

# The *aci*-nitro equilibrium of picrylacetone: a kinetic and thermodynamic study in 50:50 and 30:70 (v/v) H<sub>2</sub>O–Me<sub>2</sub>SO mixtures †

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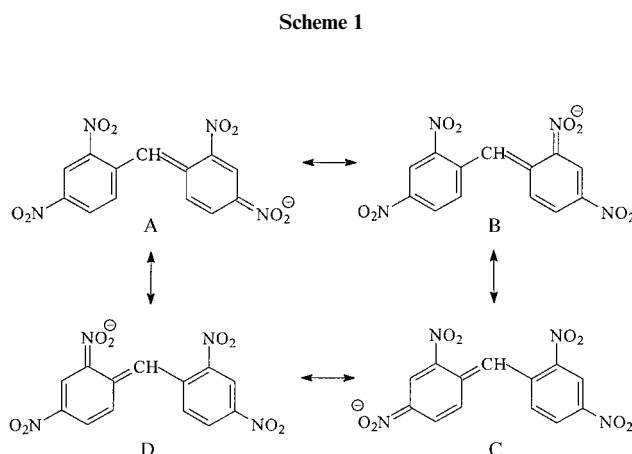
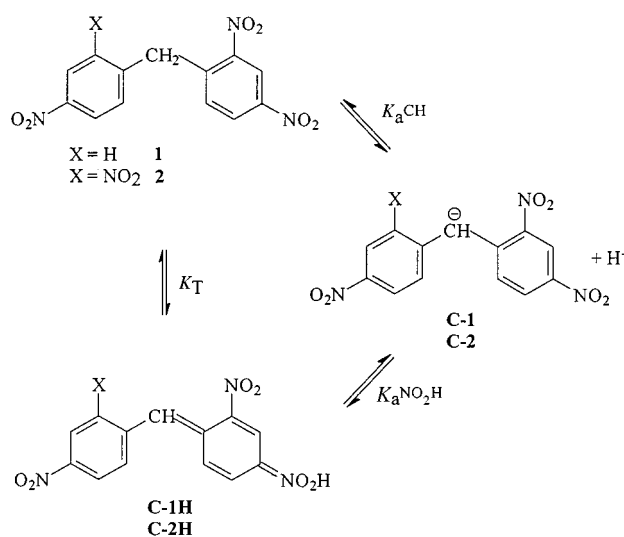
Received (in Cambridge) 1st June 1998, Accepted 17th September 1998

Rates of deprotonation of picrylacetone (**3a**) by a variety of bases B (phenoxide and carboxylate ions, primary amines, OH<sup>-</sup>, H<sub>2</sub>O) and of reprotonation of the resulting carbanion (**C-3a**) by the conjugate acids BH have been measured in 50:50 and 30:70 (v/v) H<sub>2</sub>O–Me<sub>2</sub>SO mixtures at 25 °C. In contrast with the situation in phenol and amine buffers, where only one relaxation time corresponding to a simple equilibrium approach according to **3a** + B ⇌ **C-3a** + BH is observed, a fast equilibrium protonation of the carbanion **C-3a** is found to precede its conversion to **3a** at low pH in a number of carboxylic acid buffers and HCl solutions. The resulting short-lived nitronic acid species **C-3aH** has been characterized by UV–Visible stopped-flow spectrophotometry and all data (pK<sub>a</sub><sup>NO<sub>2</sub>H</sup>, pK<sub>a</sub><sup>CH</sup>, pK<sub>T</sub>) pertaining to the *aci*-nitro equilibrium of **3a** in the two solvent mixtures studied could be determined. A notable solvent effect shown to be consistent with the preferential stabilization of the large polarizable carbanion **C-3a** by Me<sub>2</sub>SO is observed on pK<sub>a</sub><sup>NO<sub>2</sub>H</sup> and pK<sub>a</sub><sup>CH</sup>, but not on pK<sub>T</sub>, on going from 50 to 70% Me<sub>2</sub>SO. The solvent dependence and the magnitude of the intrinsic reactivity of **3a**, as determined from the Brønsted plots for the various types of catalysts in the two solvent mixtures, are also found to agree with **C-3a** being an sp<sup>2</sup>-hybridized carbanion whose negative charge is largely dispersed through the picryl ring.

## Introduction

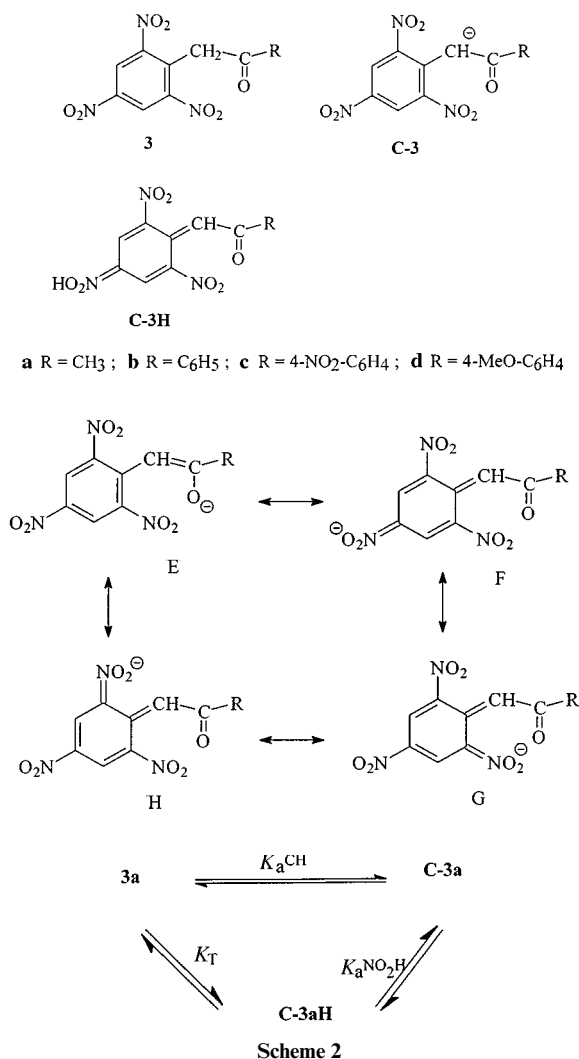
In recent years, we have been interested in delineating the factors governing the thermodynamics and kinetics of ionization of benzyl-type carbon acids whose activation arises exclusively from the presence of NO<sub>2</sub> groups in the phenyl ring, *e.g.* **1** and **2**.<sup>1</sup> Interestingly, we found that such carbon acids exhibit Marcus intrinsic reactivities which rank amongst the lowest so far reported for the ionization of carbon acids, *e.g.* log k<sub>0</sub><sup>R<sub>2</sub>COOH</sup> = -1.10 for **1** and log k<sub>0</sub><sup>R<sub>2</sub>COOH</sup> = -0.50 for **2** in a 50% H<sub>2</sub>O–50% Me<sub>2</sub>SO (v/v) mixture. Such negative log k<sub>0</sub> values clearly demonstrated that the major feature determining the reactivity of **1** and **2** is that these compounds afforded strongly resonance-stabilized sp<sup>2</sup>-hybridized carbanions, *i.e.* **C-1** and **C-2**, with a large dispersion of the negative charge over the two phenyl rings, especially on the negative oxygen atoms of the NO<sub>2</sub> groups (*e.g.* structures A–D for **C-2**).<sup>2,3</sup> In this regard, a kinetic and thermodynamic study of the reprotonation of the carbanion **C-2** in acidic medium in methanol was very revealing, providing evidence for the transient formation of a nitronic acid that we formulated as **C-2H**.<sup>4</sup> Although we failed in characterizing **C-2H** by UV–Visible spectrophotometry, the K<sub>a</sub><sup>CH</sup>, K<sub>a</sub><sup>NO<sub>2</sub>H</sup> and K<sub>T</sub> values pertaining to Scheme 1 could be derived.<sup>4</sup> So far, *aci*-nitro equilibria involving nitrotoluene-type carbon acids have been essentially studied photochemically.<sup>5–7</sup>

NMR studies of the deprotonation of picrylketones **3a–d** in pure Me<sub>2</sub>SO have revealed that these carbon acids exist essentially in their trinitro forms rather than as the nitronic acids in neutral media and that the exocyclic carbonyl functionality plays a minor role in the stabilization of the conjugate carbanions **C-3a–d**.<sup>8,9</sup> In other words, the weight of the enolate



† Supplementary data (SUPPL. NO. 57439, 16 pp.) is available from the British Library. For details of the Supplementary Publications Scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, available via the RSC Web page (<http://www.rsc.org/authors>).

resonance structure E is negligible as compared with that of the three trinitrocyclohexadienyl structures F–H. Kinetic data recently obtained for the deprotonation of **3a–d** at high pH in phenoxide buffers and dilute NaOH solutions in a 50% H<sub>2</sub>O–50% Me<sub>2</sub>SO (v/v) mixture agreed with this conclusion.<sup>9</sup> Interestingly, these studies have suggested that protonation of carbanions **C3a–d** might also occur at low pH to give rise to short-lived benzylic-type nitronic acids of type **C-3H**. This led us to reinvestigate the kinetics of the interconversion of **3a** and **C-3a** over a very large pH range, using carboxylic acid, primary amine and phenol buffers as well as dilute HCl and NaOH or NMe<sub>4</sub>OH solutions in two solvent mixtures, namely 50% H<sub>2</sub>O–50% Me<sub>2</sub>SO and 30% H<sub>2</sub>O–70% Me<sub>2</sub>SO (v/v). In this paper we report on our successful UV–Visible characterization of the nitronic acid **C-3aH** by stopped-flow spectrophotometry and our determination of all kinetic and thermodynamic parameters pertaining to Scheme 2, including the  $K_T$  values for the *aci*-nitro equilibrium of **3a**.

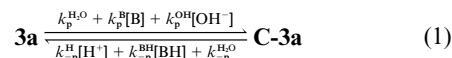


**a** R = CH<sub>3</sub>; **b** R = C<sub>6</sub>H<sub>5</sub>; **c** R = 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>; **d** R = 4-MeO-C<sub>6</sub>H<sub>4</sub>

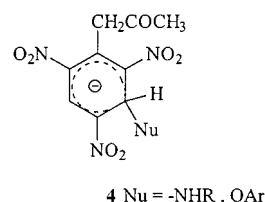
determination of the  $pK_a^{CH}$  values of **3a**, using 2-cyanophenol and 4-cyanophenol buffers in 50% Me<sub>2</sub>SO and methoxyacetic and acetic acid buffers in 70% Me<sub>2</sub>SO:  $pK_a^{CH} = 8.02$  in 50% Me<sub>2</sub>SO;<sup>9a</sup>  $pK_a^{CH} = 6.60$  in 70% Me<sub>2</sub>SO.

#### Interconversion of **3a** and **C-3a** in NaOH (NMe<sub>4</sub>OH in 70% Me<sub>2</sub>SO), primary amine and phenol buffers

In agreement with a direct equilibrium approach according to eqn. (1), stopped-flow experiments revealed that only one



relaxation time was associated with the interconversion of **3a** and **C-3a** in all phenol and primary amine buffers and NMe<sub>4</sub>OH solutions employed in 70% Me<sub>2</sub>SO. A similar situation held for primary amine buffers in 50% H<sub>2</sub>O, except for the aminoacetonitrile buffers. Interestingly, no evidence for a fast initial attack of the phenoxide or the amine reagents at an unsubstituted position of the picryl ring of **3a** to form transient  $\sigma$ -adducts of type **4** could be observed under the experimental conditions used.<sup>10–12</sup> The observed pseudo-first-order rate constants,  $k_{obsd}$ , measured in the different buffer or OH<sup>-</sup> solutions studied, are collected in Tables S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub> and S<sub>4</sub>.<sup>†</sup>



Analysis of the data in Tables S<sub>1</sub>–S<sub>4</sub><sup>†</sup> indicated that only the buffer base (B) and/or the hydroxide ion pathway(s) were important in determining  $k_{obsd}$  in the phenol buffer and NMe<sub>4</sub>OH solutions used in 70% Me<sub>2</sub>SO [eqn. (2)]. The corre-

$$k_{obsd} = k_p^{OH}[OH^-] + k_p^B[B] \quad (2)$$

sponding  $k_p^B$  and  $k_p^{OH}$  rate constants were therefore obtained as previously described for the same systems in 50% Me<sub>2</sub>SO.<sup>9a</sup> Use of eqn. (3) afforded the related  $k_{-p}^{BH}$  rate constants, while the

$$k_{-p}^{BH} = k_p^B \frac{K_a^{BH}}{K_a^{CH}} \quad (3)$$

rate constants  $k_p^{H,O}$  were calculated from  $k_p^{H,O} = k_p^{OH} K_s / K_a^{CH}$  where  $K_s$  is the autoprotolysis constant of the 30% H<sub>2</sub>O–70% Me<sub>2</sub>SO (v/v) mixture at  $I = 0.5 \text{ mol dm}^{-3}$  ( $pK_s = 18.02$  at 25 °C).<sup>1,13</sup>

Working out the data obtained for the amine buffers revealed that both buffer acid and base pathways contributed to  $k_{obsd}$  in systems with  $pK_a^{BH} \approx pK_a^{CH}$ , *i.e.* glycine ethyl ester, allylamine and methoxyethylamine in 50% Me<sub>2</sub>SO and glycine ethyl ester in 70% Me<sub>2</sub>SO. In agreement with eqn. (4), the corresponding

$$k_{obsd} = k_p^B[B] + k_{-p}^{BH}[BH] = [k_p^B + k_{-p}^{BH}/p][B] \quad (4)$$

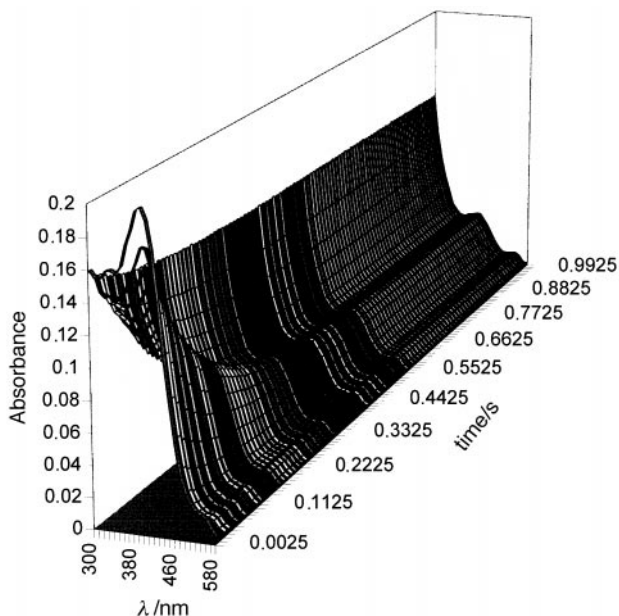
plots of  $k_{obsd}$  vs. [B] at constant pH, *i.e.* at a given  $p = [B]/[BH]$  ratio, were linear with negligible intercepts, but the slopes of these plots decreased with increasing pH. In these instances, the individual rate constants  $k_p^B$  and  $k_{-p}^{BH}$  were determined from a standard treatment of the data obtained at three or more different buffer ratios. In the other buffers, with  $pK_a^{BH} > pK_a^{CH} + 1.5$ , eqn. (4) reduced to eqn. (5), allowing a facile determination of

$$k_{obsd} = k_p^B[B] \quad (5)$$

the  $k_p^B$  values from the slopes of the various  $k_{obsd}$  vs. [B] plots

## Results

All rate and equilibrium measurements pertaining to the ionization of **3a** were made in 50% H<sub>2</sub>O–50% Me<sub>2</sub>SO and 30% H<sub>2</sub>O–70% Me<sub>2</sub>SO (v/v) at 25 °C at constant ionic strength  $I = 0.5 \text{ mol dm}^{-3}$  maintained with KCl and NMe<sub>4</sub>Cl, respectively. Pseudo-first-order conditions were used throughout with a large excess of the buffer or acid reagents over the picrylketone concentration. Interestingly, the carbanion **C-3a** exhibited a strong absorption maximum at  $\lambda_{max} = 491 \text{ nm}$ , a wavelength where neither the parent carbon acid nor the buffers absorb in the two solvent mixtures. This allowed a facile spectrophotometric



**Fig. 1** 3D-UV-Visible absorption spectra of the nitronic acid **C-3aH** in 30% H<sub>2</sub>O–70% Me<sub>2</sub>SO (v/v); *T* = 25 °C, *I* = 0.5 mol dm<sup>-3</sup> NMe<sub>4</sub>Cl; [**C-3aH**] = 1.5 × 10<sup>-4</sup> mol dm<sup>-3</sup>; [HCl] = 8 × 10<sup>-2</sup> mol dm<sup>-3</sup>. Time interval between scans: 10 ms.

obtained. The corresponding  $k_{-p}^{BH}$  values were calculated by means of eqn. (3).

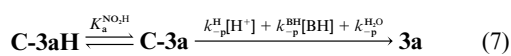
#### Interconversion of **3a** and **C-3a** in carboxylic acid buffers and HCl solutions

The simple equilibrium approach of eqn. (1) was still found to prevail when performing pH-jump experiments to study the reprotonation of **C-3a** in the pH range of 4.80–7.16 covered by buffers made up from acetic acid, methoxyacetic acid, formic acid and chloroacetic acid in 70% Me<sub>2</sub>SO. Again, the  $k_{obsd}$  data (Table S<sub>5</sub>†) were nicely accounted for in terms of eqn. (4), rewritten as eqn. (6), providing straightforward access to the related  $k_p^B$  and  $k_{-p}^{BH}$  rate constants.

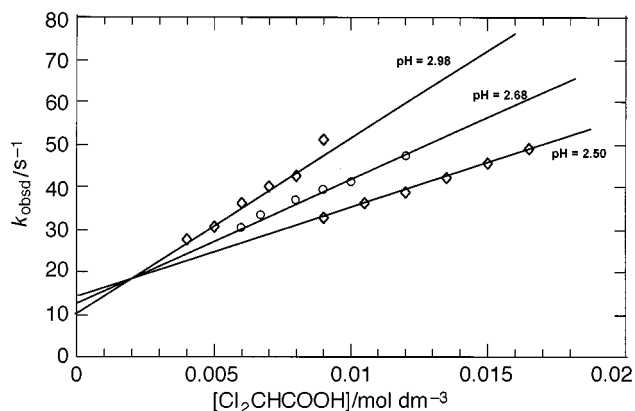
$$k_{obsd} = [p k_p^B + k_{-p}^{BH}] [BH] \quad (6)$$

In contrast, the reprotonation of **C-3a** no longer obeyed the simple equilibrium approach of eqn. (1) in the more acidic region (pH < 3.7) covered by dichloroacetic acid buffers and dilute HCl solutions (Table S<sub>6</sub>†) in 70% Me<sub>2</sub>SO, as well as in essentially all carboxylic acid buffers, aminoacetonitrile buffers and HCl solutions (pH < 6) in 50% Me<sub>2</sub>SO. Instead, the interaction consisted of two steps with the initial and instantaneous pH-dependent formation of an intermediate species X which subsequently decomposed with recovery of **3a**. Interestingly, we have been able to detect and characterize this transient species which shows an absorption maximum at  $\lambda_{max} = 400$  nm in the two solvents by fast UV-Visible spectrophotometry, as shown in Fig. 1. Complete formation of X occurs at pH ≈ 3 in 50% Me<sub>2</sub>SO but only at pH ≈ 1.5 in 70% Me<sub>2</sub>SO.

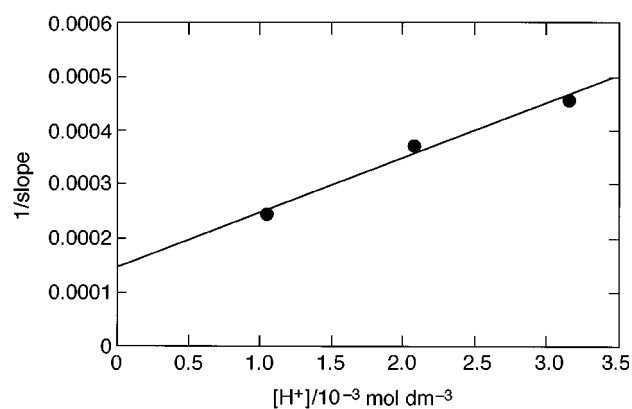
Based on various features to be considered in the discussion, there is little doubt that X may be safely identified as a nitronic acid, presumably **C-3aH**, so that the conversion of **C-3a** to **3a** at low pH must be reasonably described as shown in eqn. (7)



where  $K_a^{NO_2H}$  is the acidity constant of the nitronic acid functionality of **C-3aH**.<sup>5</sup> As pointed out in previous studies pertaining to the formation of nitronic acids from aryl-nitromethanes,<sup>14–16</sup> the measured  $k_{obsd}$  values for such a process



**Fig. 2** Effect of buffer concentration and pH on the observed rate constant,  $k_{obsd}$ , for the protonation of **C-3a** in dichloroacetic acid buffers in 30% H<sub>2</sub>O–70% Me<sub>2</sub>SO (v/v); *T* = 25 °C, *I* = 0.5 mol dm<sup>-3</sup> NMe<sub>4</sub>Cl.



**Fig. 3** Inversion plot according to eqn. (9) for protonation of **C-3a** in the pH range 2.5–2.98 in 30% H<sub>2</sub>O–70% Me<sub>2</sub>SO (v/v); *T* = 25 °C, *I* = 0.5 mol dm<sup>-3</sup> NMe<sub>4</sub>Cl.

are expected to fit eqn. (8) in the aforementioned buffer solutions.<sup>14,15</sup>

$$k_{obsd} = (k_{-p}^H [H^+] + k_{-p}^{H_2O}) \frac{K_a^{NO_2H}}{K_a^{NO_2H} + [H^+]} + k_{-p}^{BH} [BH] \frac{K_a^{NO_2H}}{K_a^{NO_2H} + [H^+]} \quad (8)$$

Eqn. (8) predicts that  $k_{obsd}$  will increase linearly with the BH concentration at a given pH, but that the slopes of these plots will decrease with increasing [H<sup>+</sup>] concentration. That this situation is actually met is illustrated in Fig. 2 which refers to the results obtained in the three dichloroacetic acid buffers studied in 70% Me<sub>2</sub>SO. Analysis of the pH dependence of the slopes of the related  $k_{obsd}$  vs. [BH] plots in terms of eqn. (9) gave a fairly

$$\frac{1}{\text{slope}} = \frac{1}{k_{-p}^{BH}} + \frac{[H^+]}{k_{-p}^{BH} K_a^{NO_2H}} \quad (9)$$

good three-points straight line (Fig. 3) from which we obtained  $k_{-p}^{CHCl_2COOH} = 6.82 \pm 0.2 \times 10^3$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>;  $k_{-p}^{CHCl_2COOH} \times K_a^{NO_2H} = 10 \pm 1$  s<sup>-1</sup> and  $pK_a^{NO_2H} = 2.83 \pm 0.1$ .

$$\frac{1}{\text{intercept}} = \frac{1}{k_{-p}^H K_a^{NO_2H}} + \frac{1}{k_{-p}^H [H^+]} \quad (10)$$

Working out similarly the data pertaining to methoxyacetic and acetic systems in 50% Me<sub>2</sub>SO afforded:  $k_{-p}^{CH_3COOH} = 2.3 \pm 0.2 \times 10^3$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>;  $k_{-p}^{CH_3OCH_2COOH} = 2.6 \pm 0.2 \times 10^4$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>;  $pK_a^{NO_2H} = 4.9 \pm 0.1$ .

**Table 1** Second-order rate constants for the ionization of **3a** in 30% H<sub>2</sub>O–70% Me<sub>2</sub>SO<sup>a,c</sup> and 50% H<sub>2</sub>O–50% Me<sub>2</sub>SO<sup>b,c</sup> (v/v) at 25 °C

|    | Buffer basic species  | 50% Me <sub>2</sub> SO |   |  | 70% Me <sub>2</sub> SO |  |   |
|----|-----------------------|------------------------|---|--|------------------------|--|---|
|    |                       | pK <sub>a</sub>        | k <sub>p</sub> <sup>Bd</sup> /dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> | k <sub>p</sub> <sup>BHd</sup> /dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> | pK <sub>a</sub>        | k <sub>p</sub> <sup>B</sup> /dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> | k <sub>p</sub> <sup>BH</sup> /dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> |
|    | OH <sup>-</sup>       | 17.34                  | 11 800  | 6.63 × 10 <sup>-6e</sup>   | 19.18                  | 47 100   | 2.1 × 10 <sup>-8f</sup>   |
| 1  | Phenoxide ion         | 11.21                  | 3 400   | 2.19   | 12.44                  | 33 900   | 0.048   |
| 2  | 4-Chlorophenoxide ion | 10.18                  | 1 580   | 10.93  | 11.52                  | 19 700   | 0.24  |
| 3  | 2-Bromophenoxide ion  | 9.52                   | 800   | 25   | 10.50                  | 8 000  | 1   |
| 4  | 4-Cyanophenoxide ion  | 8.45                   | 350   | 130  | 9.31                   | 3 100  | 6.05  |
| 5  | 2-Cyanophenoxide ion  | 7.97                   | 210   | 240  | 8.8                    | 1 050  | 9.7   |
| 6  | Butylamine            | 9.99                   | 500   | 5.3  | 10.13                  | 1 900  | 0.6   |
| 7  | Methoxyethylamine     | 9.11                   | 170   | 21.4   | 9.08                   | 770  | 2.6   |
| 8  | Allylamine            | 9.08                   | 220   | 14.5   | 8.94                   | 990  | 4.5   |
| 9  | Glycine ethyl ester   | 7.24                   | 31.7  | 485  | 7.04                   | 180  | 58  |
| 10 | Aminoacetonitrile     | 5.26                   | 13.3  | 7 650  | —                      | —  | —   |
| 11 | Glycinamide           | —                      | —   | —  | 8.25                   | 230  | 5.1   |
| 12 | Acetate ion           | 5.84                   | 15.2  | 2 300  | 7.16                   | 400  | 190   |
| 13 | Methoxyacetate ion    | 4.65                   | 11.1  | 2.6 × 10 <sup>4</sup>  | 5.94                   | 107  | 490   |
| 14 | Formate ion           | —                      | —   | —  | 5.52                   | 117  | 1 410   |
| 15 | Chloroacetate ion     | —                      | —   | —  | 4.80                   | 33.1   | 2 100   |
| 16 | Dichloroacetate ion   | —                      | —   | —  | 2.98                   | 1.63   | 6 800   |
|    | H <sub>2</sub> O      | -1.44                  | 1.06 × 10 <sup>-3g</sup>  | 3.06 × 10 <sup>6</sup>   | -1.16                  | 3.8 × 10 <sup>-4h</sup>  | 2.2 × 10 <sup>4</sup>   |

<sup>a</sup> I = 0.5 mol dm<sup>-3</sup> NMe<sub>4</sub>Cl. <sup>b</sup> I = 0.5 mol dm<sup>-3</sup> KCl. <sup>c</sup> Experimental error in the rate constants ±4% or better; in pK<sub>a</sub><sup>CH</sup> and pK<sub>a</sub><sup>BH</sup> ±0.05 pK units; in the calculated rate constants ±10%. <sup>d</sup> Data for phenoxide and acetate buffers taken from ref. 9a. <sup>e</sup> k<sub>p</sub><sup>H<sub>2</sub>O</sup>/27.6 calculated with k<sub>p</sub><sup>H<sub>2</sub>O</sup> = k<sub>p</sub><sup>OH</sup> K<sub>s</sub>/K<sub>a</sub><sup>CH</sup> (pK<sub>s</sub> = 15.83). <sup>f</sup> k<sub>p</sub><sup>H<sub>2</sub>O</sup>/14.6 calculated with k<sub>p</sub><sup>H<sub>2</sub>O</sup> = k<sub>p</sub><sup>OH</sup> K<sub>s</sub>/K<sub>a</sub><sup>CH</sup> (pK<sub>s</sub> = 18.02). <sup>g</sup> k<sub>p</sub><sup>H<sub>2</sub>O</sup>/27.6 calculated with k<sub>p</sub><sup>H<sub>2</sub>O</sup> = K<sub>a</sub><sup>CH</sup> k<sub>p</sub><sup>H</sup> /14.6 calculated with k<sub>p</sub><sup>H<sub>2</sub>O</sup> = K<sub>a</sub><sup>CH</sup> k<sub>p</sub><sup>H</sup>.

In agreement with a negligible solvent contribution (k<sub>p</sub><sup>H<sub>2</sub>O</sup>) in the pH ranges at hand in the two solvent mixtures, the intercepts of the k<sub>obsd</sub> vs. [BH] plots were found to fit eqn. (10), leading to k<sub>p</sub><sup>H</sup> = 2.2 ± 0.2 × 10<sup>4</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>; k<sub>p</sub><sup>H</sup> × K<sub>a</sub><sup>NO<sub>2</sub>H</sup> = 19 ± 1 s<sup>-1</sup> and pK<sub>a</sub><sup>NO<sub>2</sub>H</sup> = 3.06 ± 0.1 in 70% Me<sub>2</sub>SO; k<sub>p</sub><sup>H</sup> = 3.06 ± 0.2 × 10<sup>6</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>; k<sub>p</sub><sup>H</sup> × K<sub>a</sub><sup>NO<sub>2</sub>H</sup> = 30.3 ± 5 s<sup>-1</sup> and pK<sub>a</sub><sup>NO<sub>2</sub>H</sup> = 5 ± 0.2 in 50% Me<sub>2</sub>SO. Since, for a given buffer system the above analysis was necessarily based on the study of a limited number of buffer ratios in each solvent mixture, the rough agreement between the pK<sub>a</sub><sup>NO<sub>2</sub>H</sup> values deduced from eqns. (9) and (10) is satisfactory. Interestingly, these pK<sub>a</sub><sup>NO<sub>2</sub>H</sup> values imply that the k<sub>obsd</sub> values must in each solvent reach a plateau in the most acidic media where we have [H<sup>+</sup>] ≫ K<sub>a</sub><sup>NO<sub>2</sub>H</sup>. This situation is actually borne out by the data given in Table S<sub>6</sub> which show that the k<sub>obsd</sub> values level off in the most concentrated HCl solutions studied in 50 and 70% Me<sub>2</sub>SO, e.g. k<sub>obsd</sub><sup>max</sup> = 15 ± 2 s<sup>-1</sup> in 70% Me<sub>2</sub>SO, a value which agrees well with that calculated as k<sub>p</sub><sup>H</sup> × K<sub>a</sub><sup>NO<sub>2</sub>H</sup> = 19 ± 1 s<sup>-1</sup> from eqn. (10).

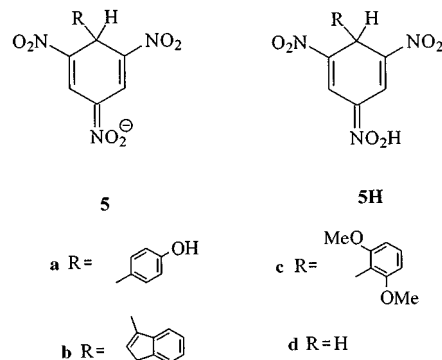
All second-order rate constants for deprotonation of **3a** and reprotonation of **C-3a** in 50 and 70% Me<sub>2</sub>SO are summarized in Table 1.

## Discussion

### The *aci*-nitro equilibrium of **3a**. Solvent effect on pK<sub>a</sub><sup>CH</sup> and pK<sub>a</sub><sup>NO<sub>2</sub>H</sup>

A detailed analysis of the proton and carbon chemical shift variations induced by the ionization of **3a** has emphasized the two following points<sup>9a</sup>: (1) the best representation of the conjugate carbanion **C-3a** is in terms of the nitronate structures F–G–H and not at all in terms of the enolate structure E; (2) within F–G–H there is a large predominance of the *para*-quinonoid structure F over the two *ortho* analogues G and H in agreement with the general observation that a *para*-NO<sub>2</sub> group is significantly more effective at resonance stabilization than is an *ortho*-NO<sub>2</sub> group.<sup>10b</sup> On this basis, one can reasonably anticipate that it is the 4-NO<sub>2</sub> group of **C-3a** which is preferentially protonated at low pH and that the resulting acid species X is the nitronic acid **C-3aH**. The situation resembles that encountered in the protonation of a number of anionic trinitro-cyclohexadienylidene structures **5** where the resulting nitronic

acids were identified as **5H**.<sup>17–19</sup> In these instances, the protonation was found to result in a marked hypsochromic shift of the absorption maxima in the electronic spectra, e.g. λ<sub>max</sub><sup>5a</sup> = 570 nm, λ<sub>max</sub><sup>5aH</sup> = 356 nm.<sup>18</sup> This situation is actually also observed for the conversion of **C-3a** (λ<sub>max</sub> = 491 nm) to **C-3aH** (λ<sub>max</sub> = 400 nm).



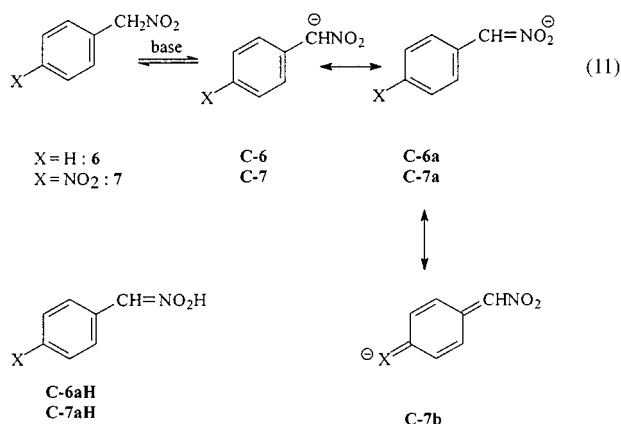
The pK<sub>a</sub><sup>CH</sup> and pK<sub>a</sub><sup>NO<sub>2</sub>H</sup> values, as well as the pK<sub>T</sub> values for the *aci*-nitro equilibrium of **3a**, as calculated from K<sub>T</sub> = K<sub>a</sub><sup>CH</sup>/K<sub>a</sub><sup>NO<sub>2</sub>H</sup>, are given in Table 2. For the purpose of comparison, this table also includes data previously reported for two benzylic carbon acids known to exhibit nitroalkane behaviour, namely phenylnitromethane **6** and (4-nitrophenyl)nitromethane **7**.<sup>14,15</sup>

A noteworthy feature emerging from Table 2 is that there is a marked contrast between the effect of solvent on the pK<sub>a</sub><sup>CH</sup> and pK<sub>a</sub><sup>NO<sub>2</sub>H</sup> values for **3a** as compared with those for **6**. In this latter instance, the resulting carbanion **C-6** has a negative charge which is largely localized onto the oxygen atoms of the exocyclic NO<sub>2</sub> group, as shown in **C-6a** [eqn. (11)].<sup>2,14</sup> As found for other oxygen acids giving rise to small anions, increasing the Me<sub>2</sub>SO content decreases the degree of hydrogen bonding solvation and therefore the stability of **C-6a**.<sup>2,14,20–22</sup> As confirmed by recent measurements of positive free energy changes for the transfer of **C-6** from water to water–Me<sub>2</sub>SO mixtures, this destabilization is the primary factor accounting for the finding that the related pK<sub>a</sub><sup>CH</sup> and pK<sub>a</sub><sup>NO<sub>2</sub>H</sup> values increase upon addition of the dipolar aprotic solvent to aqueous solu-

**Table 2** Thermodynamic parameters for the *aci*-nitro equilibrium of picrylacetone **3a** in 50:50 (v/v) and 30:70 (v/v) H<sub>2</sub>O–Me<sub>2</sub>SO mixture at 25 °C. Comparison with nitroalkane-type carbon acids

| Compound                  | 50% Me <sub>2</sub> SO        |  |                   |                          | 70% Me <sub>2</sub> SO        |  |                   |                          |
|---------------------------|-------------------------------|--|-------------------|--------------------------|-------------------------------|--|-------------------|--------------------------|
|                           | pK <sub>a</sub> <sup>CH</sup> | pK <sub>a</sub> <sup>NO<sub>2</sub>H</sup> | pK <sub>T</sub>   | [ <i>aci</i> ]/[nitro]   | pK <sub>a</sub> <sup>CH</sup> | pK <sub>a</sub> <sup>NO<sub>2</sub>H</sup> | pK <sub>T</sub>   | [ <i>aci</i> ]/[nitro]   |
| <b>3a</b>                 | 8.02                          | ≈5   | 3.02              | 3.55 × 10 <sup>-4</sup>  | 6.6                           | ≈3   | 3.34              | 4.57 × 10 <sup>-4</sup>  |
| Phenylnitromethane        | 7.93 <sup>a</sup>             | 4.75 <sup>a</sup>                          | 3.18 <sup>a</sup> | 6.61 × 10 <sup>-4a</sup> | 8.53 <sup>a</sup>             | 5.75 <sup>a</sup>                          | 2.78 <sup>a</sup> | 1.66 × 10 <sup>-4a</sup> |
| 4-Nitrophenylnitromethane | 6.02 <sup>b</sup>             | 3.36 <sup>b</sup>                          | 2.66 <sup>b</sup> | 2.18 × 10 <sup>-4b</sup> | —                             | —  | —                 | —                        |

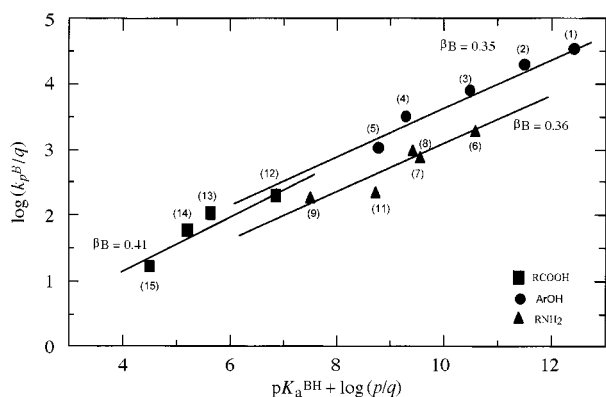
<sup>a</sup> Ref. 14 at 20 °C. <sup>b</sup> Ref. 15 at 25 °C.



tion.<sup>23</sup> In the case of **3a**, it is not an increase of ≈1 pK unit but a marked decrease of ≈2 pK units of the pK<sub>a</sub><sup>CH</sup> and pK<sub>a</sub><sup>NO<sub>2</sub>H</sup> values which is induced by the modest transfer from 50 to 70% Me<sub>2</sub>SO. In this respect, it is well known that dipolar aprotic solvents like Me<sub>2</sub>SO are very prone to stabilize large and polarizable anions.<sup>10,24,25</sup> Prototype examples are actually the nitrocyclohexadienyl anions **5** for which large negative transfer free energies have been measured in MeOH–Me<sub>2</sub>SO mixtures.<sup>26</sup> Based on the close analogy between structures **C-3** and **5**, a similar stabilization of the carbanion **C-3a** by Me<sub>2</sub>SO may be expected, consistent with the observed decreases in pK<sub>a</sub><sup>CH</sup> and pK<sub>a</sub><sup>NO<sub>2</sub>H</sup> values of **3a** on going from 50 to 70% Me<sub>2</sub>SO. Interestingly, pK<sub>a</sub><sup>CH</sup> values of other polynitrotoluene derivatives like 2,4,6-trinitrotoluene, polynitrodiphenylmethanes (e.g. **1** and **2**) or polynitrotriphenylmethanes, have also been found to decrease with increasing Me<sub>2</sub>SO content of H<sub>2</sub>O–Me<sub>2</sub>SO or MeOH–Me<sub>2</sub>SO mixtures.<sup>1b,3,27,28</sup>

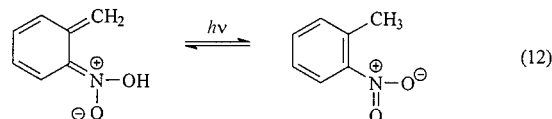
Inasmuch as they are primarily the reflection of the changes in stability of the same conjugate base, the pK<sub>a</sub><sup>CH</sup> and pK<sub>a</sub><sup>NO<sub>2</sub>H</sup> values of picrylacetone **3a** are affected to about the same extent by the solvent transfer. The same reasoning applies for the pK<sub>a</sub><sup>CH</sup> and pK<sub>a</sub><sup>NO<sub>2</sub>H</sup> values of the phenylnitromethane system.<sup>14</sup> Accordingly, the pK<sub>T</sub> values for the related *aci*-nitro equilibria suffer only slight changes on going from 50 to 70% Me<sub>2</sub>SO. In both systems, they correspond to a very small percentage of the *aci* form in the solutions, in agreement with the failure to detect the presence of **C-3aH** as well as the exocyclic nitronic acid **C-6aH** in <sup>1</sup>H and <sup>13</sup>C NMR spectra recorded using common experimental conditions in Me<sub>2</sub>SO or aqueous Me<sub>2</sub>SO mixtures. A similar situation prevailed with **C-7aH**, in the (4-nitrophenyl)nitromethane system.<sup>15</sup>

Most *aci*-nitro tautomerisms previously studied have been formulated in terms of eqn. (7) where the *C*-protonation step occurs on the intermediate nitronium ion.<sup>5,9,14</sup> However, it is worth noting that another mechanism involving direct intramolecular transfer from an *ortho*-NO<sub>2</sub>H function to the methylene carbon has been suggested to account for the photo-induced tautomerization of a number of *ortho*-nitrobenzyl structures, as exemplified in eqn. (12).<sup>5-7,29</sup> In the case of 2,4,6-trinitrobenzyl and 2,4,6-trinitrocyclohexadienyl anions, the experimental evidence (*vide supra*) is that the oxygen atoms of the *para*-nitro groups are notably more basic than those of the



**Fig. 4** Brønsted plots for deprotonation of **3a** by phenoxide and carboxylate ions and primary amines in 30% H<sub>2</sub>O–70% Me<sub>2</sub>SO (v/v); T = 25 °C, I = 0.5 mol dm<sup>-3</sup> NMe<sub>4</sub>Cl. The numbering of the catalysts is given in Table 1.

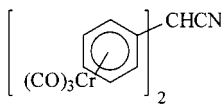
*ortho*-nitro groups, so that the mechanism of eqn. (12) does not seem reasonable.



**Reactivity of 3a.** Fig. 4 shows statistically corrected Brønsted plots obtained for deprotonation of **3a** by various primary amines, phenoxide and carboxylate buffers employed in 70% Me<sub>2</sub>SO. These plots, as well as the Brønsted plot for primary amines in 50% Me<sub>2</sub>SO (not shown, Fig. S<sub>1</sub>), show qualitative and quantitative features that are quite similar to those found in the deprotonation of a number of carbon acids in the same solvents.<sup>1-3,9,14,15,20,21,30</sup> For example, the Brønsted β<sub>B</sub> value for carboxylate buffers (β<sub>B</sub> = 0.41) is larger than for amine buffers (β<sub>B</sub> = 0.36) and the reactivity order ArO<sup>-</sup> > RCOO<sup>-</sup> > RNH<sub>2</sub> prevails for a given ΔpK<sub>a</sub> + log(p/q) value. This latter trend has been shown to result from the different contributions of the desolvation and/or solvation changes pertaining to the various buffer base or acid species which take place along the reaction coordinate of the proton transfer.<sup>1-3,9,14,30</sup>

Based on the classical definition of the intrinsic rate constant,<sup>2,31</sup> i.e. k<sub>0</sub> = k<sub>p</sub><sup>B</sup> when pK<sub>a</sub><sup>BH</sup> + log(p/q) = pK<sub>a</sub><sup>CH</sup>, the log k<sub>0</sub> values for ionization of **3a** by the different families of catalysts were readily determined from Fig. 4 and S<sub>1</sub>: log k<sub>0</sub><sup>ArOH</sup> = 2.43; log k<sub>0</sub><sup>RCOOH</sup> = 2.25; log k<sub>0</sub><sup>RNH<sub>2</sub></sup> = 1.82 in 70% Me<sub>2</sub>SO; log k<sub>0</sub><sup>RNH<sub>2</sub></sup> = 1.98 in 50% Me<sub>2</sub>SO. As can be seen in Table 3, which includes similar data for a few representative carbon acid structures, the intrinsic reactivity of **3a** is rather low, comparing well with those measured for a number of polynitrobenzyl-type carbon acids, including the three related picrylketones **3b–d**, in the same solvent.<sup>1,9b,27</sup> In this regard, there is no doubt that the low intrinsic reactivity of **3a** as well as of **3b–d** reflects the fact that there is a need for a high structural, electronic and solvational reorganization in forming the sp<sup>2</sup>-hybridized cyclohexadienyl carbanions **C-3**. The reason why carbon acids like **3a–d** which

**Table 3** Intrinsic rate constant ( $\log k_0^{\text{RNH}_2}$ ) for ionization of representative carbon acid structures in 50:50 and 30:70 (v/v)  $\text{H}_2\text{O}$ - $\text{Me}_2\text{SO}$  mixtures<sup>a,b</sup>

| Carbon acid  | 50% $\text{Me}_2\text{SO}$ | 70% $\text{Me}_2\text{SO}$ |
|--|----------------------------|----------------------------|
| $\text{RCH}(\text{CN})_2^a$  | ~7                         | —                          |
| 9-Cyanofluorene ( <b>9</b> ) <sup>b,e</sup>  | 3.76                       | 3.57 <sup>c</sup>          |
| 9-Methoxycarbonylfuorene ( <b>10</b> ) <sup>b,e</sup>  | 2.84                       | 3.09 <sup>d</sup>          |
|  ( <b>11</b> ) <sup>b,e</sup> | 2.94                       | 2.65                       |
| 2,4-Dinitrophenylacetone nitrile ( <b>8</b> ) <sup>b,f</sup>   | 2.76                       | 2.54 <sup>c</sup>          |
| Indane-1,3-dione <sup>b,e</sup>  | 2.44                       | 2.59                       |
| Acetylacetone <sup>b,e</sup>   | 2.06                       | 2.91 <sup>c</sup>          |
| Picrylacetone ( <b>3a</b> ) <sup>a,g</sup>   | 1.98                       | 1.82                       |
| Picrylacetophenone ( <b>3b</b> ) <sup>a,h</sup>  | 1.86                       | —                          |
| Nitromethane <sup>b</sup>  | 0 <sup>i</sup>             | 2.77 <sup>d</sup>          |
| Phenylnitromethane <sup>b</sup>  | -1 <sup>i</sup>            | 0.97 <sup>d</sup>          |
| 2,2',4,4'-Tetranitrodiphenylmethane  | -0.65 <sup>j</sup>         | —                          |
| 2,4,4'-Trinitrophenylmethane   | -1.15 <sup>j</sup>         | —                          |

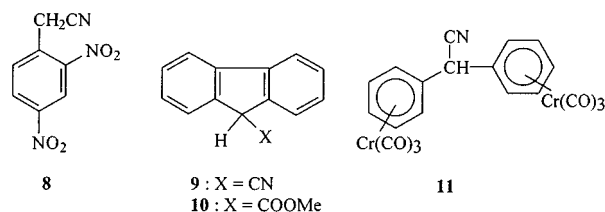
<sup>a</sup>  $T = 25^\circ\text{C}$ . <sup>b</sup>  $T = 20^\circ\text{C}$ . <sup>c</sup> Ref. 33. <sup>d</sup> In 90%  $\text{Me}_2\text{SO}$ . <sup>e</sup> Ref. 28. <sup>f</sup> Ref. 3. <sup>g</sup> This work;  $\log k_0^{\text{ArOH}} = 2.37$  in 50%  $\text{Me}_2\text{SO}$ ;  $\log k_0^{\text{ArOH}} = 2.43$ ,  $\log k_0^{\text{RCOOH}} = 2.25$  in 70%  $\text{Me}_2\text{SO}$ . <sup>h</sup> Calculated from ref. 9b by assuming that  $\log k_0^{\text{RNH}_2} = \log k_0^{\text{RRNH}} - 0.39$  as found for **3a**. <sup>i</sup> Ref. 21. <sup>j</sup> Ref. 1a.

form resonance-stabilized carbanions have much lower intrinsic reactivities than carbon acids like nitriles of the type  $\text{RR}'\text{-CHCN}$  which form purely inductively stabilized carbanions is that the development of resonance but not of inductive effects lags behind proton transfer at the transition state.<sup>2</sup> Interestingly, we note that the  $\log k_0$  values for **3a** are lower by 1 to 2 log units than those of a carbonyl compound like indane-1,3-dione,<sup>30</sup> in accordance with the evidence that it is the picryl ring and not the exocyclic ketone moiety which contributes dominantly to the delocalization of the negative charge of the carbanion **C-3a**, as shown in the resonance structures F-H. On the other hand, the  $\log k_0$  values for **3a** are markedly higher than those for nitroalkanes like nitromethane or phenylnitromethane.<sup>2,14,21</sup> In these two latter compounds, the structural reorganization required to form the conjugate  $\text{sp}^2$ -hybridized nitronate carbanion is reduced compared to that involved in the formation of **C-3a** but the strong localization of the charge onto the oxygen atoms of the only nitro group is more favorable to hydrogen-bond solvation.<sup>2,14,21</sup> Inasmuch as solvation also develops behind proton transfer at the transition state, this factor adds to the decrease in the intrinsic reactivity of nitromethane and phenylnitromethane.<sup>2</sup>

Notwithstanding the experimental uncertainty of the  $\log k_0$  values quoted in Table 3, the finding that the intrinsic reactivity of **3a** tends to decrease slightly on going from 50 to 70%  $\text{Me}_2\text{SO}$  is worthy of comment. The question of how the effect of increasing the  $\text{Me}_2\text{SO}$  content of  $\text{H}_2\text{O}$ - $\text{Me}_2\text{SO}$  mixtures may affect the intrinsic reactivity of carbon acids has been recently addressed by Bernasconi, and it has been concluded that the observed behaviour must be the reflection of two main competing factors.<sup>3</sup> One is the stabilization of the polarizable transition state by the polarizable dipolar aprotic solvent which increases the intrinsic reactivity. The other is the difference in solvation of the carbanion in the different solvent mixtures and the fact that, at the transition state, the solvation of the carbanion lags behind proton transfer, leading to a decrease in  $k_0$ . Depending upon the balance between these two factors, two contrasting situations can therefore be envisaged.<sup>3</sup> The first relates to carbanions like nitronate or enolate-type carbanions which are very prone to hydrogen-bond solvation and, hence, suffer a progressive desolvation when the  $\text{Me}_2\text{SO}$  concentration is increased. In this instance, the solvational lag enhances  $k_0$ , as does at the same time the preferential stabilization of the transition state by  $\text{Me}_2\text{SO}$ . This leads necessarily to a regular increase in the

intrinsic reactivity, especially for nitroalkanes. Thus, a transfer from water to 90%  $\text{Me}_2\text{SO}$  induces a strong increase of 3.6 log units in  $k_0$  for ionization of nitromethane by secondary amines.<sup>14</sup> Interestingly, a substantial change of 1 log unit in  $k_0$  is observed in this system when going only from 50 to 70%  $\text{Me}_2\text{SO}$ . The intrinsic reactivities of carbonyl compounds respond similarly to the solvent change but the magnitude of the enhancement in  $k_0$  is reduced, e.g. the intrinsic reactivity of acetylacetone increases only 10-fold on going from water to 90%  $\text{Me}_2\text{SO}$ .<sup>28,32</sup>

The second situation corresponds to carbon acids like 2,4-dinitrophenylacetone nitrile **8**, the 9-cyano- and 9-methoxycarbonylfuorenes **9** and **10** or the ( $\alpha$ -cyanodiphenylmethane)-bis[tricarbonylchromium(0)] compound **11** which give rise to large polarizable carbanions.<sup>14,28,33</sup> These are better solvated in  $\text{Me}_2\text{SO}$ -rich solvents as evidenced by the measurement of negative activity coefficients for their transfer from water to  $\text{Me}_2\text{SO}$ .<sup>3,23,28</sup> In this case, the solvational lag decreases  $k_0$ , thereby compensating for the enhancing effect of the first factor. Accordingly, the  $\log k_0$  values for this group of compounds are either unaffected or slightly decrease on going to the less aqueous solvents, e.g. the  $k_0$  value for ionization of **11** by primary or secondary amines decreases by a factor of 2 on going from 50 to 70%  $\text{Me}_2\text{SO}$ , while that for ionization of **9** by the same catalysts is essentially the same in 50 and 90%  $\text{Me}_2\text{SO}$ . Interestingly, Table 3 shows that it is this situation which prevails in the case of **3a**, with only a modest decrease of a factor 1.5 of  $\log k_0^{\text{RNH}_2}$  on going from 50 to 70%  $\text{Me}_2\text{SO}$ . Obviously, this behaviour is consistent with the fact that the negative charge of the carbanion **C-3a** is extensively delocalized through the picryl ring (structures F-H), a situation which is notably similar to that reported for the 2,4-dinitrophenylacetone nitrile carbanion whose negative charge is predominantly dispersed through a 2,4-dinitrophenyl ring. As mentioned earlier, the favoured solvation of **C-3a** by  $\text{Me}_2\text{SO}$  is also reflected by a marked decrease in the  $\text{p}K_{\text{a}}^{\text{CH}}$  and  $\text{p}K_{\text{a}}^{\text{NO}_2\text{H}}$  values of **3a** on going from 50 to 70%  $\text{Me}_2\text{SO}$ .



## Experimental

### Materials

2,4,6-Trinitrophenylacetone was synthesized according to a previously reported method.<sup>34</sup> After recrystallisation from chloroform: mp  $94^\circ\text{C}$  (lit. mp  $89^\circ\text{C}$ ).<sup>34</sup> Solvents were purified and solutions made up as described previously.<sup>4,9,15</sup> Buffers were purified commercial products.

### Measurements

Kinetic measurements were carried out with an Applied Photophysics Ltd stopped flow spectrophotometer equipped with a thermostatted cell compartment ( $25 \pm 0.2^\circ\text{C}$ ). Pseudo-first-order rate constants summarized in Tables  $\text{S}_1$ - $\text{S}_6$  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 **3a** up to at least 90% of the overall reaction.

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