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Steric Effects on the Intrinsic Reactivity of Nitrotriphenylmethanes

François Terrier,*,†,‡ Taoufik Boubaker,† Lan Xiao,‡ and Patrick G. Farrell*,§

UA CNRS 403, ENSCP, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France, Département de Chimie, Université de Versailles, 45 Avenue des Etats-Unis, 78000 Versailles, France, and Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, P.Q., Canada H3A 2K6

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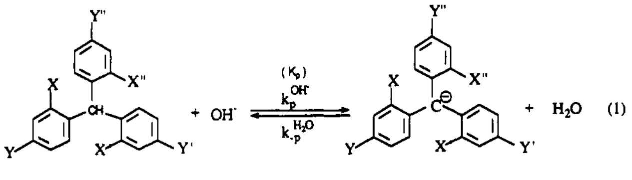
Rate constants (k_p^B, k_{-p}^{BH}) for the reversible deprotonation of (2,2′,2″,4,4′,4″-hexanitrotriphenyl), (2,2′,4,4′,4″-pentanitrotriphenyl), (2,4,4′,4″-tetranitrotriphenyl), and (4,4′,4″-trinitrotriphenyl)methanes (**1a–d**) by primary aliphatic amines and piperidine and morpholine as well as by phenoxide anions and hydroxide anion have been measured in 50% H_2O–50% Me_2SO and 20% H_2O–80% Me_2SO at 25 °C. Addition of a first ortho-nitro group to **1d** to form **1c** increases markedly the thermodynamic acidity ($\Delta pK = 3.88$ in 80% Me_2SO); concomitantly, there is a relatively modest increase in the kinetic acidity (k_p^{OH}) but a large decrease in the rate of carbanion reprotonation by the solvent ($k_{-p}^{H_2O}$). This result is consistent with a preferential stabilization of the (2,4,4′,4″-tetranitrophenyl)methyl carbanion (**C-2c**) by the 2,4-dinitrophenyl ring. Contrasting with this behavior, the introduction of the second and third *o*-nitro groups has the effect to further enhance the thermodynamic acidity, while decreasing both the k_p^B and k_{-p}^{BH} values to an unexpected extent. It is suggested that the anomalous variations of k_p^B and k_{-p}^{BH} on going from **1c** to **1b** to **1a** are the reflection of the unfavorable steric interactions which arise from the accumulation of *o*-nitro groups in the triphenylmethane system. There are two other remarkable manifestations of these steric effects: the first is the finding of extremely low intrinsic reactivities for **1b** and **1a**; the log k_0 value for **1a** is among the lowest reported values for the ionization of a carbon acid; the second is the observation of a reversal in the order of catalytic efficiency of the amine catalysts. While primary amines are normally less reactive than secondary amines in the ionization of **1d** and **1c**, they become markedly more reactive in the ionization of **1b** and **1a**. Steric effects are also suggested to be responsible for the finding of an abnormal dependence of the β_B values upon the solvent composition.

Introduction

We have recently reported a study of the ionization of the series of (polynitrotriphenyl)methanes **1a–f** according to eq 1 in various H_2O–Me_2SO solutions.[1] While the thermodynamic acidity of the exocyclic CH group, as measured by the equilibrium constants K_p, increases regularly on successive addition of the three *p*-nitro groups and then of the three *o*-nitro groups onto the phenyl rings of the unsubstituted derivative **1g**, the kinetic acidity, as measured by the rate of deprotonation by hydroxide ion, does not exhibit similar behavior. This rate constant (k_p^{OH}) increases, as expected, on going from the mononitro- (**1f**) to the tetranitro-substituted (**1c**) derivative but it does not suffer any appreciable variation on going from **1c** to the pentanitro compound **1b** and it falls drastically on going from **1b** to the hexanitro derivative **1a**. This result, together with the finding of an abnormally low $k_{-p}^{H_2O}$ rate constant for reprotonation of the carbanion **C-1a** by the solvent was taken as evidence for a remarkable effect of steric hindrance to approach of hydroxide ion at the exocyclic carbon of **1a** and of water at the exocyclic carbon of the hexanitrotriphenylmethyl carbanion **C-1a**.[1]



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 more information on the role of steric effects in this particular series of carbon acids—the carbanion of the unsubstituted triphenylmethane is known to be nonplanar with a propeller arrangement of the three phenyl rings around an essentially sp² exocyclic carbon[2-4]—we have extended our kinetic measurements to the ionization of **1a–1d** by various phenoxide and primary and secondary amine reagents in 50% H_2O–50% Me_2SO and 20% H_2O–80% Me_2SO (v/v). In the following text, we show that the increased steric demand of these catalysts results in some remarkable inversions of reactivity. Also of interest is the finding of especially low intrinsic reactivities for **1a–1d**.[5,6]

Results

Rates for the reversible deprotonation of **1a–1d** according to the general equation (2) were measured at 25 °C in 50% H_2O–50% Me_2SO and 20% H_2O–80% Me_2SO, using buffer solutions which were made up from the various amine and phenol reagents studied. Dilute NMe_4OH

$$1 \underset{k_{-p}^{H}[H^+] + k_{-p}^{BH}[BH] + k_{-p}^{H_2O}}{\overset{k_p^{H_2O} + k_p^{B}[B] + k_p^{OH}[OH^-]}{\rightleftarrows}} C\text{-}1 \qquad (2)$$

$$(pK_a^{CH})$$

$$k_{obsd} = k_p^{H_2O} + k_p^{OH}[OH^-] + k_p^B[B] + k_{-p}^{H_2O} + k_{-p}^{H}[H^+] + k_{-p}^{BH}[BH] \quad (3)$$

and HCl solutions were also used. In all cases, the ionic strength was kept constant at $I = 0.50$ M with NMe_4Cl, and the rates were determined under pseudo-first-order conditions with a large excess of the buffer, base, or acid reagent over the substrate concentration (3×10^{-5} M). Under these experimental conditions, the observed rate

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[†] ENSCP.
[‡] Université de Versailles.
[§] McGill University.

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Table I. Rate Constants for the Ionization of (2,2′,2″,4,4′,4″-Hexanitrotriphenyl)-, (2,2′,4,4′,4″-Pentanitrotriphenyl)-, and (2,4,4′,4″-Tetranitrotriphenyl)methanes in 50% H_2O–50% Me_2SO[a]

		1a (pK_a^{CH} = 8.25)		1b (pK_a^{CH} = 9.11)		1c (pK_a^{CH} = 10.86)	
buffer (basic species)	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}
1. H_2O	-1.44	8.25×10^{-9} [b]	40.5	1.70×10^{-8} [b]	606	4.05×10^{-9} [b]	8100
2. aminoacetonitrile	5.26	9.20×10^{-5} [c]	9.30×10^{-2}	4.66×10^{-4} [c]	3.3	1.05×10^{-4} [c]	42
3. glycine ethyl ester	7.24	8.40×10^{-4}	6.76×10^{-3}	5.12×10^{-3} [c]	0.38	1.70×10^{-3} [c]	7.1
4. glycinamide	8.01	1.75×10^{-3}	3.21×10^{-3}	0.026	0.225	3.10×10^{-3} [c]	2.2
5. allylamine	9.08	4.29×10^{-3}	5.90×10^{-4}			1.59×10^{-2} [c]	0.96
6. 2-methoxyethylamine	9.11	4.47×10^{-3}	6.30×10^{-4}	3.9×10^{-2}	4.5×10^{-2}	1.62×10^{-2} [c]	0.91
7. *n*-butylamine	9.99	1.21×10^{-2}	2.20×10^{-4} [c]	0.147	1.93×10^{-2}	4×10^{-2}	0.26
8. morpholine	8.23	2.65×10^{-4}	2.85×10^{-4}	6×10^{-3}	4.1×10^{-2}	5.11×10^{-3} [c]	2.18
9. piperidine	10.38	5.28×10^{-3}	3.91×10^{-5} [c]	7.8×10^{-2}	4.2×10^{-3} [c]	0.15	0.36
10. OH^-	17.27	23.8	2.26×10^{-8} [d]	118	8.14×10^{-7} [d]	122	4.73×10^{-5} [d]

[a] I = 0.5 M NMe_4Cl, t = 25 °C; experimental error in the rate constants ±4% or better; in pK_a^{BH} and pK_a^{CH} ±0.05 pK unit; in the calculated rate constants ≤10%. [b] $k_p^{H_2O}/27.6$ with $k_p^{H_2O}$ calculated from K_a^{CH} k_{-p}^{H}. [c] Calculated from k_{-p}^{BH} or k_p^B via eq 10. [d] $k_{-p}^{H_2O}/27.6$ with $k_{-p}^{H_2O}$ calculated from $k_p^{OH}Ks/K_a^{CH}$ with pK_s = 15.83 (see Experimental Section).

constant, k_{obsd}, for the approach to equilibrium (2) is given by eq 3. In this equation k_p^{OH}, k_p^B, and $k_p^{H_2O}$ are the rate constants referring to the deprotonation of 1 by hydroxide ion, the buffer base species, and the solvent, respectively, while k_{-p}^{H}, k_{-p}^{BH}, and $k_{-p}^{H_2O}$ are the rate constants referring to the protonation of the carbanions **C-1** by hydronium ion, the buffer acid species, and the solvent, respectively.

The reactions were monitored by following spectrophotometrically the appearance or disappearance of the absorption of the stable conjugated carbanions **C1a–C1d** at or near λ_{max}, e.g., in 20% H_2O–80% Me_2SO: 740 nm ($\epsilon = 3.43 \times 10^4$ L·mol^{-1} cm^{-1}) for **C-1a**; 680 nm ($\epsilon = 2.83 \times 10^4$ L·mol^{-1} cm^{-1}) for **C-1b**; 666 nm ($\epsilon = 2.67 \times 10^4$ L·mol^{-1} cm^{-1}) for **C-1c**; 800 nm ($\epsilon = 2.16 \times 10^4$ L·mol^{-1} cm^{-1}) for **C-1d**. Depending upon the pH of the solutions studied, equilibrium (2) was approached from the reactant side (pH > pK_a^{CH}) or from the product side by means of pH-jump experiments (pH < pK_a^{CH}). In general, experiments were conducted at two and sometimes three buffer ratios with k_{obsd} being determined for each ratio at 6–8 different buffer concentrations (Tables S1 and S2).[7] In the various systems, e.g., the reactions of **1a** (pK_a^{CH} = 8.25) with glycinamide (pK_a^{BH} = 8.01) and of **1c** (pK_a^{CH} = 10.86) with piperidine (pK_a^{BH} = 10.38) in 50% H_2O–50% Me_2SO or the reactions of **1b** (pK_a^{CH} = 7.06) with glycine ethyl ester (pK_a^{BH} = 7.70) and **1c** (pK_a^{CH} = 8.96) with glycinamide (pK_a^{BH} = 8.69) and methoxyethylamine (pK_a^{BH} = 9.54) in 20% H_2O–80% Me_2SO, 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.

The procedures used in evaluating the various rate constants involved in eq 3 from the measured k_{obsd} values were essentially the same as those described in previous proton-transfer studies.[8-10] The results for the ionization of **1a–1c** in 50% H_2O–50% Me_2SO and of **1a–1d** in 20% H_2O–80% Me_2SO are summarized in Tables I and II, respectively. For buffers with $pK_a^{BH} > pK_a^{CH} + 1$ (or $pK_a^{BH} < pK_a^{CH} - 1$), the quoted k_{-p}^{BH} (or k_p^B) values were calculated by means of eq 4.

$$k_p^B = k_{-p}^{BH}\frac{K_a^{CH}}{K_a^{BH}} \qquad (4)$$

Discussion

Effect of Nitro Substitution on Equilibrium Acidities. On the basis of pK_a^{CH} measurements carried out in 30% H_2O–70% Me_2SO, we have previously discussed the changes in the acidity of the exocyclic CH group brought about by the successive introduction of an ortho nitro group into each of the phenyl rings of (4,4′,4″-trinitrotriphenyl)methane **1d**.[1] Assuming that the propeller arrangement of the three phenyl rings around the central sp^2-hybridized carbon is retained on going from the unsubstituted carbanion **C-1g** to the substituted triphenylmethyl analogs **C-1f–C-1a**, only one activated phenyl ring can be in the most favorable position for effective conjugation with this sp^2 carbon at any given time.[2-4,11] Accordingly, we have attributed the relatively strong increase in acidity (ΔpK^{CH} = 2.96) observed in this solvent mixture on going from **1d** to **1c** to the fact that the tetranitro carbanion **C-2c** can benefit from a preferential stabilization of its negative charge by the more activated 2,4-dinitrophenyl ring. In accord with the above idea that conjugation of the exocyclic sp^2 carbon with more than one 2,4-dinitrophenyl ring is not possible, the changes in the acidity caused by the introduction of more *o*-nitro groups in **1c** to give **1b** and **1a** were reduced: $\Delta pK_{a\,1c}^{\,1b}$ = 2.25; $\Delta pK_{a\,1b}^{\,1a}$ = 0.48 in 70% Me_2SO.

The pK_a^{CH} values measured in 80% Me_2SO lead to a similar ΔpK_a pattern with, however, a much greater effect of the first *o*-nitro group ($\Delta pK_{a\,1d}^{\,1c}$ = 3.88) than was found in 70% Me_2SO. This result is the reflection of the increase in the Me_2SO content of the mixtures. In the field of carbon acids, a decrease in the pK_a values on transfer from water to Me_2SO is normally observed for compounds giving rise to carbanions with highly delocalized negative charge.[1,5c,12-16] In this regard, it is noteworthy that the pK_a^{CH} values for the ionization of **1a**, **1b**, and **1c**, which all benefit from a possible delocalization of the negative charge of their conjugated carbanions through a dinitrophenyl ring, are decreased to about the same extent on going from 70 to 80% Me_2SO ($\Delta pK_a \approx$ 0.7–0.9). In contrast, the pK_a value for the less acidic trinitro derivative **1d**, which gives a carbanion stabilized by delocalization of

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[7] See paragraph concerning supplementary material at the end of this paper.

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Table II. Rate Constants for the Ionization of (2,2′,2″,4,4′,4″-Hexanitrotriphenyl)-, (2,2′,4,4′,4″-Pentanitrotriphenyl)-, (2,4,4′,4″-Tetranitrotriphenyl)-, and (4,4′,4″-Trinitrotriphenyl)methanes in 20% H_2O–80% Me_2SO[a]

buffer (basic species)	pK_a^{BH}	1a (pK_a^{CH} = 6.53)		1b (pK_a^{CH} = 7.06)		1c (pK_a^{CH} = 8.96)		1d (pK_a^{CH} = 12.84)	
		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_2O	−1.05	$5.63 \times 10^{-8\,b}$	2.12	$3.30 \times 10^{-7\,b}$	42.2	$6.86 \times 10^{-8\,b}$	695	$5.51 \times 10^{-10\,b}$	4.2×10^{4}
2. aminoacetonitrile	5.64	4.5×10^{-3}	3.15×10^{-2}	$6.84 \times 10^{-3\,c}$	0.18	$4.02 \times 10^{-3\,c}$	8.4	$3.47 \times 10^{-5\,c}$	550
3. glycine ethyl ester	7.70	1.6×10^{-2}	$1.08 \times 10^{-3\,c}$	3.5×10^{-2}	8.2×10^{-3}	$8.29 \times 10^{-2\,c}$	1.51	$8.91 \times 10^{-4\,c}$	123
4. glycinamide	8.69	2.5×10^{-2}	$1.73 \times 10^{-4\,c}$	0.152	$3.56 \times 10^{-3\,c}$	0.22	0.33	$3 \times 10^{-3\,c}$	42.5
6. 2-methoxyethylamine	9.54	6×10^{-2}	$5.86 \times 10^{-5\,c}$	0.31	$1.02 \times 10^{-3\,c}$	0.51	0.17	$1.16 \times 10^{-2\,c}$	23.25
7. *n*-butylamine	10.27	0.11	$2 \times 10^{-5\,c}$	0.59	$3.64 \times 10^{-4\,c}$	1.17	$5.7 \times 10^{-2\,c}$	$2.96 \times 10^{-2\,c}$	11
8. morpholine	8.48	4.85×10^{-3}	$5.44 \times 10^{-5\,c}$	3.2×10^{-2}	$1.21 \times 10^{-3\,c}$	0.20	0.60	$3.05 \times 10^{-3\,c}$	70
9. piperidine	10.16	1.54×10^{-2}	$3.6 \times 10^{-6\,c}$	0.2	$1.58 \times 10^{-4\,c}$	1.23	$7.7 \times 10^{-2\,c}$	$3.11 \times 10^{-2\,c}$	14.88
11. 2-cyanophenoxide ion	9.53	1.10	$1.1 \times 10^{-3\,c}$	2.32	$7.86 \times 10^{-3\,c}$	4.5	1.5	$7.15 \times 10^{-2\,c}$	146
12. 4-cyanophenoxide ion	10.22	1.58	$3.22 \times 10^{-4\,c}$	4.7	$3.25 \times 10^{-3\,c}$	8.05	0.44^{c}	0.164^{c}	68.5
13. 2-bromophenoxide ion	11.37	5.62	$8.12 \times 10^{-5\,c}$	20.2	$9.89 \times 10^{-4\,c}$	50.12	0.20^{c}	0.82^{c}	24.24
14. 4-chlorophenoxide ion	12.45	8.1	$9.73 \times 10^{-6\,c}$	35.5	$1.45 \times 10^{-4\,c}$	160	$5.2 \times 10^{-2\,c}$	4.2	11.5
15. phenoxide ion	13.59	40	$3.47 \times 10^{-6\,c}$	165	$4.87 \times 10^{-5\,c}$	530	$1.24 \times 10^{-2\,c}$	16	3
10. OH^-	21.21	2220	$4.58 \times 10^{-12\,d}$	16 300	$1.14 \times 10^{-10\,d}$	15 200	$8.43 \times 10^{-9\,d}$	2160	$9.1 \times 10^{-6\,d}$

[a] I = 0.5 M NMe_4Cl; t = 25 °C; experimental error in the rate constants ±4% or better; in pK_a^{BH} and pK_a^{CH} ± 0.05 pK units; in the calculated rate constants ≤10%. [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 eq 10. [d] $k_{-p}^{H_2O}/11.11$ with $k_{-p}^{H_2O}$ calculated from $k_p^{OH}K_s/K_a^{CH}$ with pK_s = 20.17 (see Experimental Section).

its negative charge through a less activated 4-nitrophenyl ring, is essentially unaffected by the solvent transfer (ΔpK_a = 0.05). This behavior accounts for the greater $\Delta pK_{a\,1d}^{1c}$ value found in 80% Me_2SO.

Effect of Nitro Substitution on Kinetic Acidities. Evidence for F-Strain. Inspection of Tables I and II shows that the regular increase in the thermodynamic acidity that we observed on going from **1d** to **1a** is not paralleled by a similar regular increase in the rates of proton abstraction by hydroxide ion (k_p^{OH}) or any other base (k_p^B, $k_p^{H_2O}$). In 80% Me_2SO, introduction of a first *o*-nitro group in **1d** to give **1c** increases the rate constant k_p^{OH} by a factor of 7 whereas generating a large pK_a decrease (ΔpK_a = 3.88). A most unexpected feature, however, is the finding that k_p^{OH} remains essentially unchanged on addition of the second *o*-nitro group to form **1b** and then decreases by a factor of 5–7 on introduction of the third *o*-nitro group to give the more acidic derivative **1a**. Even more significant changes are observed in looking at the k_p^B values pertaining to the deprotonation of **1a**–**1d** by all amines and phenoxide anions used as base catalysts. Thus, following a marked (30-fold) increase on going from the trinitro (**1d**) to the tetranitro (**1c**) compound, the k_p^B value for unsubstituted phenoxide ion decreases by a factor of 3 on going from **1c** to the pentanitro (**1b**) derivative before suffering another 4-fold decrease on addition of the last *o*-nitro group to form the hexanitro (**1a**) compound.

Before suggesting an explanation for the anomalous variations in k_p^B, it is of interest to consider the concomitant effect of the nitrosubstitution on the rates of carbanion reprotonation (k_{-p}^H, k_{-p}^{BH}, $k_{-p}^{H_2O}$). Such rate constants are known to be normally governed by the extent of charge delocalization.[1,8] First, Table II shows that the addition of the first *o*-nitro group to **1d** to give **1c** results in a large (ca. 100-fold) decrease in the k_{-p} rate constants. This important decrease is consistent with the much greater charge stabilization of the carbanion **C-1c** by a 2,4-dinitrophenyl ring than of the carbanion **C-1d** by a 4-nitrophenyl ring. Contrasting with this behavior, the large changes in k_{-p} observed on going from **1c** to **1b** to **1a**, e.g., k_{-p}^{BH} (**1c**)/k_{-p}^{BH} (**1b**) = 487 and k_{-p}^{BH} (**1b**)/k_{-p}^{BH} (**1a**) = 44 for reprotonation by piperidinium ion in 80% Me_2SO, cannot be understood in terms of an increased resonance stabilization of the carbanions **C-1b** and **C-1a** compared to the carbanion **C-1c**. Effective conjugation of the exocyclic sp^2 carbon occurs with one 2,4-dinitrophenyl ring in the three species.

We suggest that the more reasonable explanation for the above anomalous variations in the k_p and k_{-p} values is in terms of additional unfavorable steric interactions arising from the accumulation of *o*-nitro groups in the triphenylmethane system. On the basis of the observed trends, these steric interactions are clearly operating both in the starting carbon acids and in the carbanions and can be viewed as steric hindrance to the approach of the base (OH^-, ArO^-, RNH_2, RR′NH, H_2O) or acid (H_3O^+, ArOH, RNH_3^+ $RR'NH_2^+$, H_2O) reagent to exocyclic carbon (F-strain).

Brönsted Plots. Figures 1 and 2 show that satisfactory Brönsted plots are obtained on plotting the log k_p^B values for deprotonation of a given carbon acid by a homogeneous family of bases. This suggests that the steric factors pertaining to the reactions remain essentially constant when the basicity of the reagent is varied within a particular series of catalysts. The fact that three distinct Brönsted lines referring to phenoxide ions and primary and secondary amines can be drawn for each carbon system is in accord with many previous findings that structurally different base catalysts of similar pK_a's can exhibit ap-

Table III. Bönsted Coefficients and Intrinsic Rate Constants for the Ionization of the Triphenylmethanes 1a–1d in 50% H_2O–50% Me_2SO and 20% H_2O–80% Me_2SO

basic species, B		hexanitro **1a**	pentanitro **1b**	tetranitro **1c**	trinitro **1d**
		50% H_2O–50% Me_2SO			
	pK_a^{CH}	8.25	9.11	10.86	
RNH_2	β_B	0.47 ± 0.01	0.53 ± 0.03	0.55 ± 0.01	–
	log k_o	−2.95 ± 0.02	−1.55 ± 0.06	−1.15 ± 0.02	–
RR′NH	β_B	0.60 ± 0.04	0.52 ± 0.03	0.67 ± 0.06	–
	log k_o	−3.75 ± 0.10	−1.95 ± 0.05	−0.70 ± 0.15	
		20% H_2O–80% Me_2SO			
	pK_a^{CH}	6.53	7.06	8.96	12.84
RNH_2	β_B	0.30 ± 0.04	0.43 ± 0.02	0.53 ± 0.02	0.63 ± 0.01
	log k_o	−2.42 ± 0.10	−1.87 ± 0.05	−0.82 ± 0.03	−0.15 ± 0.05
RR′NH	β_B	0.30 ± 0.02	0.47 ± 0.02	0.47 ± 0.03	0.60 ± 0.03
	log k_o	−3.02 ± 0.05	−2.25 ± 0.05	−0.65 ± 0.08	0 ± 0.10
ArO^-	β_B	0.40 ± 0.04	0.44 ± 0.02	0.53 ± 0.02	0.59 ± 0.01
	log k_o	−1.20 ± 0.10	−0.82 ± 0.05	0.35 ± 0.05	0.75 ± 0.03

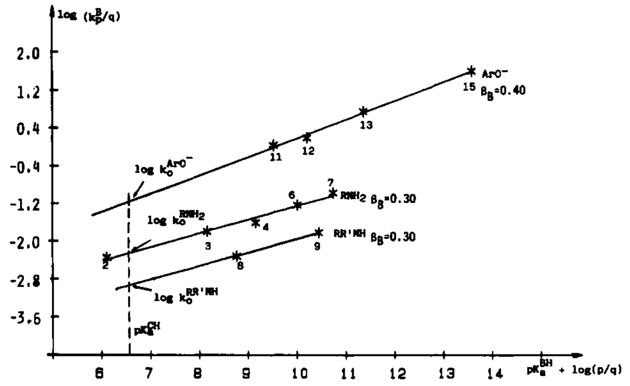

Figure 1. Statistically corrected Brönsted plots for the deprotonation of **1a** by phenoxide and amine bases in 20% H_2O–80% Me_2SO (v/v), t = 25 °C, I = 0.5 M NMe_4Cl. The numbering of the catalysts is indicated in Table II.

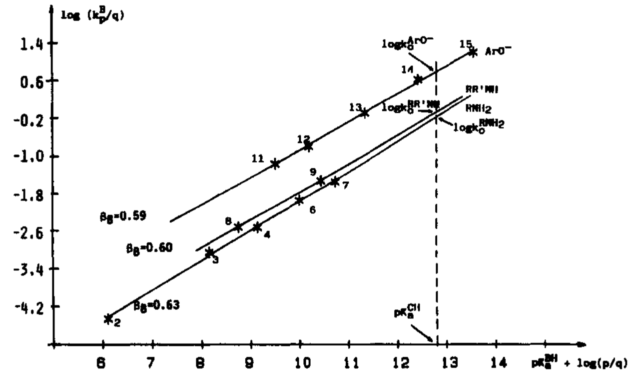

Figure 2. Statistically corrected Brönsted plots for the deprotonation of **1d** by phenoxide and amine bases in 20% H_2O–80% Me_2SO (v/v), t = 25 °C, I = 0.5 M NMe_4Cl. The numbering of the catalysts is indicated in Table II.

preciable differences in the efficiency with which they assist proton transfers to/from a carbon atom.[1,5,7-9,17-21]

There is, however, an unusual result which emerges from a comparison of the Brönsted plots in Figures 1 and 2. It is the fact that the differences in the catalytic efficiencies of the three classes of catalysts show major variations on going from the trinitro-substituted triphenylmethane **1d** to the hexanitro-substituted triphenylmethane **1a**. Figure 2 exemplifies the reactivity sequence $ArO^- > RR'NH > RNH_2$ found for **1c** and **1d**, consistent with the behavior commonly found in the ionization of carbon acids.[1,5,8,9,17-23] The greatest reactivity of secondary amines compared to primary amines is now a well-known phenomenon that has been explained by the fact that the solvation of ammonium ions decreases in the order $RNH_3^+ > RR'NH_2^+$, coupled with a late development of this solvation along the reaction coordinate.[1,5,19,23] In contrast, Figure 1 shows the reactivity order $ArO^- > RNH_2 > RR'NH$ which is observed for **1a** and **1b**. While occasional anomalies in the relative reactivities of these two classes of catalysts have been reported,[18a,21a,24] large inversions of this type are rare and there is no doubt that they are the reflection of the increased steric effects to the approach of the exocyclic carbon of **1a** and **1b** caused by the accumulation of *o*-nitro groups in the three phenyl rings. The phenomenon is expected to be more accentuated for the more bulky secondary amines than for the primary amines, accounting for the observed reactivity pattern.

When considering the role of steric effects in governing the reactivity of the triphenylmethane derivatives **1a**–**1d**, it is interesting to recall that the $k_p^{RR'NH}/k_p^{RNH_2}$ ratios which measure the reactivity difference between secondary and primary amines are generally in the range 5–10 for the ionization of carbon acids.[5,19,20,25] That these ratios are equal to 0.4 and 0.2 in the case of **1b** and **1a**, respectively, gives a measure of the importance of the F-strain effect in these derivatives. In addition, it is perhaps of significance to note that secondary amines are only slightly more reactive than primary amines in the deprotonation reactions of **1c** and **1d**: $k_p^{RR'NH}/k_p^{RNH_2} \approx 1.5$ in both systems. This low value suggests that F-strain is probably operating to some extent in the reactions involving a triphenylmethane derivative like **1d** which has no *o*-nitro substituents. A similar conclusion was previously formulated by Streitwieser and Hammons who found that the rate of hydrogen isotope exchange of triphenylmethane is slower

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than expected from a log k_{exch} vs pK_a correlation established for different hydrocarbons.[26]

Table III shows that the Brönsted β_B values for primary and secondary amines, as well as phenoxide anions, tend to decrease on going from **1d** (β_{RNH_2} = 0.63; $\beta_{RR'NH}$ = 0.60; β_{ArO^-} = 0.59) to **1a** (β_{RNH_2} = 0.30; $\beta_{RR'NH}$ = 0.30; β_{ArO^-} = 0.40) in 80% Me_2SO, i.e., going from the less to the more thermodynamically favored reactions. This trend is consistent with the reactivity–selectivity principle.[19d,27] In contrast, a comparison of the results obtained for the ionization of **1a**–**1c** by primary and secondary amines in the two solvent mixtures studied reveals a rather uncommon solvent dependence of the β_B values. In all carbon acid systems previously studied in H_2O–Me_2SO mixtures,[19b–e] β_B was found to increase with increasing Me_2SO content. Since measurements of solvent activity coefficients have revealed that the solvent effect on the stability of ammonium ions tends to increase with decreasing the p$K_a^{NH^+}$ values,[5,19b,e,28] the increase in β_B was readily understood as a solvation effect.[5,28] In the present triphenylmethane systems, the β_B values pertaining to the two classes of amine catalysts are subject to a marked decrease on going from 50 to 80% Me_2SO, the effect being especially important in the case of **1a**, i.e. β_{RNH_2} = 0.47 and 0.30 in 50 and 80% Me_2SO, respectively. This behavior suggests that a new factor is playing a major role in our systems which was not present in earlier studies. Since the major difference between the triphenylmethane derivatives and other carbon acids considered so far is the large steric hindrance, one possible explanation for the abnormal solvent dependence of β_B is that this steric hindrance influences the timing of the solvation of the developing ammonium ions.

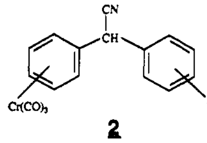
While it is clear that more information regarding the effect of such solvent transfers on the β_B values in highly crowded systems is needed before one can speculate further on the above suggestion, it is interesting to emphasize another puzzling observation regarding the Brönsted β_B values for the **1a** system. As pointed out in an earlier paper,[29] the β_{RNH_2} and $\beta_{RR'NH}$ values for ionization of **1a** are markedly different in 50% Me_2SO (β_{RNH_2} = 0.47; $\beta_{RR'NH}$ = 0.60). Notwithstanding that the $\beta_{RR'NH}$ values correspond to two-point Brönsted slopes so that their significance is perhaps questionable, we note in Table III that this difference in the two parameters disappears on going to 80% Me_2SO (β_{RNH_2} = 0.30; $\beta_{RR'NH}$ = 0.30). In general, β_{RNH_2} and $\beta_{RR'NH}$ for deprotonation of carbon acids are essentially similar,[1,5,19–25] as it is actually found for the **1b**–**1d** systems. Since **1a** is the most crowded triphenylmethane in our series, it seems again reasonable to attribute the different β_{RNH_2} and $\beta_{RR'NH}$ values for this derivative in 50% Me_2SO to the exceptional steric hindrance which prevails in **1a**.

Intrinsic Reactivities. Intrinsic rate constants (in the Marcus sense)[5,6,28] for **1a**–**1d**, obtained from Brönsted plots as $k_o = k_p^B/q$ when pK_a^{BH} + log p/q = pK_a^{CH} are given in Table III. These rate constants are remarkably low compared with those reported for a number of carbon acids in H_2O–Me_2SO mixtures.[5,19,20,25] We note in particular that the log k_o values measured with reference to ionization of **1a**–**1d** by primary or secondary amines are all ≤0 and 2–4 orders of magnitude lower than those reported for nitro-substituted benzylic-type carbon acids under similar experimental conditions, e.g., log $k_o^{RR'NH}$ = −0.25 and +1.75 for phenylnitromethane in 50 and 90% Me_2SO, respectively;[19c] log $k_o^{RR'NH}$ = +2.70 and +3.70 for (2,4-dinitrophenyl)acetonitrile and (4-nitrophenyl)acetonitrile, respectively, in 50% Me_2SO.[19a] The log $k_o^{RR'NH}$ value for **1a** in 50% Me_2SO reflects one of the highest intrinsic barriers ever observed for the ionization of a carbon acid.[5,28]

In the absence of steric effects, low intrinsic rate constants are normally observed in those carbon acid ionizations that either occur with extensive solvent reorganization and/or give rise to highly delocalized sp2-hybridized carbanions.[5,8,19,20,28] As mentioned previously, the unsubstituted triphenylmethyl carbanion **C-1g** (λ_{max} = 495 nm in Me_2SO)[30] can be considered to be considerably delocalized with a propeller-like conformation, giving maximum delocalization possible with the steric inhibition of the rings to full coplanarity.[2–4,11] Introduction of the *p*-nitro groups in **C-1g** to form **C-1d** should not markedly affect this conformational situation while enhancing the resonance stabilization of the negative charge of the carbanion. The finding that **C-1d** is a very stable species and has an intense absorption maximum at λ = 800 nm in 80% Me_2SO supports this idea. There is therefore little doubt that the formation of this carbanion involves considerable structural-electronic-solvational reorganization and that it is this factor which contributes for the most part to the low intrinsic reactivity of **1d**. Steric hindrance to approach of base reagents from the exocyclic carbon will not be the overriding factor determining the intrinsic barrier in this case.

Going from **1d** to **1c** results in a 4-fold reduction in k_o with no concomitant change in the relative catalytic efficiencies of primary and secondary amines. Accordingly, this lowering of k_o can be understood in terms of the additional resonance stabilization of the negative charge caused by the presence of a 2,4-dinitrophenyl ring in **C-1c**. In contrast, there is no way of accounting for the further and important decreases in k_o that we observe on going from **1c** to **1b** (Δ log $k_o^{RR'NH}$ = −1.60) to **1a** (Δ log $k_o^{RR'NH}$ = −0.77) on the basis of an increased resonance stabilization of the carbanions **C-1b** and **C-1a**. These important decreases must therefore originate from the unfavorable steric effects discussed above.

While steric hindrance has been postulated in the ionization reactions of some diphenylmethanes derivatives, e.g., **2**[31] or **3**,[8a] the effect on k_o was found to be rather small and did not result in marked changes in the relative reactivities of catalysts like primary and secondary amines. Our finding that k_o undergoes a significant lowering on going from **1d** to **1a** is therefore of particular interest in the understanding of the factors affecting the intrinsic reactivities of carbon acids.



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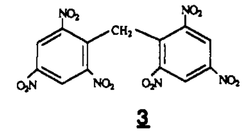

3

Experimental Section

Materials. All four (nitrotriphenyl)methanes **1a**–**1d** were available from a recent study.[1] Solvents were purified and solutions made up as described previously.[20] Buffers were purified commercial products.

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Measurements. Fast kinetic measurements were carried out with a Durrum stopped-flow spectrophotometer equipped with a thermostated cell compartment (25 ± 0.2 °C). Slow rates were measured with a conventional UV–vis Kontron Uvikon spectrophotometer. All rates were reproducible to within ±3% or better. pH Determinations in water–Me_2SO mixtures containing 0.5 M NMe_4Cl were carried out at 25 °C using the same procedure as that previously described.[20] A Tacussel Isis 20000 electron pH meter was used for this purpose. The autoprotolysis constants of the 50% H_2O–50% Me_2SO–0.5 M NMe_4Cl and 20% H_2O–80% Me_2SO–0.5 M NMe_4Cl mixtures were known from previous studies: $pK_s = 15.83$ and 20.17 in 50% and 80% Me_2SO, respectively, at 25 °C.[1,16,20]

Acknowledgment. We are grateful to Professeur C. F. Bernasconi for helpful suggestions during the preparation of this article.

Registry No. **1a**, 3626-18-4; **1b**, 80134-75-4; **1c**, 132283-06-8; **1d**, 603-49-6; aminoacetonitrile, 540-61-4; glycine ethyl ester, 459-73-4; glycinamide, 598-41-4; 2-methoxyethylamine, 109-85-3; *n*-butylamine, 109-73-9; morpholine, 110-91-8; piperidine, 110-89-4; 2-cyanophenoxide ion, 72332-14-0; 4-cyanophenoxide ion, 14609-76-8; 2-bromophenoxide ion, 1121-17-1; 4-chlorophenoxide ion, 24573-38-4; phenoxide ion, 3229-70-7.

Supplementary Material Available: Kinetic data in the form of Tables S1–S2 (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Polar Effects in Reactions of Carbon-Centered Radicals with Diazonium Salts: Free-Radical Diazocoupling

Francesco Minisci,* Fausta Coppa, Francesca Fontana, Giuseppe Pianese, and Lihua Zhao

Dipartimento di Chimica del Politecnico, piazza Leonardo da Vinci 32, 20133 Milano, Italy

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Carbon-centered radicals react with diazonium salts by addition, leading under reductive conditions to azo derivatives (free-radical diazocoupling), or by electron-transfer in chain processes. The reaction is highly sensitive to polar effects and it has been investigated by three different processes: (i) alkyl radicals, generated from alkyl iodides, H_2O_2, Fe(II) salt, and DMSO, have been utilized to develop a new general synthesis of alkylarylazo compounds; (ii) the reaction of aryl radicals with diazonium salts in the presence of Ti(III) or Fe(II) salts has been investigated, also in relation to the fact that the reaction products (azoarenes and biaryls) are often detected as side products in classical organic reactions of diazonium salts, catalyzed by Cu(I) salts, such as the Sandmeyer, Meerwein, and Pschorr reactions; (iii) adducts from addition of aryl radicals to vinyl acetate or vinyl ether react with diazonium salts either by diazocoupling reaction or by electron-transfer; a general synthesis of [α-(acyloxy)alkyl]arylazo compounds has been developed.

Polar effects in free-radical reactions are particularly marked when charged species are involved; in these cases, highly selective syntheses can be achieved.[1] In this account we report new syntheses of azo compounds by reductive addition of carbon-centered radicals to diazonium salts; the role of polar effects in such reactions is discussed.

Results

(i) Diazocoupling of Diazonium Salts by Alkyl Iodides, H_2O_2, Fe(II) Salts, and DMSO. A new reaction leading to alkylarylazo compounds has been developed according to eq 1

$$ArN_2^+ + RI + MeSOMe + H_2O_2 + 2Fe^{2+} \rightarrow ArN{=}NR + MeI + MeSO_2H + 2Fe^{3+} + OH^- \quad (1)$$

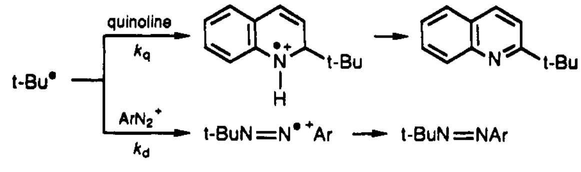
The reaction was carried out in DMSO at 0–5 °C; it proved suitable for primary, secondary and tertiary alkyl iodides, as shown by the results reported in Table I, while the presence of electron-withdrawing groups in the α-position on the alkyl iodide (e.g. ICH_2COOR, ICH_2COCH_3, ICH_2CN, $ICH(COOR)_2$, etc.) prevents the formation of the azo compound.

A competitive experiment, performed in the presence of protonated quinoline (Scheme I) allowed us to evaluate the rate constant for the addition of the *tert*-butyl radical to the diazonium salt.

Table I. Formation of RN=NAr According to eq 1

Ar	R	procedure	yield, %
Ph	t-Bu	A	68
Ph	t-Bu	B	62
Ph	i-Pr	A	51
Ph	i-Pr	C	65
Ph	i-Bu	C	61
p-ClPh	t-Bu	A	70
p-ClPh	t-Bu	B	63
p-ClPh	cyclohexyl	A	56
p-ClPh	i-Pr	C	66
p-MePh	t-Bu	B	63
p-MePh	cyclohexyl	C	62
p-MePh	i-Pr	A	52
p-MeOPh	t-Bu	A	54
p-MeOPh	cyclohexyl	A	46
o-ClPh	t-Bu	A	72
o-ClPh	cyclohexyl	C	64
o-ClPh	i-Pr	C	66
o-ClPh	n-Bu	C	36

Scheme I



The *p*-chlorobenzenediazonium salt proved to be 12.2 times more reactive than protonated quinoline toward the *tert*-butyl radical, and from the known value of k_q (4.1 ×

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