4Cl. [c] Reference 9; no constant ionic strength. [d] Extrapolated values from data in ref 10. [e] Reference 12. [f] $\Delta pK_a = pK_a^{i+1} - pK_a^{i}$ where i = no. of NO_2 groups.

intercepts which had values consistent with the $k_{-p}^{H}[H^+]$ contributions expected from the k_{-p}^{H} values determined in HCl solutions.

$$k_{obsd} = k_{-p}^{H}[H^+] + \left(k_{-p}^{BH} + \frac{k_p^{B}K_a^{BH}}{[H^+]}\right)[BH] \quad (6)$$

In phenol buffers, which have pK_a^{BH} in the range 7.40–11.47, eq 2 reduces to 7. In the case of **1a**, the k_{-p}^{BH} and $k_{-p}^{H_2O}$ terms were negligible under all circumstances and the determination of k_p^{B} from eq 7 was straightforward.

$$k_{obsd} = k_p^{OH}[OH^-] + k_p^{B}[B] + k_{-p}^{BH}[BH] + k_{-p}^{H_2O} \quad (7)$$

A similar situation holds for **1b** in buffers of pH > 10. In less basic buffers, the k_{obsd} data for **1b** were analyzed in terms of a contribution of both the $k_p^{B}[B]$ and $k_{-p}^{BH}[BH]$ terms. The contribution of the $k_p^{OH}[OH^-]$ term led to intercepts which were too small to give reliable information up to pH 11 in both systems.

All rate constants for the ionization of **1a** and **1b** according to eq 1 are summarized in Table I, along with the corresponding parameters for **1c** and **1d** in 50% H_2O–50% DMSO. For buffers with $pK_a^{BH} \gg pK_a^{CH}$ (or $pK_a^{BH} \ll pK_a^{CH}$), the k_{-p}^{BH} (or k_p^{B}) values indicated were calculated by means of eq 8.

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

Discussion

Effect of Nitro Substitution on Equilibrium and Kinetic Acidities. Kinetic acidities as measured by the rates of proton abstraction by hydroxide ion (k_p^{OH}) and equilibrium acidities (pK_a^{CH}) determined in 50% H_2O–50% DMSO for the hexa- and pentanitrodiphenylmethanes (**1a** and **1b**) are compared in Table II with analogous data previously reported for the tetra-, tri- and dinitro-substituted analogues **1c**, **1d**, and **1e**, respectively. Also given in Table II are the rates of reprotonation of the corresponding carbanions **C-1a**–**C-1e** by the solvent ($k_{-p}^{H_2O}$) as well as estimated rate and equilibrium parameters for 4-nitrodiphenylmethane (**1f**) (pK_a^{CH}, k_p^{OH}, $k_{-p}^{H_2O}$) and diphenylmethane **1g** (pK_a^{CH}). For **1f**, the quoted pK_a, k_p^{OH}, and $k_{-p}^{H_2O}$ values have been extrapolated from measurements in 90 and 95% DMSO by assuming that the solvent effect on these parameters is approximately the same as that observed on the similar parameters for **1e**.[9,10] For **1g**, the quoted pK_a value is that determined in DMSO since it has been noted that the equilibrium acidities of nonactivated carbon acids with delocalized conjugate bases suffer only small variations on transfer from a protic to a dipolar aprotic solvent.[11,12]

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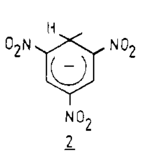
The most striking feature of Table II is not the expected finding that the equilibrium acidity of **1g** increases with increasing the number of nitro groups but the fact that the ΔpK values measuring the acid-strengthening effect of each additional nitro group are not consistent with common observations. From previous work, it is known that an *o*-nitro group is significantly less effective at resonance stabilization of negative charge than is a *p*-nitro group and that even in the absence of steric hindrance the acidifying effect of an additional substitution by a similar substituent is less than that of the previous one because of the so-called resonance saturation effect.[5,13] On these grounds, one would have anticipated decreases in the ΔpK values which become progressively smaller since going from **1g** to **1a** involves two successive *p*-nitro substitutions followed by four successive *o*-nitro substitutions. Contrasting with this idea, Table II shows normal decreases in the ΔpK values only as one proceeds from **1g** to **1c**. Going from **1c** to **1b** and from **1b** to **1a** results in much greater enhancements in the equilibrium acidity than expected.

Interestingly, the breakdown in the ΔpK pattern occurs on addition of a third *o*-nitro group in the diphenylmethane moiety, suggesting that its origin is the loss of the planar arrangement of the two phenyl rings in the penta- and hexanitro-substituted carbanions **C-1b** and **C-1a**. As demonstrated elsewhere, conjugation of the sp^2-hybridized exocyclic carbon of **C-1a** and **C-1b** can occur with only one aromatic ring, the latter being preferentially the picryl ring in the case of the dissymetric carbanion **C-1b**.[6] Accordingly, **1a** and **1b** should behave as α-(2,4,6-trinitrophenyl)- and α-(2,4-dinitrophenyl)-substituted 2,4,6-trinitrotoluenes rather than polynitrodiphenylmethanes.

Because σ-complex formation at the unsubstituted 3-position competes strongly with ionization of the methyl group in basic media, no direct measurement of pK_a^{CH} has been reported for 2,4,6-trinitrotoluene (TNT) in 50% H_2O–50% DMSO.[5,14-16] However, a fairly reliable value of 10.5 can be derived for this pK_a by combining data previously obtained for TNT in MeOH–DMSO mixtures and the related 2,4-dinitrotoluene (DNT) in both MeOH-DMSO and H_2O–DMSO mixtures and assuming a similar acidity difference in a given solvent mixture.[17] Based on this value, the increases in acidity caused by α-(2,4,6-trinitrophenyl) and α-(2,4-dinitrophenyl) substitution of the methyl group of TNT can be evaluated as being ca. 5.5 and 2.8 pK units, respectively. Such acidifying $-I$ effects are certainly large but they could perhaps be anticipated since even negatively charged 2,4,6-trinitrocyclohexadienate and 2,4-dinitrocyclohexadienate moieties of type **2** and **3** have been found to exert a significant electron-withdrawing effect, increasing the acidity of AH-type acids by about 2.5 and 0.70 pK units, respectively.[18] It is interesting, however, that the 2,4,6-trinitrophenyl and 2,4-dinitrophenyl substituents are considerably *less* acidifying when they do not lead to resonance stabilization of the carbanion than when they are involved in such resonance stabilization. Changes in pK_a values for ionization of the methyl group caused by introduction of *p*- and *o*-nitro groups to toluene are illustrative in this regard: toluene ($pK_a \approx 42$) < 4-nitrotoluene ($pK_a \approx 23$) < 2,4-dinitrotoluene ($pK_a \approx 15$) < 2,4,6-trinitrotoluene ($pK_a \approx 10.5$).[17a,19,20] Clearly, we have here a very effective resonance stabilization of the resulting carbanions by the corresponding nitrophenyl moieties while at the same time we see the influence of the saturation effect previously noted on going from **1g** to **1c**. To be noted is that **1a** and **1b** are among the strongest benzylic-type carbon acids known to date. In particular, both **1a** and **1b** are more acidic than phenylnitromethane or 2,4-dinitrophenylacetonitrile **4** and **5** which bear activating groups directly attached to the acidic site: $pK_a^4 = 7.93$ and $pK_a^5 = 8.06$ in 50% H_2O–50% DMSO.[21]



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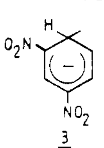

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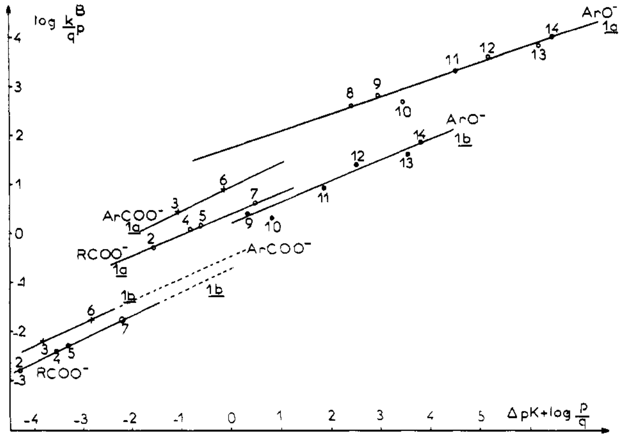
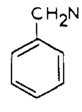
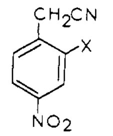


Figure 2. Statistically corrected Brønsted plots for the deprotonation of **1a** and **1b** by various carboxylate and phenoxide ions in 50% H_2O–50% DMSO (v/v); t = 25 °C, I = 0.5 M NMe_4Cl. The numbering of the catalysts is indicated in Table I.



4



5a X = NO_2
5b X = H

The increases in the equilibrium acidity brought about by the successive introduction of the *p*- and *o*-nitro groups in **1g** are in part the result of regular increases in the rate constant k_p^{OH}. Notwithstanding possible changes in transition-state structures for reactions occurring over a large pK range (vide infra), the regular increase in k_p^{OH} suggests that the accumulation of *o*-nitro groups in the two phenyl rings of **1g** causes no appreciable steric hindrance to proton abstraction by hydroxide ion. On the other hand, it is worth noting that it is the changes in $k_{-p}^{H_2O}$ which govern the changes in the ΔpK's, consistent with the idea

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(20) The quoted pK_a values refer to DMSO for toluene and 4-nitrotoluene but to 50:50 (v/v) H_2O–DMSO for 2,4-dinitrotoluene and 2,4,6-trinitrotoluene. However, a possible solvent effect is not expected to affect significantly our reasoning.

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Table III. β_B (α_{BH}) Values and Intrinsic Rate Constants for the Ionization of 1a–d in 50% H_2O–50% DMSO at 25 °C

	1a			1b			1c			1d		
base	β_B	α_{BH}	log k_0	β_B	α_{BH}	log k_0	β_B	α_{BH}	log k_0	β_B	α_{BH}	log k_0
ArO^-	0.35	0.65	1.75	0.42	0.58	0.23	0.41	0.59	0.50	0.46	0.54	0.00
$ArCOO^-$	0.48	0.52	0.96	0.43	0.57	−0.52	0.48	0.52	−0.50	0.48	0.52	−0.80
$RCOO^-$	0.43	0.57	0.41	0.48	0.52	−0.68	0.48	0.52	−0.60	0.48	0.52	−1.10

that rates of carbanion reprotonation are primarily dependent upon the extent of resonance stabilization. The strong decrease in $k_{-p}^{H_2O}$ observed on going from the tetranitro to the pentanitro system indicates that loss of concomitant charge delocalization over both phenyl rings in C-1b is overcompensated by the greater anion stabilizing effect of a conjugated 2,4,6-trinitrophenyl ring as compared with a 2,4-dinitrophenyl ring.

Brønsted Plots. Figure 2 shows Brønsted plots for the deprotonation of 1a and 1b by carboxylate and phenoxide ions in 50% H_2O–50% DMSO. As can be seen, each family of buffers defines its own Brønsted plots. For a given $\Delta pK + \log (p/q)$ value, the relative reactivity order is aryl oxide (ArO^-) ions > benzoate ($ArCOO^-$) ions > aliphatic carboxylate ($RCOO^-$) ions, consistent with results obtained for the ionization of 1c and 1d.[3] Interestingly, the difference in the catalytic efficiencies of ArO^- and $RCOO^-$ ions does not show major variations on going from the trinitro-substituted diphenylmethane 1d to the hexanitro-substituted diphenylmethane 1a. This suggests that steric effects do not really play a major role in governing the proton-transfer rates of eq 1.

Other noteworthy observations are the following: (1) The Brønsted β_B values for carboxylate and phenoxide ions tend to decrease on going from 1d ($\beta_B^{RCOO^-} = 0.48$; $\beta_B^{ArO^-} = 0.46$) to 1a ($\beta_B^{RCOO^-} = 0.43$; $\beta_B^{ArO^-} = 0.35$), i.e. on going from the less to the more thermodynamically favored reaction (Table III). This trend is consistent with the reactivity–selectivity principle.[22] (2) The points for OH^- (not shown) deviate negatively from all Brønsted lines drawn in Figure 2. For example, the deviations for the 1a and 1b systems are of 1.38 and 1.22 log units, respectively, from the plots defined by the aliphatic carboxylate ions. Such values are typical for the reduced reactivity of the strongly solvated hydroxide ion in the ionization of carbon acids.[22c–24] (3) A slight but real negative deviation of the point for *p*-cyanophenoxide ion is found in the aryl oxide Brønsted plots of Figure 2. This deviation is reminiscent of that observed in the study of other carbon acids, e.g. 1c and 1d, or in reactions such as nucleophilic additions to carbonyl centers.[25] We will come back to this point later in our discussion.

Intrinsic Reactivities. Intrinsic rate constants (in the Marcus sense) for 1a and 1b, obtained from Brønsted plots as $k_o = k_p^B/q$ when $\Delta pK + \log (p/q) = 0$ are given in Table III, together with those for 1c and 1d.[3] The intrinsic reactivities of 1a–d are all remarkably low compared with those reported for a number of carbon acids in the same solvent mixture.[19,22c,24,27] Using the log k_o values for ionization by $RCOO^-$ ions as the reference, it appears in particular that the intrinsic reactivities of 1a–d are 2–4 orders of magnitude lower than those of the nitrophenylacetonitriles 5a and 5b: log $k_o^{5a} = 2.70$; log $k_o^{5b} = 3.70$.[21b,28]

Since steric effects apparently do not govern the ionization of 1a–1d to a notable extent (vide supra), there is little doubt that the low intrinsic reactivities of 1a–d must largely reflect the need for a high structural–electronic–solvational reorganization in forming the sp^2-hybridized carbanions C-1a–C-1d. In fact, the results can be readily understood in terms of the Principle of Nonperfect Synchronization (PNS) formulated by Bernasconi.[2] According to this principle, the intrinsic rate constant, of a reaction k_0 decreases if a product stabilizing factor, e.g. resonance and solvation, develops late but increases if this factor develops early along the reaction coordinate.[2] By the same reasoning, a reactant stabilizing factor will decrease k_0 if it is lost early but will increase k_o if it is lost late.[2] For the deprotonation of a carbon acid, it is well recognized that essential factors governing the stabilization of a resulting sp^2-hybridized carbanion are resonance and solvation which both lag behind the proton transfer.[1e,2,29–36] Low intrinsic reactivities therefore imply extensive structural and solvational reorganization for strongly resonance stabilized carbanions.[2]

In the case of C-1c and C-1d which have two coplanar phenyl rings or almost so, the resonance structures A–D show that extensive delocalization of the negative charge can occur. This implies considerable bond-length changes as well as an appreciable solvational demand from the nitro groups where a large fraction of the negative charge must ultimately reside. In contrast, charge delocalization may be formally viewed as if it is restricted to one picryl ring in both the penta- and hexanitro carbanions C-1b and C-1a (resonance structures E–G, vide supra).[37] This implies a reduction in the contribution of the overall bond-length changes to the reorganization but the lesser charge dispersion combined with the especially high capacity of a trinitro-substituted phenyl ring to delocalize charge must increase the electron density on each of the nitro groups in the conjugated ring relative to that in C-1c and C-1d. Hence, it seems reasonable to expect an enhanced solvational demand for C-1a and C-1b as compared with C-1c and C-1d. This effect may compensate for the loss in charge dispersion, accounting for the observation that the intrinsic reactivities of 1a and 1b remain more comparable to those of 1c and 1d than to those of 5a and 5b. Because

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[28] The $k_o^{RCOO^-}$ value for 4b is considered to be the same as that found with piperidine and morpholine by analogy with 4a.

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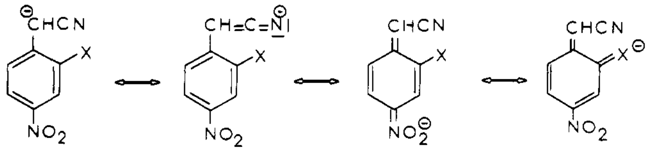
[37] Assuming rapid electronic rearrangement between the two noncoplanar aromatic rings, one could also view the symmetric carbanion C-1a as being an anion which possesses two independent picryl rings, each delocalizing half of the negative charge. Thus, bond-length changes would be greater than anticipated in the situation where the delocalization is restricted to one picryl ring but the effect would be partially offset by reduced solvation.

of the presence of the activating cyano group upon the exocyclic carbon, these latter compounds give carbanions **C-5a** and **C-5b**, respectively, with a negative charge which is only partially delocalized in the nitrosubstituted phenyl ring.[21b] This leads to reduced reorganization upon ionization of **5a** and **5b**, which manifests itself in higher intrinsic reactivities than those for **1a–d**.



C-5a X=NO$_2$
C-5b X=H

While they are all typical for formation of strongly resonance stabilized carbanions, the log k_o values show interesting variations within the **1a–d** series. First, we note that k_o for **1d** is lower than for **1c** by about 0.5 log unit. One can think of two possible reasons for this difference, the first being that the mutual coplanarity of the two phenyl rings is not so complete in **C-1c** as in **C-1d**, thereby resulting in somewhat reduced conjugation in the former carbanion.[6] A more satisfactory way to explain the enhanced k_o value for **1c** relates, however, to the demonstration by Bernasconi that an increase in k_o for a carbon acid has to be expected when a substituent effect causes a disproportionately large variation on the rate (k_p^B) compared to the equilibrium constant.[2,21b] As can be seen in Table II, the effect of adding a second *o*-nitro group to **1d** to form **1c** causes similar increases in both the rate constant for proton abstraction (k_p^B) and the equilibrium acidity (pK_a^{CH}). This implies that this nitro group stabilizes the developing negative charge (which in the transition state is mainly localized on carbon) to about the same extent as it contributes to the stabilization of the carbanion. This results in a large α_{CH} value (vide infra) and an increased k_0 value which reflects the fact that a product stabilizing factor has developed early in the transition state.[2,21b,24]

Going from **1c** to **1b** leaves k_o essentially unaffected apart from a small decrease with the phenoxide bases. This suggests that there is an approximate balance between the decrease in charge dispersion due to loss of coplanarity in **C-1b** and the enhanced solvational demand of the nitro groups in the conjugated picryl ring of this carbanion (resonance structures E ↔ F ↔ G). On the other hand, there is a ca. 12-fold increase in k_o on going from **1b** to **1a**, these give structurally related carbanions, and this clearly calls for a nonsteric explanation. We note that the acidifying effect resulting from the addition of the fourth *o*-nitro group derives largely from an increase in the k_p^B values (Table I)—a situation which is reminiscent of that encountered in comparing **1d** to **1c**. This shows that there is a factor in **1a** which is nearly as effective in stabilizing the developing negative charge at the carbon atom in the transition state as in stabilizing the carbanion **C-1a** itself. Viewing **1a** and **1b** as α-(2,4,6-trinitrophenyl)- and α-(2,4-dinitrophenyl)-2,4,6-trinitrotoluenes, we believe that this factor is probably the greater $-I$ effect exerted by a picryl ring as compared with a 2,4-dinitrophenyl ring. While this greater electronic effect has no reason to operate very differently in the transition state and the carbanion, it enhances k_o as found in comparing the pair **1c–1d**.[2]

A common manifestation of imbalance in the transition states for ionization of carbon acids giving rise to strongly stabilized carbanions is that the Brønsted α_{CH} value obtained by varying the pK_a^{CH} of the carbon acid is different from the β_B value obtained by varying pK_a^{BH}.[2,3] Here, we can only obtain an order of magnitude for α_{CH} pertaining to each of the pairs **1a-1b** and **1c-1d** from the ratios $\Delta \log k_p^B/\Delta pK_a^{CH}$. For acetic acid as the reference catalyst, we thus calculate $\alpha_{CH} = 0.89$ and 0.99 for the pair **1a–1b** and the pair **1c–1d**, respectively. Measuring the extent of the imbalance as $I = \beta_B - \alpha_{CH}$,[2,3,21b] then negative values equal to −0.43[38] and −0.51, respectively, can be calculated. Such values are indeed typical for systems in which there is a considerable lag in structural–electronic–solvational reorganization behind proton transfer in the transition state.[2]

As a result of the observed differences in the Brønsted plots of Figure 2, greater intrinsic reactivities are obtained for ionization of **1a–d** by phenoxide than carboxylate ions. This trend can be largely understood in terms of the desolvation of these ions which must develop early along the reaction coordinate of reactions (1).[2,22c,24] As pointed out previously, this requirement which is observed in other nucleophilic reactions, e.g. nucleophilic additions to carbonyl groups,[39–42] leads to a depressing effect on the intrinsic reactivity which is proportional to the energetic cost of the desolvation.[2,39] Because of the greater possibility of delocalization of its negative charge, an ArO^- ion has a lower hydrogen-bond solvation than a $RCOO^-$ ion of similar basicity, and thus the k_o values are higher for the ionization of **1a–d** by phenoxide than by carboxylate ions. In agreement with this view, it has been found that $RCOO^-$ and ArO^- ions exhibit more comparable behavior when the ionization of carbon acids is studied in solvents in which hydrogen-bonding solvation is decreased compared to aqueous solutions, e.g. methanol.[4,43]

That the observed rate constants for deprotonation of **1a–d** by *p*-cyanophenoxide ion show definite negative deviations from the Brønsted plots defined by other phenoxide ions in 50% H_2O–50% DMSO (see Figure 2) may also be a reflection of a solvation effect. Bordwell and Taft have pointed out that π-acceptor substituents such as *p*-CN or *p*-NO_2 have an appreciable hydrogen-bonding solvation.[44–46] This would make the prior desolvation of the *p*-cyanophenoxide ion energetically more expensive than it would be if there were no charge delocalization onto the N atom, i.e. the cyano group exhibited only a polar effect. This phenomenon has been called a substituent–solvation-assisted-resonance effect,[44–46] but it can also be considered as a PNS effect modifying the polar substituent effect.[2]

Experimental Section

Materials. All nitrodiphenylmethanes studied were synthetized according to standard procedures: 2,2′,4,4′,6,6′-hexanitrodiphenylmethane, mp 231 °C (lit.[47] mp 232 °C); 2,2′,4,4′,6-pentanitrodiphenylmethane, mp 209–211 °C (lit.[47] mp 208–210 °C); 2,2′,4,4′-tetranitrodiphenylmethane, mp 179 °C (lit.[48] mp 182 °C); 2,4,4′-trinitrodiphenylmethane, mp 111 °C (lit.[49] mp 110–111

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[38] Value calculated by using an average β_B value for **1a** and **1b**.

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°C); 4,4′-dinitrodiphenylmethane, mp 181 °C (lit.[50] mp 181–182 °C); 4-nitrodiphenylmethane, mp 32 °C (lit.[51,52] mp 29–32 °C). Solvents were purified and solutions made up as described previously.[3] Buffers were purified commercial products.

Measurements. Kinetic studies were made using a Durrum stopped-flow spectrophotometer, with a thermostatted cell compartment (25 ± 0.2 °C). Some slow kinetic measurements were made using a Shimadzu UV-160 spectrophotometer. pH determinations in water–DMSO mixtures containing 0.5 M NMe_4Cl were carried out at 25 °C using the same procedure as that previously described.[3] A Tacussel Isis 20000 electronic pH meter was used for this purpose.

Registry No. **1a**, 32255-27-9; **1b**, 32255-28-0; **C-1a**, 126083-71-4; **C-1b**, 126083-72-5.

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A Dichotomy in the Nitration of Fluoranthene with NO_2/N_2O_4: Mechanistic and Toxicological Implications

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The nitration of fluoranthene with nitrogen dioxide can occur by two distinctive reaction pathways. These paths can be distinguished by product analysis, since fluoranthene is a nonalternant hydrocarbon. Free-radical nitration and electrophilic nitration give different products. In solvents with dielectric constants lower than that of CH_2Cl_2 and in the absence of acid catalysis, the exclusive reaction pathway is homolytic in nature. The products of the homolytic reaction pathway can be interpreted as arising via a multiple-step addition–elimination mechanism and are notable for the formation of 2-nitrofluoranthene (the major product in CCl_4 but absent under electrophilic nitration conditions) and the unusually large amounts of the expected 1,2-dinitrofluoranthene and 1,3-dinitrofluoranthene. The ionic reaction pathway is subject to both Lewis and Brønsted acid catalysis, particularly in CH_2Cl_2, and is inhibited by nonnucleophilic bases like 2,6-di-*tert*-butylpyridine. At temperatures lower than 25 °C, the ionic reaction pathway predominates, even in CCl_4. 2-Nitrofluoranthene is a marker for the free-radical nitration of fluoranthene, and its presence in polluted tropospheric air suggests that free-radical nitration by NO_2 may occur under atmospheric conditions.

The reactions of polycyclic aromatic hydrocarbons (PAH) with nitrating agents have received much attention recently due to the potential for the formation of nitro-PAH in urban atmospheres[2–5] and the mutagenic and/or carcinogenic properties of many of these compounds.[6,7] Nitro-PAH are thought to arise from a variety of human activities including fossil fuel combustion and biomass burning. However, certain nitro-PAH that cannot be explained in terms of the conventional nitration mechanism have been identified in airborne particulate matter.[4,8,9] For example, 2-nitrofluoranthene (2NF), despite being the most abundant and ubiquitous nitro-PAH pollutant,[4,8,9] has not been observed in combustion emissions.[3] It also did not appear to be produced under various nitration conditions;[10,11] however, recently 2NF has been identified as a product under homolytic nitration conditions,[12–15] and it was proposed that 2NF arises from radical reactions in polluted tropospheric ambient air.[4,8,9,13,14]

Despite the numerous works devoted to nitration of PAH, reports on the reaction of PAH with NO_2/N_2O_4 are often controversial, and mechanisms involving electron-transfer, radical, or electrophilic substitution have been proposed.[16] We have recently reported on the radical nitration of fluoranthene, **1**, with NO_2/N_2O_4 in CCl_4.[14] We proposed the use of **1** as a mechanistic probe for distinguishing between radical and electrophilic nitration because, being a nonalternant hydrocarbon, it gives a markedly different product distribution according to the type of reaction mechanism. Thus, the positional reactivity found with nitronium ion mediated nitration follows the order 3 > 8 > 7 > 1 > 2, in agreement with the theoretical calculations involving an intermediate σ-complex that

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