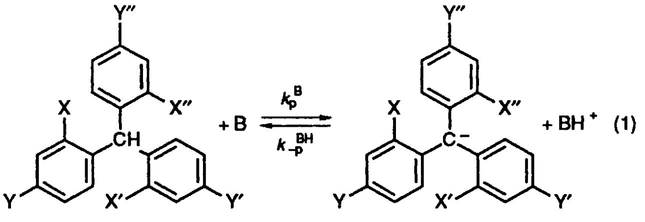
Highly Sterically hindered Carbon Acids: The Intrinsic Reactivity of 5,5′,5″-Trimethyl- and 3,3′,3″,5,5′,5″-Hexamethyl-2,2′,2″,4,4′,4″-Hexanitrotriphenylmethanes

François Terrier,*[a,b] Lan Xiao,[c] Patrick G. Farrell[c] and Danielle Moskowitz[c]
[a] *UA CNRS 403, Ecole Nationale Supérieure de Chimie de Paris, 11 Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*
[b] *Department of Chemistry, University of Versailles, 45, Avenue des Etats-Unis, 78000-Versailles, France*
[c] *Department of Chemistry, McGill University, 801, Sherbrooke Street West, Montreal, Canada*

Rate constants (k_p^B, k_{-p}^{BH}) for the reversible deprotonation of 5,5′,5″-trimethyl- and 3,3′,3″,5,5′,5″-hexamethyl-2,2′,2″,4,4′,4″-hexanitrotriphenylmethanes (**2** and **3**) by primary aliphatic amines, piperidine and morpholine as well as by phenoxide anions and hydroxide anion have been measured in H_2O–Me_2SO (20:80) at 25 °C. Comparison of the results obtained with those for 2,2′,2″,4,4′,4″-hexanitrotriphenylmethane (**1a**) shows that the introduction of methyl groups in positions adjacent to the nitro groups decreases markedly the thermodynamic acidity of the exocyclic CH group: $\Delta pK_{a_{1a}}^{2} = 1.68$; $\Delta pK_{a_{1a}}^{3} = 6.48$. It is suggested that these decreases are very likely the reflection of a twisting of the nitro groups out of their attached aromatic planes and therefore of a reduced resonance stabilization of the conjugated carbanions **C-2** and **C-3**. Other important steric effects are operating in the ionization of **2** and **3**. These arise from the accumulation of *ortho*-nitro groups in the triphenylmethane system which makes the approach of the base reagents from the exocyclic carbon of **2** and **3** very difficult. The finding of extremely low intrinsic reactivities for **2** and **3** and the observation of a much greater catalytic efficiency of primary amines than of secondary amines in assisting the proton transfers are the two most striking manifestations of these F-strain effects.

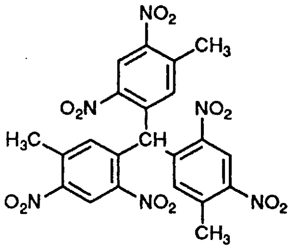
We have recently reported thorough thermodynamic and kinetic studies of the ionization of the series of nitrotriphenylmethanes **1a–f** by various base reagents [eqn. (1)] in different H_2O–Me_2SO mixtures.[1,2] The successive introduction of *para*-nitro groups and then *ortho*-nitro groups in the three phenyl rings of the parent unsubstituted derivative **1g** was found to result in a regular increase in the thermodynamic acidity (K_a) but not in the kinetic acidity (k_p^B) of the exocyclic CH group. While the latter is normally enhanced on going from the mononitro (**1f**) to the tetranitro (**1c**) compound, it suffers a marked decrease on going from **1c** to the more acidic penta- and hexa-nitro compounds **1b** and **1a**. This abnormal pattern in the k_p^B values has been attributed to the fact that the accumulation of *ortho*-nitro groups in the phenyl rings causes considerable steric hindrance to proton abstraction by the base reagents. A spectacular manifestion of this steric hindrance was the finding of especially low intrinsic reactivities for **1a** and **1b**.[2]



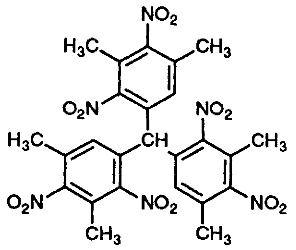
1 **C-1**

a X = X′ = X″ = Y = Y′ = Y″ = NO_2
b X = X′ = Y = Y′ = Y″ = NO_2, X″ = H
c X = Y = Y′ = Y″ = NO_2, X′ = X″ = H
d Y = Y′ = Y″ = NO_2, X = X′ = X″ = H
e Y = Y′ = NO_2, X = X′ = X″ = Y″ = H
f Y = NO_2, X = X′ = X″ = Y′ = Y″ = H
g X = X′ = X″ = Y = Y′ = Y″ = H

To obtain further information on the effect of steric hindrance in this particular series of carbon acids—the carbanion of the unsubstituted triphenylmethane is known to be non-planar with a propeller arrangement of the three phenyl rings around an essentially sp² exocyclic carbon[3–6]—we have extended our kinetic and thermodynamic investigations to other highly-substituted triphenylmethanes. In this paper, we report a study of the reversible deprotonation of 5,5′,5″-trimethyl- and 3,3′,3″,5,5′,5″-hexamethyl-2,2′,2″,4,4′,4″-hexanitrotriphenylmethanes **2** and **3** [tris(5-methyl-2,4-dinitrophenyl)- and tris-(3,5-dimethyl-2,4-dinitrophenyl)methanes] by various base reagents (amines, phenoxide ions, OH^-) under similar conditions to those used for **1a** in H_2O–Me_2SO (20:80). The introduction of methyl groups in positions adjacent to the nitro groups in the phenyl rings of **1a** is found to markedly decrease the thermodynamic acidity of the CH group. We will suggest that this behaviour is very likely the consequence of a notable twisting of the nitro groups out of the aromatic planes and therefore of the reduced capability of these groups to stabilize the conjugated carbanions through resonance interaction. In addition, our results provide further evidence that steric hindrance to approach of the base reagents from the exocyclic carbon is a major feature of the ionization of tri-*ortho*-substituted triphenylmethane derivatives.



2



3

Results

Rates and pK_a^{CH} values for the reversible deprotonation of **2** and **3** according to general eqn. (2) were measured in H_2O–Me_2SO

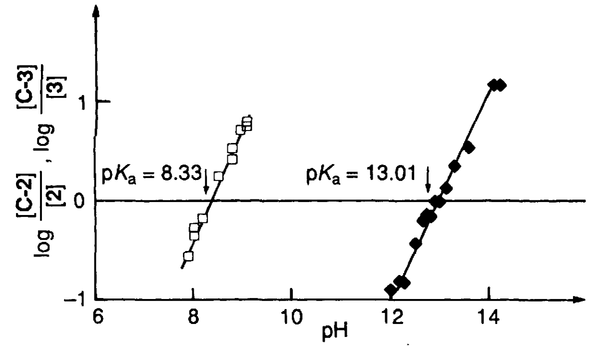


Fig. 1 The variation of the ratio of ionized to non-ionized triphenylmethanes **2** (pK_a = 8.33) and **3** (pK_a = 13.01) as a function of pH in H_2O–Me_2SO (20:80); T = 25 °C; I = 0.5 mol dm^{-3} NMe_4Cl

(20:80) (v/v) by monitoring spectrophotometrically the appearance or disappearance of the absorption of the conjugated carbanions **C-2** and **C-3** at or near λ_{max}: 660 nm (ε = 29 700 dm^3 mol^{-1} cm^{-1}) for **C-2**; 700 nm (ε = 17 400 dm^3 mol^{-1} cm^{-1}) for **C-3**. Use of H_2O–Me_2SO mixtures with a lower Me_2SO content was precluded by the low solubility of **2** and **3** in these solvents. Experiments were carried out using various buffer solutions made up from primary and secondary amines as well as phenols. Dilute NMe_4OH and HCl solutions were also used. In all cases, the ionic strength was kept constant at 0.5 mol dm^{-3} with NMe_4Cl.

$$\mathbf{2}\ (\text{or } \mathbf{3}) \underset{k^{H}_{-p}[H^+] + k^{BH}_{-p}[BH] + k^{H_2O}_{-p}}{\overset{k_p^{H_2O} + k_p^B[B] + k_p{}^{OH}[OH^-]}{\rightleftharpoons}} \mathbf{C\text{-}2}\ (\text{or } \mathbf{C\text{-}3}) \qquad (2)$$

The pK_a^{CH} values of **2** and **3** were first determined from observed optical density variations at λ_{max} of **C-2** and **C-3** obtained at equilibrium as a function of pH. In agreement with eqn. (3), excellent straight lines with unit slopes were obtained on plotting the log values of the ratio of the concentrations of ionized to non-ionized triphenylmethanes (**2** and **3**) as a function of pH (Fig. 1). We thus readily obtain: pK_a^{CH} = 8.33 for **2**; pK_a^{CH} = 13.01 for **3**.

$$\log \frac{[C\text{-}2]}{[2]} = \text{pH} - \text{p}K_a \qquad (3)$$

Rates of proton transfer were determined under pseudo-first-order conditions with a large excess of the buffer, base or acid reagent over the substrate concentration (*ca.* 2 × 10^{-5} mol dm^{-3}). Under these conditions, the observed rate constant, k_{obsd}, for the approach to equilibrium (2) was given by eqn. (4). In this equation, k_p^{OH}, k_p^B and $k_p^{H_2O}$ are the rate constants referring to the deprotonation of **2** or **3** by hydroxide ion, the buffer base species and the solvent, respectively, while k^H_{-p}, k^{BH}_{-p} and $k^{H_2O}_{-p}$ are the rate constants referring to the protonation of the carbanions **C-2** and **C-3** by hydronium ion, the buffer acid species and the solvent, respectively.

Depending upon the pH of the solutions studied, equilibrium (2) was experimentally approached by mixing a neutral solution of **2** (or **3**) with the appropriate NMe_4OH or buffer solutions (pH ≥ pK_a^{CH}) or by mixing a freshly prepared 0.01 mol dm^{-3} NMe_4OH solution of the carbanions **C-2** (or **C-3**) with the appropriate buffer or acid solutions (pH ≤ pK_a^{CH}). In the case of **2** (pK_a^{CH} = 8.33), the equilibrium could be approached from both reactant and product sides in the following buffers: glycine ethyl ester (pK_a^{BH} = 7.70), morpholine (pK_a^{CH} = 8.48), glycinamide (pK_a^{BH} = 8.69). A similar situation prevailed in the case of **3** (pK_a^{BH} = 13.01) with *p*-chlorophenoxide (pK_a^{BH} = 12.45) and phenoxide (pK_a^{BH} = 13.59) buffers. In these instances, the rate data obtained in the two series of experiments for a given buffer were identical within experimental error. All observed first-order rate constants for the ionization of **2** and **3** are summarised in Tables S1 and S2 given as Supplementary material [sup. pub. no. 56887 (5 pp)].*

The procedures used in evaluating the various rate constants involved in eqn. (4) were essentially the same as those described

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

in previous proton-transfer studies.[1,2,7,8] All rate constants for reaction (2) in H_2O–Me_2SO (20:80) are summarized in Table 1. For buffers with pK_a^{BH} > pK_a^{CH} + 1 (or pK_a^{BH} < pK_a^{CH} − 1), the quoted k^{BH}_{-p} (or k_p^B) values were calculated by means of eqn. (5).

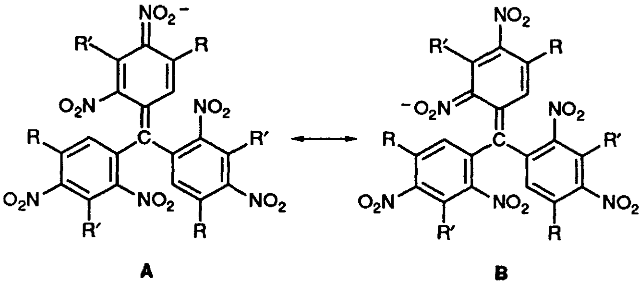
$$k_p^B = k^{BH}_{-p} \frac{K_a^{CH}}{K_a^{BH}} \qquad (5)$$

Discussion

Table 2 compares the pK_a^{CH} values as well as some rate constants for deprotonation of **2** and **3** by some representative base reagents (B) with similar data obtained in H_2O–Me_2SO (20:80) for the ionization of 2,2′,2″,4,4′,4″-hexanitrotriphenylmethane **1a**.[2] Also given are the rate constants k^{BH}_{-p} for reprotonation of the carbanions **C-2**, **C-3** and **C-1a** by the conjugated acids BH.

As can be seen, introduction of a first methyl group *ortho* to the *p*-nitro group in each of the three phenyl rings of **1a** to give **2**, results in a decrease of 1.8 pK units in the thermodynamic acidity of the exocyclic CH group. Interestingly, this effect is large but it is considerably less than that brought about by the introduction of the second series of methyl groups which are all located in a position *ortho* to the two nitro groups: **3** is a weaker acid than **2** by 4.68 pK units, having a pK_a value (13.01) close to that measured for the ionization of 4,4′,4″-trinitrotriphenylmethane **1d** (12.84) in the same H_2O–Me_2SO mixture.[1] The large influence of the methyl groups is likely to be understood in terms of a much weaker resonance stabilization of the carbanions **C-2** and **C-3**, especially the latter, by the *ortho* and *para*-nitro groups rather than in terms of the weak electron-donating contributions of these substituents. The reasons are the following.

It is well known that triphenylmethyl anions have a non-planar propeller structure,[3–6] and can have only one phenyl ring in the most favourable position for conjugation with the exocyclic sp^2 carbon atom at any given time. Accordingly, the high thermodynamic acidity of **1a** arises for the most part from a very effective stabilization of **C-1a** through the two resonance structures A and B (R = R′ = H) of one 2,4-dinitrophenyl ring, the acidifying effects of the two other activated rings being mainly inductive in nature.[2] However, X-ray crystallographic studies have revealed that the presence of a substituent,



---

* For details of the Supplementary Publications scheme, see 'Instructions for Authors', 1992, *J. Chem. Soc., Perkin Trans. 2*, in the January issue.

Table 1 Rate constants for the ionization of 5,5′,5″-trimethyl- and 3,3′,3″,5,5′,5″-hexamethyl-2,2′,2″,4,4′,4″-hexanitrotriphenylmethanes (**2** and **3**) in H_2O–Me_2SO (20:80)[a]

			2 (pK_a^{CH} = 8.33)		**3** (pK_a^{CH} = 13.01)	
	Buffer (basic species)	pK_a^{BH}	k_p^B/ $dm^3\ mol^{-1}\ s^{-1}$	k_{-p}^{BH}/ $dm^3\ mol^{-1}\ s^{-1}$	k_p^B/ $dm^3\ mol^{-1}\ s^{-1}$	k_{-p}^{BH}/ $dm^3\ mol^{-1}\ s^{-1}$
1	H_2O	−1.05	1.56×10^{-8} [b]	37	9.81×10^{-10} [b]	1.13×10^5
2	Aminoacetonitrile	5.64	1.15×10^{-4} [c]	5.65×10^{-2}	1.20×10^{-6} [c]	28
3	Glycine ethyl ester	7.70	1.07×10^{-3}	4.26×10^{-3}	1.8×10^{-5} [c]	3.81
4	Glycinamide	8.69	3.53×10^{-3}	2.34×10^{-3}	1.32×10^{-4} [c]	2.79
5	2-Methoxyethylamine	9.54	7.96×10^{-3}	4.91×10^{-4} [c]	2.48×10^{-4} [c]	0.733
6	*n*-Butylamine	10.27	1.68×10^{-2}	1.93×10^{-4} [e]	8.39×10^{-4} [c]	0.46
7	Morpholine	8.48	4.5×10^{-4}	3×10^{-4}	6.79×10^{-6}	0.23
8	Piperidine	10.16	2.62×10^{-3}	3.88×10^{-5} [e]	6.35×10^{-5}	4.48×10^{-2}
9	2-Cyanophenoxide ion	9.53	0.096	7.89×10^{-3}	6.82×10^{-4} [c]	2.06
10	4-Cyanophenoxide ion	10.22	0.125	1.61×10^{-3}	8.37×10^{-4} [c]	0.52
11	2-Bromophenoxide ion	11.37	2.06	1.88×10^{-3}	8.29×10^{-3} [c]	0.362
12	4-Chlorophenoxide ion	12.45	2.76	—	0.025	0.066
13	Phenoxide ion	13.59	29.8	1.74×10^{-4}	0.256	3.7×10^{-2}
14	OH^-	21.21	239	3.11×10^{-11} [d]	67	4.13×10^{-7} [d]

[a] I = 0.5 mol dm^{-3} NMe_4Cl, T = 25 °C; experimental error in the rate constants: ±5% or better; in pK_a^{BH} and pK_a^{CH}: ±0.05 pK unit; in the calculated rate constants: ±15%. [b] $k_p^{H_2O}/11.11$ with $k_p^{H_2O}$ calculated from $K_a^{CH}k_{-p}^{H}$. [c] Calculated from k_{-p}^{BH} or k_p^B *via* eqn. (5). [d] $k_{-p}^{H_2O}/11.1$ with $k_{-p}^{H_2O}$ calculated from $k_p^{OH}K_s/K_a^{CH}$ with pK_s = 20.17 (see experimental section).

Table 2 Comparison of some representative rate and equilibrium parameters for the ionization of **2** and **3** with similar data for 4,4′,4″-trinitro- (**1d**) and 2,2′,2″,4,4′,4″-hexanitro- (**1a**) triphenylmethanes in H_2O–Me_2SO (20:80)[a,b]

	1d (pK_a^{CH} = 12.84)		**1a** (pK_a^{CH} = 6.53)		**2** (pK_a^{CH} = 8.33)		**3** (pK_a^{CH} = 13.01)	
Buffer base	k_p^B/ $dm^3\ mol^{-1}\ s^{-1}$	k_{-p}^{BH}/ $dm^3\ mol^{-1}\ s^{-1}$	k_p^B/ $dm^3\ mol^{-1}\ s^{-1}$	k_{-p}^{BH}/ $dm^3\ mol^{-1}\ s^{-1}$	k_p^B/ $dm^3\ mol^{-1}\ s^{-1}$	k_{-p}^{BH}/ $dm^3\ mol^{-1}\ s^{-1}$	k_p^B/ $dm^3\ mol^{-1}\ s^{-1}$	k_{-p}^{BH}/ $dm^3\ mol^{-1}\ s^{-1}$
H_2O[c]	5.51×10^{-10}	4.2×10^4	5.63×10^{-8}	2.12	1.56×10^{-8}	37	9.81×10^{-10}	1.13×10^5
n-Butylamine	2.69×10^{-2}	11	0.11	2×10^{-5}	1.68×10^{-2}	1.93×10^{-4}	8.39×10^{-4}	0.46
Piperidine	3.11×10^{-2}	14.88	1.54×10^{-2}	3.6×10^{-6}	2.62×10^{-3}	3.88×10^{-5}	6.35×10^{-5}	4.48×10^{-2}
Phenoxide ion	16	3	40	3.47×10^{-6}	29.8	1.74×10^{-4}	0.256	3.7×10^{-2}
OH^-[d]	2160	9.1×10^{-6}	2220	4.58×10^{-12}	239	3.11×10^{-11}	67	4.13×10^{-7}

[a] Data for **1a** and **1d** are taken from ref. 2. [b] T = 25 °C, I = 0.5 mol dm^{-3} NMe_4Cl. [c] $k_p^B = k_p^{H_2O}/11.11$. [d] $k_{-p}^{BH} = k_{-p}^{H_2O}/11.11$.

especially an alkyl (CH_3) or an alkoxy (OCH_3) group in a position adjacent to the nitro group in a phenyl ring, generally induces a twisting of the latter substituent out of the aromatic plane.[9–17] Twist angles of NO_2 groups in the range 35–60° have been found when there is only one substituent in an adjacent position but greater angles of twist have been measured for nitro groups located between two adjacent substituents.[10–18] For example, the two nitro groups surrounding the methyl group of 2,4,6-trinitrotoluene in its orthorhombic form are rotated by 60° and 45°, respectively, out of the phenyl ring while the 2-, 4- and 6-nitro groups of 2,4,6-trinitro-*m*-xylene are twisted by 75°2, 35°7 and 35°7, respectively.[15,18]

Based on these findings, it seems reasonable to assume that the *para*-nitro groups are somewhat tilted out of their respective aromatic rings in the trimethyl substituted triphenylmethane **2** as well as in the conjugated carbanion **C-2**. These nitro groups are thus less efficient at delocalizing the negative charge of **C-2** *via* structure A (R = CH_3, R′ = H), thereby reducing the overall resonance stabilization of this carbanion compared to that of **C-1a** and causing the 1.8 pK unit decrease in the acidity observed on going from **1a** to **2**. The situation must be worse in **C-3** since both resonance structures A and B (R = R′ = CH_3) are now sterically hindered by the twisting or the nitro groups. As a matter of fact, a much larger decrease in acidity occurs on going from **2** to **3**. The finding of a relatively weak absorption coefficient for **C-3** (ε = 17 400 $dm^3\ mol^{-1}\ cm^{-1}$) compared to that for **C-2** (ε = 29 700 $dm^3\ mol^{-1}\ cm^{-1}$) or **C-1a** (ε = 34 300 $dm^3\ mol^{-1}\ cm^{-1}$) supports the view of a notably reduced resonance stabilization of **C-3**.

An analysis of the changes in pK_a^{CH} in terms of those in the rate constants for the various pathways contributing to the equilibrium formation of **C-1a**, **C-2** and **C-3** is also instructive. Table 2 shows that the decrease in CH acidity caused by the introduction of the first series of methyl groups in **1a** to give **2** is due to a 8–10 fold decrease in the kinetic acidity (k_p^{OH}, k_p^B) and a concomitant and similar increase in the rate constants $k_{-p}^{H_2O}$ or k_{-p}^{BH}. In contrast, the large pK_a decrease (ΔpK_a = 4.68) observed on going from **2** to **3** is essentially the reflection of a large increase in the rate constants $k_{-p}^{H_2O}$ or k_{-p}^{BH} for carbanion reprotonation: $k_{-p\,3}^{H_2O}/k_{-p\,2}^{H_2O} = 10^4$; $k_{-p\,3}^{BuNH_3^+}/k_{-p\,2}^{BuNH_3^+} = 2380$; $k_{-p\,3}^{Pip\cdot H^+}/k_{-p\,2}^{Pip\cdot H^+} = 1150$. Since it is known that the rates of carbanion reprotonation by the solvent or any general acid are primarily dependent upon the extent of charge delocalization, this result adds to the evidence that there is a considerable steric inhibition to resonance of the two nitro groups in **C-3**.

Brönsted Plots. Intrinsic Reactivities.—Figs. 2 and 3 show Brönsted plots for the deprotonation of **2** and **3** by the various catalysts studied. As can be seen, each family of buffers defines its own Brönsted plots. This is in accord with many previous reports that structurally different catalysts of similar pK_a values can exhibit appreciable differences in the efficiency with which they assist proton transfers to/from a carbon atom.[19–26] For a given ΔpK_a + log (p/q) value, the relative reactivity order is aryloxide (ArO^-) > primary amines (RNH_2) > secondary amines (RR′NH).

While the greater catalytic efficiency of aryloxide bases

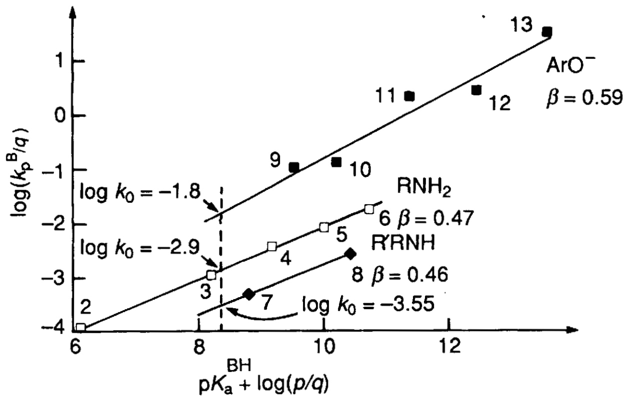


Fig. 2 Statistically-corrected Brönsted plots for the deprotonation of **2** by phenoxide and amine bases in H_2O–Me_2SO (20:80); T = 25 °C, I = 0.5 mol dm^{-3} NMe_4Cl. The numbering of the catalysts is indicated in Table 1.

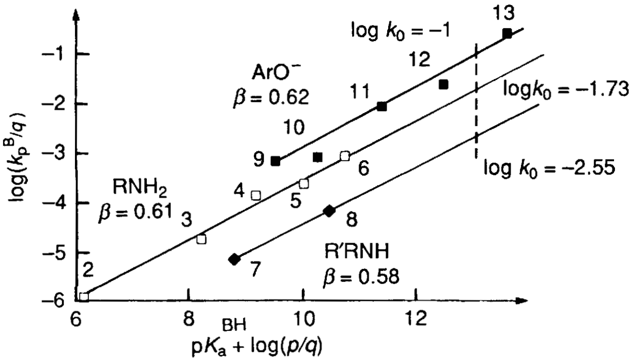


Fig. 3 Statistically-corrected Brönsted plots for the deprotonation of **3** by phenoxide and amine bases in H_2O–Me_2SO (20:80); T = 25 °C, I = 0.5 mol dm^{-3} NMe_4Cl. The numbering of the catalysts is indicated in Table 1.

compared to amine bases is consistent with the behaviour commonly found in the ionization of carbon acids,[7,26] the greater reactivity of primary amines compared to secondary amines is a very unusual result.[20–25] In general, primary amines are much less reactive than secondary amines because of a greater need for solvation of developing primary than secondary ammonium ions, coupled with a late development of this solvation along the reaction coordinate.[20–25] It turns out, however, that we have recently found a similar inversion in reactivity of the two classes of amines in the study of the ionization of the non-methyl-substituted hexanitro derivative **1a**.[2] In this case, a detailed analysis of the kinetic results has provided convincing evidence that the inversion was the reflection of a difficult approach of the base reagents from the exocyclic carbon caused by the accumulation of *ortho*-nitro groups in the three phenyl rings of **1a**, the effect being greater for the more bulky secondary amines. There is no doubt that this explanation also holds for **2** and **3**. In this regard, we note that the $k_p^{RNH_2}/k_p^{RR'NH}$ ratios which measure the reactivity difference between primary and secondary amines are equal to 4 and 7 for **2** and **3**, as compared with values of 4–5 for **1a**.

As an illustration of this conclusion, we note in Table 2 that all the k_p^B rate constants for the ionization of **3** are markedly lower than those found for the similarly acidic 4,4′,4″-trinitrotriphenylmethane derivative **1d** which has no *ortho*-nitro groups, *e.g.* $k_{p\,\mathbf{1d}}^{BuNH_2}/k_{p\,\mathbf{3}}^{BuNH_2} = 32$, $k_{p\,\mathbf{1d}}^{Pip}/k_{p\,\mathbf{3}}^{Pip} = 490$. It is therefore because the corresponding k_{-p}^{BH} rate constants for reprotonation of **C-3** are also significantly lower than those for reprotonation of the 4,4′,4″-trinitrophenylmethyl carbanion **C-1d** that the thermodynamic acidities of **1d** and **3** are similar. In as much as there are no notable F-strain effects in the ionization reactions of **1d**,[1] the finding of a greater value for the $k_{p\,\mathbf{1d}}^{Pip}/k_{p\,\mathbf{3}}^{Pip}$ ratio than for the $k_{p\,\mathbf{1d}}^{BuNH_2}/k_{p\,\mathbf{3}}^{BuNH_2}$ ratio is in itself evidence for the aforementioned greater steric inhibition to the approach of the more bulky secondary amines.

Table 3 shows that the Brönsted β_B values for the three classes of catalysts increase on going from the more to the less thermodynamically-favoured reaction, *e.g.* $\beta_{RNH_2}^{\mathbf{1a}} = 0.30$, $\beta_{RNH_2}^{\mathbf{2}} = 0.47$, $\beta_{RNH_2}^{\mathbf{3}} = 0.61$. This trend is in accord with the reactivity–selectivity principle.[27] Consistent with general behaviour is the finding of similar β_{RNH_2} and $\beta_{RR'NH}$ values for the ionization of **2** as well as of **3** in H_2O–Me_2SO (20:80).[20–25] Unfortunately, the very low stability of these substrates at lower Me_2SO contents did not allow us to confirm the anomalous variations observed in the β_{RNH_2} and $\beta_{RR'NH}$ values for the deprotonation of **1a** in H_2O–Me_2SO (50:50).[1]

Values of the intrinsic rate constants (in the Marcus sense)[20,28,29] for **2** and **3**, as determined from the Brönsted plots of Figs. 2 and 3 as $k_o = k_p^B/q$ when $pK_a^{BH} + \log p/q = pK_a^{CH}$ are also given in Table 3. These rate constants are very low and of the same order of magnitude as that found for **1a**.[1] As demonstrated for this compound, they imply such high intrinsic barriers that they cannot be understood in the only terms of the considerable structural-electronic-solvational reorganization which is known to accompany the formation of a nitro-substituted triphenylmethyl anion.[1,2,4–6,30] Therefore, another factor contributes to decrease the k_o values and this factor is presumably the operation of important F-strain effects. An interesting result, however, is the approximately 10-fold increase of k_o on going from **2** to **3**. This increase fits well the idea that the presence of the methyl groups causes the twisting of the nitro groups in **C-3**, thereby decreasing the degree of resonance stabilization of this carbanion and enhancing the corresponding k_o value.

Experimental

Materials.—Solvents were purified and solutions made up as described previously.[2,7] Buffers were purified commercial products. Tris(5-methyl-2,4-dinitrophenyl)methane (**2**) and tris(3,5-dimethyl-2,4-dinitrophenyl)methane (**3**) were obtained by nitration of tris-*m*-tolylmethane and tris-3,5-xylylmethane, respectively,[31] as follows.

The methylated triphenylmethane (1.0 g) was ground as finely as possible and added to 25 cm^3 of conc. H_2SO_4. The mixture was cooled to *ca.* −40 °C in an propan-2-ol/CO_2 bath and 25 cm^3 of fuming nitric acid (d = 1.52) were gradually added, maintaining efficient stirring. The mixture, which became rapidly dark brown, was stirred at −40 °C for 15 min, then allowed to warm to room temperature. The trimethyl compound was stirred for a further 6 h at room temperature whereas the hexamethyl compound was stirred for the same time at 80 °C. The solution was then poured onto ice and the precipitate filtered and thoroughly washed with water to give crude yields of 1.77 g (trimethyl) and 1.65 g (hexamethyl).

Recrystallization of the trimethyl derivative from ethanol gave 1.23 g (63%) of white, microcrystals of tris(5-methyl-2,4-dinitrophenyl)methane (**2**): m.p. 272 °C; mass spectrum (obsd.), *m*/*z* 556.0825 (reference $C_{13}F_{21}$); $C_{22}H_{16}N_6O_{12}$ requires 556.082 62; δ_H ([$^2H_6$]acetone; Me_4Si) 8.81 (3 H, s, 3-H), 7.63 (3 H, s, 6-H), 7.02 (1 H, s, CH) and 2.56 (9 H, s, CH_3).

Recrystallization of the hexamethyl derivative from *N*,*N*-dimethylformamide gave 1.34 g (73%) of white needles of tris(3,5-dimethyl-2,4-dinitrophenyl)methane (**3**): 330 °C (decomp.); mass spectrum (obsd.), *m*/*z* 598.129 75 (reference $C_{13}F_{23}$); $C_{25}H_{22}N_6O_{12}$ requires 598.129 57; δ_H ([$^2H_6$]DMSO; Me_4Si), 7.22 (3 H, s, 6-H), 5.43 (1 H, s, CH), 2.33 (9 H, s, CH_3) and 2.17 (9 H, s, CH_3).

Table 3 Brönsted coefficients and intrinsic rate constants for the ionization of the hexanitrotriphenylmethanes **1a**, **1d**, **2** and **3** in H_2O–Me_2SO (20:80)

	1a $pK_a^{CH} = 6.53$		**2** $pK_a^{CH} = 8.33$		**3** $pK_a^{CH} = 13.01$		**1d** $pK_a^{CH} = 12.84$	
Base	β_B	log k_o	β_B	log k_o	β_B	log k_o	β_B	log k_o
RNH_2	0.30	−2.42	0.47	−2.90	0.61	−1.73	0.63	−0.15
RR′NH	0.30	−3.02	0.46	−3.55	0.58	−2.55	0.60	0
ArO^-	0.40	−1.20	0.59	−1.80	0.62	−1.00	0.59	0.75

Measurements.—Fast kinetic measurements were carried out with a Durrum stopped-flow spectrophotometer equipped with a thermostatted cell compartment (25 ± 0.2 °C). Slow rates were measured with a conventional UV–VIS Kontron Uvikon spectrophotometer. All rates were reproducible to within ±5%. pH and pK_a determinations in the 20–80 (v/v) H_2O–Me_2SO mixture containing 0.5 mol dm^{-3} NMe_4Cl were carried out at 25 °C using the same procedures as those previously described. A Tacussel Isis 20 000 electronic pH meter was used for this purpose. The autoprotolysis constant of this solvent mixture was known from previous studies: $pK_a = 20.17$ at 25 °C.[2]

The high resolution mass spectra were obtained on a VG ZAB-2F-HS sector mass spectrometer in the direct-inlet mode. Measurements were carried out with a resolving power of 10^4 by electron impact (70 eV, 100 μA). Source temperature was 240 °C in each experiment with a probe temperature of 195 and 185 °C, respectively for the xylyl and tolyl derivatives. ^1H NMR spectra were recorded on a Bruker AM-250 spectrometer equipped with an Aspect 3000 computer. Chemical shifts are reported in parts per million (δ, *J* values in Hz), relative to internal Me_4Si.

References

1 F. Terrier, H. Q. Xie, J. Lelièvre, T. Boubaker and P. G. Farrell, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1899.
2 F. Terrier, T. Boubaker, L. Xiao and P. G. Farrell, *J. Org. Chem.*, 1992, **57**, in the press.
3 J. F. Brooks and G. D. Stucky, *J. Am. Chem. Soc.*, 1972, **94**, 7333.
4 S. E. Browne, S. E. Asher, E. H. Cornwall, J. K. Frisoli, I. J. Harris, E. A. Salot, E. A. Sauter, M. A. Trecoske and P. S. Veale, *J. Am. Chem. Soc.*, 1984, **106**, 1432.
5 W. Clegg and J. C. Lockhart, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1621.
6 K. Bowden and S. I. J. Hirani, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1885.
7 F. Terrier, J. Lelièvre, A. P. Chatrousse and P. G. Farrel, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1479.
8 F. Terrier, D. Croisat, A. P. Chatrousse, M. J. Pouet, J. C. Hallé and G. Jacob, *J. Org. Chem.*, 1992, **57**, in the press.
9 F. Benedetti, D. R. Marshall, C. J. M. Stirling and J. L. Zeng, *J. Chem. Soc., Chem. Commun.*, 1982, 918.
10 W. R. Carper, L. P. Davis and M. W. Extine, *J. Phys. Chem.*, 1982, **86**, 459.
11 S. C. Nyburg, C. H. Faerman, L. Prasad, D. Palleros and N. S. Nudelman, *Acta Crystallogr., Sect. C*, 1987, **43**, 686.
12 (*a*) P. Coppens and G. M. Schmidt, *Acta Crystallogr.*, 1964, **17**, 222; (*b*) P. Coppens, *Acta Crystallogr.*, 1964, **17**, 573.
13 M. Sax, P. Beurskens and S. Chu, *Acta Crystallogr.*, 1965, **18**, 252.
14 J. Trotter, *Acta Crystallogr.*, 1959, **12**, 605.
15 F. Gérard and A. Hardy, *Acta Crystallogr., Sect. C*, 1988, **44**, 1283.
16 C. M. Grammacioli, R. Destro and M. Simonetta, *Acta Crystallogr., Sect. B*, 1968, **24**, 129.
17 G. Clifford and D. S. Dudis, *Acta Crystallogr., Sect. C*, 1990, **46**, 650.
18 J. H. Bryden, *Acta Crystallogr., Sect. B*, 1972, **28**, 1395.
19 F. Terrier, H. Q. Xie and P. G. Farrell, *J. Org. Chem.*, 1990, **55**, 2610.
20 (*a*) C. F. Bernasconi, *Ad. Phys. Org. Chem.*, 1991, **27**, 119; (*b*) *Acc. Chem. Res.*, 1987, **20**, 301; (*c*) *Pure Appl. Chem.*, 1982, **54**, 2335.
21 T. A. Spencer, M. C. R. Kendall and I. D. Reingold, *J. Am. Chem.*, 1972, **94**, 1250.
22 (*a*) J. Hine and J. Mulders, *J. Org. Chem.*, 1967, **32**, 2200; (*b*) J. Hine, J. Mulders, J. G. Houston and J. P. Idoux, *J. Org. Chem.*, 1967, **32**, 2205.
23 (*a*) R. P. Bell in *The Proton in Chemistry*, 2nd edn., Cornell University, Ithaca, New York, 1973, ch. 10; (*b*) R. P. Bell and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1949, 1288.
24 (*a*) C. F. Bernasconi and S. A. Hibdon, *J. Am. Chem. Soc.*, 1983, **105**, 4343; (*b*) C. F. Bernasconi and R. D. Bunnell, *Isr. J. Chem.*, 1985, **26**, 420; (*c*) C. F. Bernasconi and P. Paschalis, *J. Am. Chem. Soc.*, 1986, **108**, 2969; (*d*) C. F. Bernasconi, R. D. Bunnell and F. Terrier, *J. Am. Chem. Soc.*, 1988, **120**, 6514; (*e*) C. F. Bernasconi, D. A. V. Kliner, A. J. Mullin and J. X. Ni, *J. Org. Chem.*, 1988, **53**, 3342; (*f*) C. F. Bernasconi, D. A. A. Ohlberg and M. W. Stronach, *J. Org. Chem.*, 1991, **56**, 3016.
25 (*a*) D. Stefanidis and J. W. Bunting, *J. Am. Chem. Soc.*, 1991, **113**, 991; (*b*) J. W. Bunting and D. Stefanidis, *J. Am. Chem. Soc.*, 1990, **112**, 779.
26 F. Terrier, A. P. Chatrousse, E. Kizilian, N. V. Ignatev and L. M. Yagupolskii, *Bull. Soc. Chim. Fr.*, 1989, 627.
27 (*a*) A. Pross, *Adv. Phys. Org. Chem.*, 1977, **14**, 69; (*b*) B. Giese, *Angew. Chem. Int. Ed. Engl.*, 1977, **16**, 125.
28 (*a*) R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891; (*b*) A. O. Cohen and R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 4249.
29 C. F. Bernasconi, *Tetrahedron*, 1985, **41**, 3219.
30 C. D. Ritchie and R. E. Ushold, *J. Am. Chem. Soc.*, 1967, **89**, 2960.
31 G. W. Wheland and A. A. Danish, *J. Am. Chem. Soc.*, 1940, **62**, 1125.

Paper 2/02040H
Received 22nd *April* 1992
Accepted 29*th April* 1992