The low intrinsic reactivity of picrylacetone: an index for the π-acceptor capability of a 2,4,6-trinitrophenyl structure

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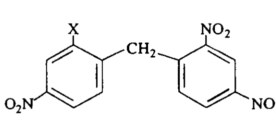
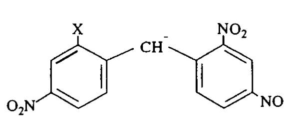
Rates of deprotonation of picrylacetone, *i.e.*, 2,4,6-trinitrophenylacetone 4, by a variety of bases B (phenoxide and carboxylate ions, OH^-) and of protonation of the resulting carbanion (C-4) by the conjugated acids BH^+ have been measured in a 50%H_2O–50%Me_2SO (v/v) mixture at 25 °C. The intrinsic reactivity (in the Marcus sense) of 4, as determined from the Brønsted plot for phenoxide reactions ($\beta^{ArO} = 0.38$) is low: $\log k_0^{ArO} = 2.37$. This value is more typical for the formation of a strongly resonance-stabilized benzyl-type carbanion than for that of an enolate-type carbanion and it may be regarded as a good measure of the high π-acceptor capability of a conjugated 2,4,6-trinitrophenyl structure. Definitive evidence that the negative charge of C-4 is essentially delocalized through the picryl moiety comes from the observation that this carbanion undergoes instantaneous protonation at its *p*-nitro group at low pH (pH < 6). The pK'_a value associated with the ionization of the resulting nitronic acid (C-4H) is ≈5, which compares well with similar data previously reported in the literature.

Introduction

It is now well recognized that there is a close though inverse relationship between the intrinsic reactivity (in the Marcus sense) of a carbon acid and the importance of the structural and solvational reorganization that is required to form the conjugate carbanionic species.[1,2] The greater the resonance stabilization of the resulting carbanion, the greater, in general, are the structural and solvation changes involved in the ionization process and the lower the intrinsic reactivity ($\log k_0$) of the carbon acid.[1–3] On this basis, the location of the intrinsic reactivity of a given carbon acid on the $\log k_0$ scale can help clarify the electronic mode of action of its activating structure.[4–6]

In recent years, we have paid attention to benzylic-type structures which give rise to conjugate carbanions with a high potential for delocalization of the negative charge through remote electron-withdrawing groups.[7,8] The ionization of (2,4-dinitrophenyl)(4-nitrophenyl)methane 1 and bis(2,4-dinitrophenyl)methane 2 is representative of such systems. As evidenced by NMR and UV–VIS spectroscopy,[7] it affords essentially planar carbanions (C-1, C-2) whose negative charge is highly dispersed over the two phenyl rings, as illustrated by resonance contributors A–D. Consistent with the idea that the formation of C-1 and C-2 occurs along with an extensive structural reorganization, was the finding that the deprotonation of 1 and 2 is associated with intrinsic barriers which are amongst the highest so far measured for carbon acids; for ionization by phenoxide bases: $\log k_0 = 0.50$ for 1; $\log k_0 = 0$ for 2 in 50% H_2O–50%Me_2SO.[8b]

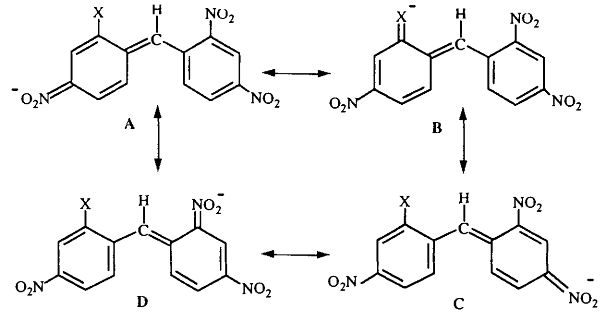




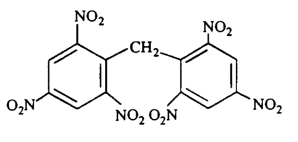
1 X=H C-1

2 X=NO_2 C-2

Although there is ample evidence of its strong ability to accommodate a negative charge, notably in σ-adduct formation and related nucleophilic aromatic substitution processes,[9] the π-acceptor capability of a 2,4,6-trinitrophenyl moiety has not been assessed by means of the $\log k_0$ scale for carbon acids. Owing to its tendency to undergo base addition at C3 prior to or concomitantly with ionization of its methyl group, as well as to the relatively low equilibrium constants associated with the two processes in protic media, the intrinsic reactivity of 2,4,6-trinitrotoluene (TNT) is difficult to measure directly.[10–13] Following our study of 1 and 2, we recently looked at the ionization behaviour of bis(2,4,6-trinitrophenyl)methane 3. In this system, the presence of the four *ortho*-nitro groups prevents mutual coplanarity of the two phenyl rings in the conjugate carbanion C-3. Hence, charge delocalization can occur in only one of the two picryl rings at a given time, making it possible to consider 3 as an α-(2,4,6-trinitrophenyl)-substituted 2,4,6-trinitrotoluene. Interestingly, a low $\log k_0$ value was measured, using phenoxide bases, for this derivative ($\log k_0^{ArO} = 1.75$ in 50%H_2O–50%Me_2SO) but whether this value is really a good reflection of the π-acceptor capability of a 2,4,6-trinitrophenyl moiety or not needed further confirmation.[8b]



In this paper we report a kinetic and thermodynamic study of the ionization of picrylacetone, *i.e.*, 2,4,6-trinitrophenylacetone 4, by hydroxide ion and various phenoxide and carboxylate anions in 50%H_2O–50%Me_2SO [eqn. (1)]. In accordance with the idea that the negative charge of the resulting carbanion is essentially delocalized through the picryl ring, we report kinetic and spectroscopic evidence that C-4 undergoes instantaneous protonation at its *p*-nitro group to give a nitronic acid in



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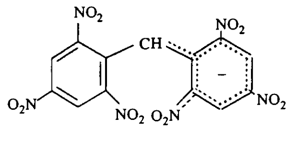
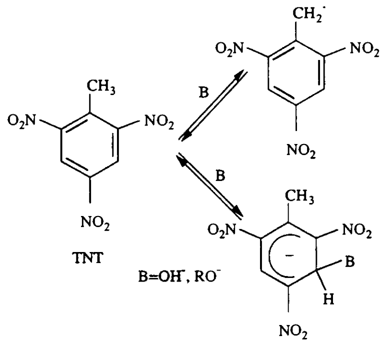
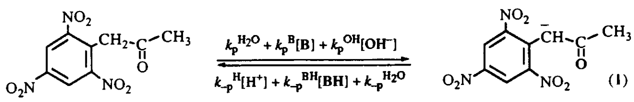


C-3





4 C-4

solutions of low pH. Based on this, it is suggested that the low intrinsic reactivity measured for **4** provides an appropriate measure of the strong $-M$ effect of a conjugated 2,4,6-trinitrophenyl structure.

Results

General features

All rate and equilibrium measurements pertaining to the reversible deprotonation of **4** according to the general equation (1) were carried out in 50%H$_2$O–50%Me$_2$SO (v/v) at 25 °C and constant ionic strength of 0.5 mol dm^{-3} maintained with KCl. Pseudo-first-order conditions were used throughout with a large excess of the buffer, base or acid reagents over the substrate concentration (3 × 10^{-5} mol dm^{-3}). In eqn. (1), k_p^{OH}, k_p^B and $k_p^{H_2O}$ are the rate constants referring to the deprotonation of **4** by hydroxide ion, the buffer base species (B = ArO$^-$, RCOO$^-$) and the solvent, respectively, while k_{-p}^H, k_{-p}^{BH} and $k_{-p}^{H_2O}$ are the rate constants referring to the reprotonation of C-**4** by hydronium ion, the buffer acid species (BH = ArOH, RCOOH) and the solvent, respectively. Use of most primary and secondary amine buffers was precluded because of the high ability of a 2,4,6-trinitrophenyl moiety to undergo fast covalent addition of the amine reagent at an unsubstituted ring position to form relatively stable σ-adducts.[9a,14,15]

pK_a^{CH} of picrylacetone 4

The pK_a^{CH} of **4** was determined from the observed absorbance variations at λ_{max} of C-**4** (491 nm) obtained at equilibrium as a function of pH. In accordance with eqn. (2), an excellent

$$\log\frac{\text{C-4}}{4} = \text{pH} - \text{p}K_a^{CH} \qquad (2)$$

straight line with unit slope was obtained on plotting the ratio of ionized to un-ionized **4** as a function of pH (Fig. 1). We thus readily obtained pK_a^{CH} = 8.02 ± 0.04 for **4**.

Reaction of 4 in NMe$_4$OH and phenol buffer solutions

In agreement with the direct equilibrium approach according to eqn. (1), oscilloscope traces of the reaction progress obtained in stopped-flow experiments revealed that only one relaxation time is associated to the interconversion of **4** and C-**4** in phenol buffer and dilute NMe$_4$OH solutions. Table S$_1$ summarises the observed pseudo-first-order rate constants, k_{obsd}, measured under the different experimental conditions studied.†

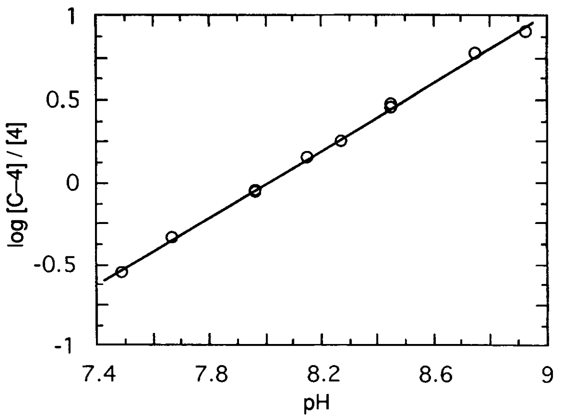


Fig. 1 Variation of the ratio of ionized to unionized picrylacetone **4** as a function of pH in 50%H$_2$O–50%Me$_2$SO (v/v); T = 25 °C, I = 0.5 mol dm^{-3} KCl

Table 1 Observed first-order rate constants, k_{obsd}, for the ionization of **4** in dilute NMe$_4$OH solutions in 50%H$_2$O–50%Me$_2$SO at 25 °C

[OH$^-$]/10^{-3} mol dm^{-3}	k_{obsd}/s^{-1}
1	8
2	25
2.5	27
3	36
4	47
5	62
6	70
7	85
7.5	88
8	94

From the k_{obsd} values obtained in NMe$_4$OH solutions (Table 1), an excellent straight line fitting the simple eqn. (3) was

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

obtained (not shown). From the slope, one could readily determine k_p^{OH} = 11 830 dm^3 mol^{-1} s^{-1}. Since the intercept was negligible, the rate constant $k_{-p}^{H_2O}$ was calculated from $k_{-p}^{H_2O} = k_p^{OH}(K_s/K_a^{CH})$ where K_s is the autoprotolysis constant of the 50:50 (v/v) H$_2$O–Me$_2$SO mixture at I = 0.5 mol dm^{-3} (pK_s = 15.83 at 25 °C):[8a] $k_{-p}^{H_2O}$ = 1.83 × 10^{-4} s^{-1}.

Analysis of the data in Table S$_1$ indicated that only the buffer pathways were important in determining k_{obsd} in the pH range 7.67–11.47 covered by the various phenol buffers employed. In agreement with eqn. (4), all plots of k_{obsd} *vs.* [B] at constant pH

$$k_{obsd} = k_p^B[B] + k_{-p}^{BH}[BH] = \left(k_p^B + \frac{k_{-p}^{BH}}{p}\right)[B] \qquad (4)$$

were linear with negligible intercepts and it is only in the relatively acidic 2-cyano- and 4-cyano-phenol buffer systems (pK_a^{BH} ≈ pK_a^{CH}) that a pH dependence of the slopes was also observed (Fig. 2). In these instances, the individual rate

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† Tables S$_1$–S$_3$ have been deposited with the British Library Sup. Pub. No. 57115 (5 pp.). For details of the supplementary publications scheme, see 'Instructions for Authors', (1996), *J. Chem. Soc., Perkin Trans. 2*, in the January issue.

Table 2 Second-order rate constants for the ionization of **4** in 50%H_2O–50%Me_2SO (v/v)[a]

Entry	Buffer (BH)	pK_a^{BH} [b]	$k_p^B/dm^3\ mol^{-1}\ s^{-1}$	$k_{-p}^{BH}/dm^3\ mol^{-1}\ s^{-1}$
1	2-cyanophenol	7.97	210	240
2	4-cyanophenol	8.45	355	132
3	2-bromophenol	9.52	795	25.1[c]
4	4-chlorophenol	10.18	1580	10.93[c]
5	phenol	11.21	3400	2.19[c]
6	4-methoxyphenol	11.47	4460	1.58[c]
7	methoxyacetic acid	4.65	11.09[c]	2.6×10^4
8	acetic acid	5.84	15.19[c]	2300
9	H_2O	17.34	11 830	6.6×10^{-6} [d]

[a] $I = 0.5$ mol dm^{-3} KCl; $T = 25$ °C; experimental error in the rate constants ± 5% or better; in pK_a^{BH}: ± 0.05 pK unit; in the calculated rate constants: ± 12%. [b] Ref. 8. [c] Calculated from eqn. (6). [d] $k_p^{H_2O}/27.6$ with $k_{-p}^{H_2O}$ calculated from $k_p^{OH}K_s/K_a^{CH}$ with $pK_s = 15.83$ [see ref. 8(*a*)].

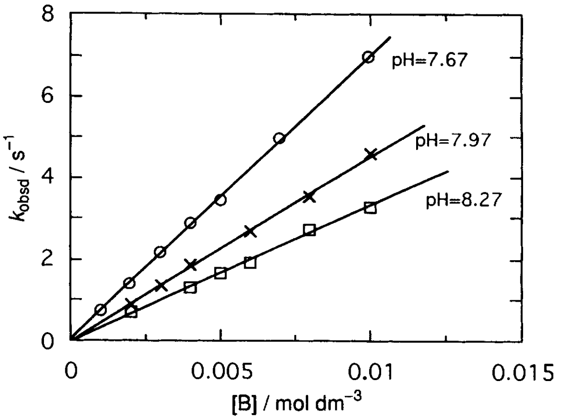


Fig. 2 Effect of buffer concentration and pH on the observed rate constant, k_{obsd}, for the deprotonation of **4** in 2-cyanophenol buffers in 50%H_2O–50%Me_2SO (v/v); $T = 25$ °C, $I = 0.5$ mol dm^{-3} KCl

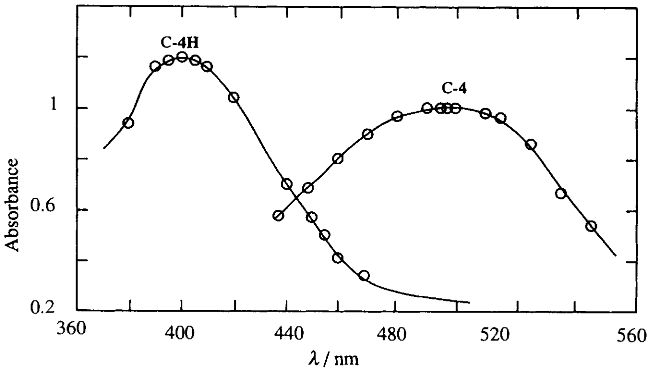


Fig. 3 UV-VIS absorption spectra of the carbanion C-4 and the nitronic acid C-4H in 50%H_2O–50%Me_2SO (v/v); $T = 25$ °C, $I = 0.5$ mol dm^{-3} KCl; [**4**] = 1.5×10^{-5} mol dm^{-3}; [C-4H] = 1.5×10^{-4} mol dm^{-3}

constants k_p^B and k_{-p}^{BH} were determined from a standard treatment of the data obtained at three different buffer ratios $p = [B]/[BH]$. In the other buffers with $pK_a^{BH} > pK_a^{CH} + 1$, eqn. (4) further reduced to eqn. (5), allowing a facile

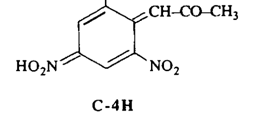
$$k_{obsd} = k_p^B[B] \tag{5}$$

determination of the k_p^B values from the slopes of the various k_{obsd} *vs.* [B] plots obtained. The corresponding k_{-p}^{BH} values were calculated by means of eqn. (6) These rate constants are summarized in Table 2.

$$k_{-p}^{BH} = k_p^B \frac{K_a^{BH}}{K_a^{CH}} \tag{6}$$

Reactions of C-4 in HCl and carboxylic acid buffer solutions

The kinetics of approach to equilibrium (1) were also investigated at pH ⩽ 6 by monitoring the disappearance of the carbanion C-4 in HCl solutions as well as in acetic acid and methoxyacetic acid buffer solutions. Under these experimental conditions, complete conversion of C-4 into **4** was observed but the oscilloscope pictures obtained by stopped-flow spectrophotometry revealed that the reprotonation process no longer occurred according to eqn. (1). Instead, they showed the instantaneous formation of an intermediate species X which subsequently decomposed to **4**. As will be discussed later, there is little doubt that X arises from protonation at an NO_2 group of C-4, most likely at the *para*-position, and is therefore the nitronic acid C-4H. Fig. 3 shows the UV-VIS absorption spectrum of X, recorded for a 5×10^{-3} mol dm^{-3} HCl solution.



(7)

Considering the fast initial formation of C-4H, an appropriate scheme for the conversion of C-4 into **4** at pH ⩽ 6 is shown in eqn. (7), where K'_a is the acidity constant of the nitronic acid functionality. Based on this, the value of the observed rate constants k_{obsd} for reprotonation of C-4 in acetic acid and methoxyacetic acid buffer solutions (Table S_2) should fit eqn. (8), in agreement with our finding that the slopes of the

$$k_{obsd} = (k_{-p}^{H}[H^+] + k_{-p}^{H_2O})\frac{K'_a}{K'_a + [H^+]} + k_{-p}^{BH}[BH]\frac{K'_a}{K'_a + [H^+]} \tag{8}$$

linear k_{obsd} *vs.* [BH] plots obtained at the different pHs studied in these buffers decrease with increasing H^+ concentration (Fig. 4). On the other hand, the pH dependence of the intercepts may be expected to obey eqn. (9) if the contribution of the solvent

$$k_{obsd}^{o} = k_{-p}^{H}[H^+]\frac{K'_a}{K'_a + [H^+]} \tag{9}$$

($k_{-p}^{H_2O}$) is negligible in eqn. (8). In accordance with this idea, a plot of $1/k_{obsd}^{o}$ *vs.* $1/[H^+]$ according to eqn. (10) is reasonably

$$\frac{1}{k_{obsd}^{o}} = \frac{1}{k_{-p}^{H}[H^+]} + \frac{1}{k_{-p}^{H}K'_a} \tag{10}$$

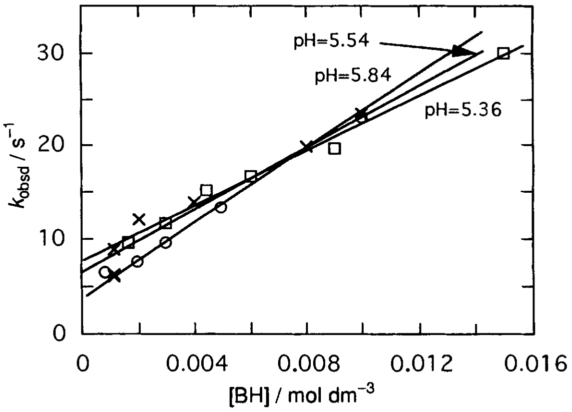


Fig. 4 Effect of buffer concentration and pH on the observed rate constant, k_{obsd}, for the protonation of the carbanion **C-4** in acetic acid buffers in 50%H_2O–50%Me_2SO (v/v); T = 25 °C, I = 0.5 mol dm^{-3} KCl

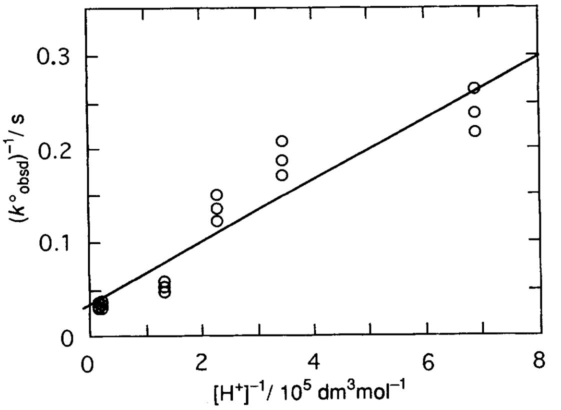


Fig. 5 Inversion plot according to eqn. (10) for protonation of the carbanion **C-4** in the pH range 4.65–5.84 in 50%H_2O–50%Me_2SO (v/v); T = 25 °C, I = 0.5 mol dm^{-3} KCl

linear (Fig. 5). This leads to the following estimates of k^{H}_{-p} and $k^{H}_{-p}\,K_a'$ from the slope and the intercept, respectively: $k^{H}_{-p} = 3.06 \pm 0.2 \times 10^6$ dm^3 mol^{-1} s^{-1} and $k^{H}_{-p}K'_a = 30.30 \pm 5$ s^{-1}. Combination of these two values affords a pK'_a value of ≈5, implying that the general expression of k_{obsd} [eqn. (8)] must reduce to $k^{H}_{-p}K'_a$ for HCl solutions of pH $\leqslant 3$. This situation is actually borne out by the data in Table S_3 which shows that the k_{obsd} values reach a plateau corresponding to $k_{obsd} = 19.5 \pm 1$ s^{-1} in the most acidic media. Although this value is only in rough agreement with that determined from eqn. (10), the interesting point is that it confirms the order of magnitude of the acidity of **C-4H**: p$K'_a = 5 \pm 0.2$.

Determination of the pH dependence of the slopes of the k_{obsd} *vs.* [BH] plots [eqn. (8)] afforded the following estimates for the k^{BH}_{-p} rate constant pertaining to the acetic acid and methoxyacetic acid buffers: $k^{CH_3COOH}_{-p}$ = 2300 dm^3 mol^{-1} s^{-1}; $k^{MeOCH_2COOH}_{-p} = 2.6 \times 10^4$ dm^3 mol^{-1} s^{-1}. These rate constants, together with the corresponding k^{B}_{p} values calculated from eqn. (6) are given in Table 2.

Discussion

Structure of the X species

Kovar and Breitmaier have previously reported NMR evidence that the negative charge of the carbanion **C-4** is essentially delocalized into the picryl ring.[16] The strong olefinic character of the exocyclic C_α carbon was clearly demonstrated by the finding that the ionization of **4** results both in large downfield variations of the C_α ($\Delta\delta$ = 57.3) and H_α ($\Delta\delta$ = 2.12) resonances and in a large increase in the $^1J_{C_\alpha H_\alpha}$ coupling constant (ΔJ = 27.3 Hz).[5,7,17,18] On the other hand, two main features supported the idea that **C-4** is best represented by the nitronate structures **E**–**G** than by the enolate structure **H**. First, the ionization of **4** induces a strong shielding of the $H_{3,5}$ protons of the picryl ring ($\Delta\delta$ = 0.69), comparable with that observed upon ionization of 2,4,6-trinitrotoluene to give the carbanion TNT$^-$ ($\Delta\delta H_{3,5}$ = 0.74).[13] Secondly, the resonances of the $C_{2,6}$ and C_4 carbons, especially the latter, move markedly to high field whereas those of the $C_{3,5}$ carbons move slightly to low field on going from **4** to **C-4**.[16] This situation is consistent with predictions based on SCFMO calculations and reminiscent of the one reported in ^{13}C studies of the formation of related polynitrobenzyl carbanions, as well as of a number of picryl σ-adducts of general structure **5**.[5,7,19–21] Interestingly, the much greater upfield shift observed for the C_4 resonance ($\Delta\delta$ = −19.7) than for the $C_{2,6}$ resonance ($\Delta\delta$ = −11) suggested that the *para*-quinoid structure **E** plays the major role in the delocalization of the negative charge of **C-4**,‡ in agreement with the well-known feature that a *p*-NO_2 group is significantly more effective at resonance stabilization of charge than is an *o*-nitro group.[9] On these grounds, one can reasonably expect that the fast reversible protonation of **C-4** will occur preferentially at the *p*-NO_2 group and that the resulting species X is the nitronic acid **C-4H**.

A few nitronic acids arising from protonation of anionic nitro-substituted cyclohexadienylide structures have been reported in the literature.[9,22–24] Typical examples are the nitronic acids **5H** and **6H** which have been characterized by UV–VIS and/or NMR spectroscopy and result from the protonation of the trinitrobenzene σ-adducts **5** and the nitrobenzofuroxan or benzofurazan σ-adducts **6** respectively.[22–24] Another and perhaps more significant example is the nitronic acid **C-2H**, which has been detected as a transient species in a protonation study of the bis(2,4-dinitrophenyl)methyl carbanion **C-2** in methanol.[25] In all cases, the protonation of the anionic structure is characterized by a marked hypsochromic shift of the absorption maximum in the electronic spectra and a similar situation is actually observed for the conversion of **C-4** (λ_{max} = 491 nm) to **C-4H** ($\lambda_{max} \doteq$ 400 nm). On the other hand, a pK'_a value of 4.25 has been measured for the ionization of the acid **C-2H** in methanol.[25] Since the acidity of an oxygen acid is commonly increased on going from a methanolic to an aqueous solution but decreased upon addition of a dipolar aprotic solvent such as Me_2SO,[26–29] our pK'_a value of ≈5 measured for the fast protonation of **C-4** in 50%H_2O–50%Me_2SO (v/v) is quite consistent with our assignment of X as the nitronic acid **C-4H**.

From the pK_a^{CH} and pK'_a values pertaining to the ionization behaviour of **4**, the equilibrium constant K_T measuring the extent of the conversion of this compound into the *aci* form according to the equilibrium **C-4** $\rightleftharpoons$ **C-4H** can be calculated: $K_T = 10^{-3}$. This corresponds to a very low percentage of the *aci* form in 50%H_2O–50%Me_2SO (v/v), accounting for our failure to detect the presence of **C-4H** in ^{1}H and ^{13}C NMR spectra recorded under experimental conditions.

Acidity of 4

The carbon acidity of TNT in 50%H_2O–50%Me_2SO (v/v) has been recently assessed: pK_a^{CH} ≈ 12.5.[30] On this basis, it

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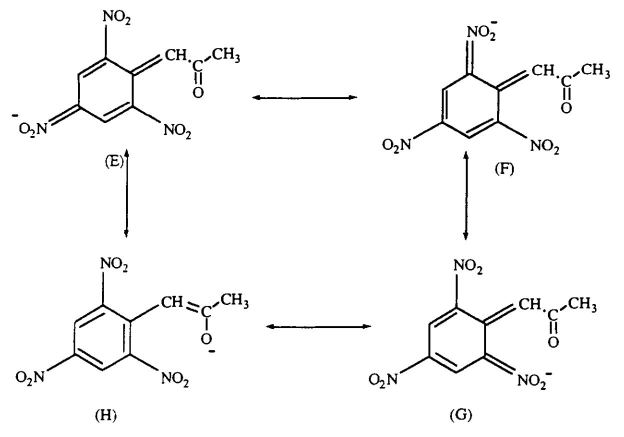
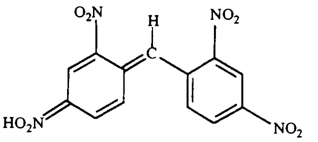
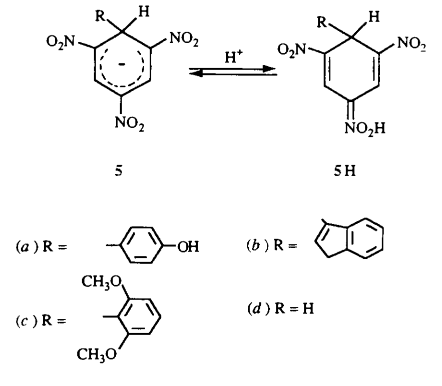
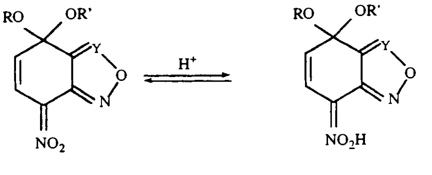
‡ A ^{1}H and ^{13}C NMR reinvestigation of the ionization of **4** in [$^2H_6$]Me_2SO has confirmed Kovar and Breitmaier's results except for a reversal in the chemical shifts of the C_4 and $C_{2,6}$ carbons of the carbanion **C-4**: δ_{C_4} = 126.82, $\delta_{C_{2,6}}$ = 139.70 as compared with δ_{C_4} = 137.85, $\delta_{C_{2,6}}$ = 130.3 in the same solvent.[16] Based on our assignments for these quaternary nitro-bearing carbons, the ionization of **4** is found to induce a much greater upfield shift of the C_4 resonance than of the $C_{2,6}$ resonance, in agreement with data recently reported for a number of related polynitrobenzyl carbanions.[7,30]





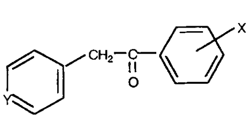
C-2H



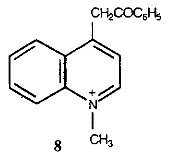


6 6H

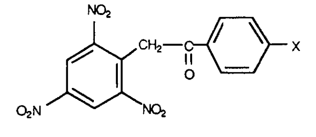
(a) Y = N, R = R′ = CH$_3$
(b) Y = N → O, R = R′ = CH$_3$
(c) Y = N, R ---- R′ = –CH$_2$–CH$_2$–
(d) Y = N → O, R ---- R′ = –CH$_2$–CH$_2$–



7 (Y = N, NR$^+$)



8



9 (X = NO$_2$, H, OCH$_3$)

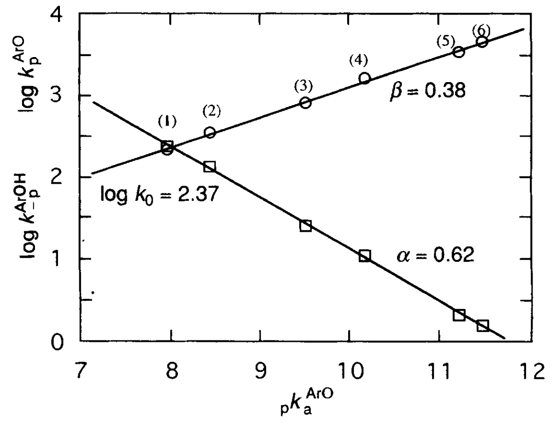


Fig. 6 Brønsted plot for the deprotonation of **4** by various phenoxide ions in 50%H$_2$O–50%Me$_2$SO (v/v); T = 25 °C, I = 0.5 mol dm^{-3} KCl. The numbering of the catalysts is given in Table 2.

appears that the substitution of one methyl hydrogen of TNT for the acetyl group to give **4** has a marked acidifying effect of 4.5 pK units. On the other hand, a pK^{CH} value of $\approx$19.2 has been reported for acetone in aqueous solution.[31–34] Notwithstanding the fact that the carbon acidity of **4** which gives rise to a carbanion with a highly delocalized negative charge, is probably one or two orders of magnitude lower in aqueous than in 50%Me$_2$SO solution,[9,11,29,35] the acidifying effect due to the substitution of a methyl hydrogen of acetone for a picryl ring may be estimated to $\approx$10 pK units. These comparisons lend additional support to the proposal that **4** behaves for the most part as a polynitrobenzyl-type substrate. For comparison, the CH-acidity of **4** is of the same order as that of phenacylpyridinium derivatives **7** (Y = NR$^+$)[6] as well as of compounds like **8** (pK_a^{CH} = 7.02).[36] Some β-diketone derivatives have also similar pK_a^{CH} values in 50%H$_2$O–50%Me$_2$SO (v/v), *e.g.*, acetylacetone (pK_a^{CH} = 9.12 at 20 °C)[28a] or dibenzoylmethane (pK_a^{CH} = 8.72 at 20 °C).[2b]

Reactivity of 4

Fig. 6 shows that the rate constants k_p^B pertaining to the deprotonation of **4** by phenoxide bases define a good Brønsted relationship. The corresponding β_B value is equal to 0.38 and compares well with those obtained for a number of carbon acids of similar pK_a^{CH} values in 50%H$_2$O–50%Me$_2$SO (v/v), *e.g.* β_B = 0.41 for **2** (pK_a^{CH} = 10.90).[8a] Using the classical definition of the intrinsic rate constant, *i.e.*, $k_0 = k_p^B$ where $\Delta pK = pK_a^{CH} - pK_a^{BH} = 0$ for phenol buffers[1,37], the log k_0^{ArO} value for the ionization of **4** can be readily determined from Fig. 6: log k_0^{ArO} = 2.37.

In the last decade, it has been clearly demonstrated that there is a strong connection between the intrinsic reactivity of a carbon acid and the extent of the structural and solvational reorganization that is required to form the conjugate carbanion.[1–6] Inasmuch as **4** behaves as a 2,4,6-trinitrobenzylic carbon acid and gives a carbanion whose negative charge undergoes a preferential delocalization through the picryl ring (structures **E**–**G**), one could reasonably expect that its intrinsic reactivity resembles that of previously studied polynitrobenzyl-type carbon acids rather than of carbonyl derivatives. As can be seen in Table 3, which summarizes a number of log k_0^{ArO} values referring to the deprotonation of representative carbon acid structures by phenoxide bases in 50%H$_2$O–50%Me$_2$SO (v/v), the intrinsic reactivity of **4** is about two orders of magnitude lower than that of similarly acidic β-dicarbonyl compounds such as acetylacetone or indane-1,3-dione.[1,2b,28] In contrast, it is of the same order as that of **3** which gives a carbanion where

Table 3 Comparison of intrinsic rate constants for deprotonation of some representative carbon acids in 50%H_2O–50%Me_2SO (v/v)

Carbon acid	Base	log k_0
$RCH(CN)_2$	RR′NH	≈7[a]
$CH_3COCH_2COCH_3$	$RCOO^-$	3.80[b]
	ArO^-	(4.60)[c]
Indan-1,3-dione	$RCOO^-$	3.18[d]
	ArO^-	4[d]
Dibenzoylmethane	RR′NH	2.36[e]
	ArO^-	(3.16)[f]
4	ArO^-	2.37
Bis(2,4,6-trinitrophenyl)methane	ArO^-	1.75[g]
CH_3NO_2	RR′NH	0.73[h]
	ArO^-	(1.6)[f]
Bis(2,4-dinitrophenyl)methane	$RCOO^-$	−0.50[g]
	ArO^-	0.50[g]
$C_6H_5NO_2$	$RCOO^-$	−0.59[h]
	ArO^-	(0.20)[c]
(2,4-Dinitrophenyl)(4-nitrophenyl)methane	$RCOO^-$	−1,10[g]
	ArO^-	0[g]

[a] Ref. 1. [b] Ref. 8(*a*). [c] Value estimated from the general observation that log k_0^{ArO} is greater than log k_0^{RCOO} by 0.8–1 log unit. [d] Ref. 8(*b*). [e] Ref. 2. [f] Value estimated on the basis that the effect of going from phenoxide to secondary amine bases is similar to the intrinsic reactivity of indane-1,3-dione and dibenzoylmethane.[2]

the negative charge has been shown to be subject primarily to delocalization through the picryl ring[7,8b] and somewhat greater than that of **2** which affords a planar diphenylmethyl carbanion whose negative charge can be dipersed through the two 2,4-dinitrophenyl rings.[8a] Also, the intrinsic reactivity of **4** compares well with that of nitromethane or phenylnitromethane which gives rise to nitronate-type carbanions where the dispersion of the negative charge over the two oxygen atoms of the NO_2 group is assisted by strong hydrogen bonding solvation.[1,3,38]

Thus, the low intrinsic reactivity of **4** agrees well with the behaviour expected for an α-substituted 2,4,6-trinitrotoluene, further confirming the idea that a 2,4,6-trinitrophenyl structure may be able to exert a strong −M effect. It should also be recalled that the ionization of carbon acids of low intrinsic reactivity has been recognized to proceed through strongly imbalanced transition states.[1] Since direct evidence that this situation prevails in the ionization of **4** cannot be obtained from our results, it is interesting to mention that we have actually found strong imbalances in the ionization of a series of picrylacetophenones **9** whose behaviour is closely related to that of **4**. We are presently completing this study and we will report these results soon.

Experimental

Materials

2,4,6-Trinitrophenylacetone was synthesized according to previously reported methods.[39] After recrystallisation from chloroform, mp = 94 °C (lit.,[39] mp 89 °C). Solvents were purified and solutions made up as described previously.[5,8] Buffers were purified commercial products.

Measurements

Kinetic measurements were carried out with a Durrum stopped-flow spectrophotometer equipped with a thermostatted cell compartment (25 ± 0.2 °C). Pseudo-first-order rate constants summarized in Tables S_1-S_3 are based upon the average value obtained from at least three repetitive runs conducted at a given pH and a given buffer composition. All reactions were found to be kinetically first-order in **4** up to at least 90% of the overall reaction.

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Paper 5/03845F
Received 14*th June* 1995
Accepted 19*th July* 1995