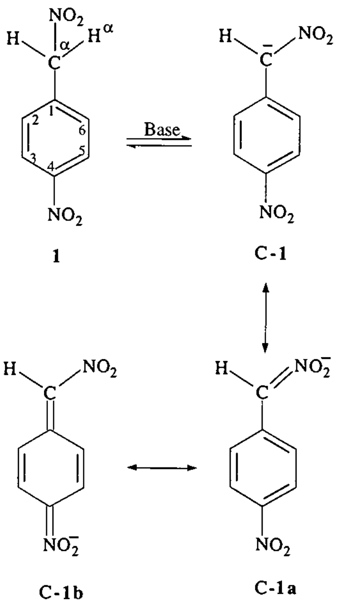
The nitroalkane behaviour of (4-nitrophenyl)nitromethane: a kinetic and structural study in H_2O–Me_2SO mixtures

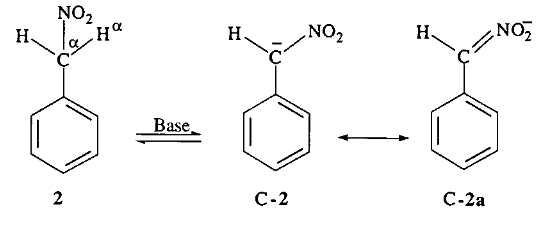
Gilles Moutiers,* Valérie Thuet and François Terrier*

Laboratoire SIRCOB (EP CNRS 102), Department of Chemistry, Bâtiment Lavoisier, University of Versailles, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France

Rates of proton abstraction from (4-nitrophenyl)nitromethane (1) by a variety of bases B (phenoxide and carboxylate ions, primary amines) and of reprotonation of the resulting carbanion (C-1) by the conjugate acids BH have been measured in a 50:50 (v/v) H_2O–Me_2SO mixture at 25 °C. In contrast with the situation at pH $\geqslant$ 4.2 where only one relaxation time corresponding to a simple equilibrium approach according to 1 + B $\rightleftharpoons$ C-1 + BH is observed, the interconversion of 1 and C-1 proceeds in two steps in acidic media. Kinetic studies as well as data obtained by ^1H and ^{13}C NMR or UV–VIS spectroscopy indicate that the first step corresponds to the protonation of the exocyclic nitro group of C-1, giving rise to the corresponding nitronic acid C-1a,H. All rate and equilibrium parameters obtained for the *aci*-nitro behaviour of 1, including the log k_0 values measuring its intrinsic reactivity towards the various types of bases studied, emphasize a nitroalkane behaviour rather than a 4-nitrotoluene behaviour of this carbon acid in 50:50 (v/v) H_2O–Me_2SO. Although they clearly reveal some contribution of the nitrophenyl ring to the stabilization of C-1 in Me_2SO, the NMR data remain consistent with a major role of the exocyclic nitro group in governing the ionization behaviour of 1 in this dipolar aprotic solvent.

The thermodynamics and kinetics of the ionization of (4-nitrophenyl)nitromethane **1** have been studied by various authors in aqueous solution,[1–4] as well as in acetonitrile,[5,6] dimethyl sulfoxide (Me_2SO)[7] or H_2O–Me_2SO mixtures.[8,9] In all instances, the overall behaviour of **1** was assumed to closely resemble that of the parent unsubstituted analogue, *i.e.* phenylnitromethane **2**.[2,10,11] This implies a large predominance of the exocyclic nitronate-type resonance contributor **C-1a** to the stabilization of the resulting carbanion.





A remarkable feature of the ionization of **1**, however, is that the UV–VIS absorption of **C-1** is considerably more sensitive to solvent changes than that of the phenylnitromethane carbanion **C-2**. Going from water to 10:90 (v/v) H_2O–Me_2SO thus results in a shift of λ_{max} from 289 nm (ε 2.14 × 10^4 dm^3 mol^{-1} cm^{-1}) to 326 nm (ε 2.23 × 10^4) for **C-2** while the corresponding change in λ_{max} of **C-1** is from 380 nm (ε 1.38 × 10^4)[8] to 462 nm (ε 1.82 × 10^4). A transfer from H_2O to acetonitrile solutions induces similarly a strong bathochromic shift for λ_{max} (**C-1**) (496 nm; $\varepsilon = 2.69 \times 10^4$).[6] Obviously, such variations in the visible absorption suggest that the contribution of the aromatic nitronate resonance contributor **C-1b** to the stabilization of **C-1** increases appreciably upon addition of a dipolar aprotic solvent to an aqueous solution. The finding that the carbon acidity (pK_a^{CH}) of **1** decreases significantly less than that of **2** on going from water to Me_2SO also supports this idea: $\Delta pK = 2.73$ for **1** and 5.44 for **2**.[2,3,7,10] However, the extent to which this trend affects the *aci*-nitro behaviour of **1** remains difficult to assess.

To obtain a better understanding of the reactivity of **1**, we have undertaken a thorough structural and kinetic investigation of the ionization of **1** under various experimental conditions. In this paper, we report on the results of both a ^1H and ^{13}C NMR analysis in various H_2O–Me_2SO mixtures, and a kinetic study in a 50:50 (v/v) H_2O–Me_2SO mixture. Major features of this work will relate to our finding that protonation of the carbanion **C-1** occurs at the exocyclic nitro group at low pH and our determination of a very low intrinsic reactivity of **1**. These results clearly show, unexpectedly perhaps, that **1** behaves as a nitroalkane-type compound in 50% aqueous Me_2SO.

Results

Structural studies

Addition of dilute potassium hydroxide to a ≈5 × 10^{-5} mol dm^{-3} solution of **1** in 50:50 (v/v) H_2O–Me_2SO gives rise to a yellow species exhibiting a strong absorption maximum at 411 nm ($\varepsilon = 1.48 \times 10^4$ dm^3 mol^{-1} cm^{-1}). Unambiguous evidence that this species is the conjugate carbanion **C-1** was obtained by carrying out a ^1H and ^{13}C NMR study of the ionization of **1** in this solvent mixture. The most pertinent data are summarized

Table 1 ^{1}H Chemical shifts for (4-nitrophenyl)nitromethane **1** and the related carbanion **C-1** in H_2O–Me_2SO mixtures and $(CD_3)_2SO$[a]

Solvent	Compound	$\delta(H^\alpha)$	$\delta(H^{3,5})$	$\delta(H^{2,6})$
$(CD_3)_2SO$	**1**	5.95	8.30	7.80
	C-1	6.84	7.97	7.80
	$\Delta\delta$	0.89	−0.33	0
30:70 H_2O–Me_2SO	**1**	5.84	8.30	7.77
	C-1	6.97	8.10	7.94
	$\Delta\delta$	1.13	−0.20	0.17
50:50 H_2O–Me_2SO	**1**	5.82	8.33	7.77
	C-1	7.05	8.15	7.98
	$\Delta\delta$	1.23	−0.18	0.21

[a] δ in ppm relative to internal reference $SiMe_4$.

in Tables 1 and 2 together with related NMR data obtained in 30:70 (v/v) H_2O–Me_2SO and in pure $(CD_3)_2SO$. At this stage, two major observations can be made: (*i*) the resonances of the exocyclic H^α and C^α atoms of **1** suffer large downfield shifts upon ionization: $\Delta\delta H^\alpha = 1.23$; $\Delta\delta C^\alpha = 35.31$ ppm; (*ii*) the spectra reveal an equivalence of the $H^{2,6}$ and $H^{3,5}$ protons as well as of the $C^{2,6}$ and $C^{3,5}$ carbons of the carbanion at probe temperature. A similar observation holds in acetonitrile at −40 °C. As will be elaborated further in the discussion, these results suggest not only that the C^α carbon of **C-1** has a strong olefinic character but also that most of the negative charge of this carbanion resides on the exocyclic nitro group in all solvents studied. In other words, the NMR data favour structure **C-1a** as the main resonance contributor for **C-1**.

Kinetic and equilibrium measurements

All rate and equilibrium measurements pertaining to the ionization of **1** according to the general equation (1) were made in

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

50:50 (v/v) H_2O–Me_2SO at 25 °C and constant ionic strength *I* of 0.5 mol dm^{-3} maintained with KCl. Pseudo-first-order conditions were used throughout with a large excess of the buffer, base (NaOH) or acid (HCl) reagents over the (4-nitrophenyl)-nitromethane concentration (≈5 × 10^{-5} mol dm^{-3}). In eqn. (1), the rate constants $k^{\mathbf{OH}}_{\mathbf{p}}$, $k^{\mathbf{B}}_{\mathbf{p}}$ and $k^{\mathbf{H_2O}}_{\mathbf{p}}$ refer to the deprotonation of **1** by OH^-, the buffer base species B (ArO^-, $RCOO^-$, RNH_2) and the solvent, respectively, while $k^{\mathbf{H}}_{-\mathrm{p}}$, $k^{\mathbf{BH}}_{-\mathrm{p}}$ and $k^{\mathbf{H_2O}}_{-\mathrm{p}}$ are the rate constants referring to the reprotonation of **C-1** by hydronium ion, the buffer acid species BH (ArOH, RCOOH, $RRNH_3^+$) and the solvent, respectively.

The $pK^{\mathbf{CH}}_{\mathbf{a}}$ value of **1** was first determined from the observed absorbance variations at $\lambda_{\mathbf{max}}$ of **C-1** obtained at equilibrium as a function of pH. These describe a clear acid–base equilibration, an excellent straight line with unit slope being obtained on plotting the log values of the ratio of ionized to non-ionized **1** as a function of pH [eqn. (2)]. From this plot (not shown), we readily obtained $pK^{\mathbf{CH}}_{\mathbf{a}} = 6.02 \pm 0.04$ for **1** (Table 3).

$$\log [\mathbf{C\text{-}1}]/[\mathbf{1}] = \mathrm{pH} - \mathrm{p}K^{\mathbf{CH}}_{\mathbf{a}} \qquad (2)$$

Depending upon the pH studied, the interconversion of **1** and **C-1** was kinetically investigated in the forward direction by mixing a neutral solution of **1** with the appropriate NaOH or buffer solutions (pH ⩾ 6) or in the reverse direction by mixing a freshly prepared 0.01 mol dm^{-3} solution of the carbanion **C-1** in NaOH with the required buffer or HCl solutions (pH ⩽ 6). In agreement with the direct equilibrium approach described by eqn. (1), oscilloscope traces of the reaction progress obtained in stopped-flow experiments revealed that only one relaxation time was associated with the interconversion in all primary amine and phenol buffers as well as in all dilute NaOH solutions employed. Some of the observed first-order rate constants, $k_{\mathbf{obs.}}$, measured under these experimental conditions are summarized in Tables S_1 and S_2 given as supplementary information.†

From the $k_{\mathbf{obs.}}$ values obtained in NaOH solutions, an excellent straight line fitting the simple equation (3) was obtained

$$k_{\mathbf{obs.}} = k^{\mathbf{OH}}_{\mathbf{p}}[\mathrm{OH}^-] \qquad (3)$$

(not shown), which afforded $k^{\mathbf{OH}}_{\mathbf{p}} = 14\,250$ dm^3 mol^{-1} s^{-1}. This allowed the calculation of the $k^{\mathbf{H_2O}}_{-\mathrm{p}}$ rate constant from $k^{\mathbf{H_2O}}_{-\mathrm{p}} = k^{\mathbf{OH}}_{\mathbf{p}}\,(K_s/K^{\mathbf{CH}}_{\mathbf{a}})$ where K_s is the autoprotolysis constant of the 50:50 H_2O–Me_2SO mixture at $I = 0.5$ mol dm^{-3} ($pK_s = 15.83$ at 25 °C):[12] $k^{\mathbf{H_2O}}_{-\mathrm{p}} = 2.2 \times 10^{-6}$ s^{-1}.

Working out the data obtained in the pH range of 7.24–9.99 covered by the primary amine and phenol buffers employed revealed that only the buffer base pathway was important in determining $k_{\mathbf{obs.}}$ in these systems. Applying eqn. (4) allowed the

$$k_{\mathbf{obs.}} = k^{\mathbf{B}}_{\mathbf{p}}[\mathrm{B}] \qquad (4)$$

various $k^{\mathbf{B}}_{\mathbf{p}}$ rate constants to be determined easily. Then, the related $k^{\mathbf{BH}}_{-\mathrm{p}}$ values were calculated by means of eqn. (5).

$$k^{\mathbf{BH}}_{-\mathrm{p}} = k^{\mathbf{B}}_{\mathbf{p}}\,K^{\mathbf{BH}}_{\mathbf{a}}/K^{\mathbf{CH}}_{\mathbf{a}} \qquad (5)$$

The simple equilibrium approach of eqn. (1) also prevailed in the pH range of 4.21–6.24 covered by buffers made up from acetic acid, formic acid, benzoic acid, 3-chlorobenzoic acid and 4-chlorobenzoic acid. The corresponding $k_{\mathbf{obs.}}$ values are summarized in supplementary Table S_3. In acetic acid buffers, both buffer base and acid pathways contributed to $k_{\mathbf{obs.}}$ with the data fitting eqn. (6). In agreement with this equation, plots of $k_{\mathbf{obs.}}$ *vs.*

$$k_{\mathbf{obs.}} = k^{\mathbf{B}}_{\mathbf{p}}[\mathrm{B}] + k^{\mathbf{BH}}_{-\mathrm{p}}[\mathrm{BH}] = [p\,k^{\mathbf{B}}_{\mathbf{p}} + k^{\mathbf{BH}}_{-\mathrm{p}}][\mathrm{BH}] \qquad (6)$$

$[CH_3COOH]$ 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 decreasing pH. From a standard treatment of the data, the following $k^{\mathbf{AcOH}}_{-\mathrm{p}}$ and $k^{\mathbf{AcOH}}_{\mathbf{p}}$ values were obtained: $k^{\mathbf{AcOH}}_{-\mathrm{p}} = 1.91$ dm^3 mol^{-1} s^{-1}; $k^{\mathbf{AcOH}}_{\mathbf{p}} = 1.05$ dm^3 mol^{-1} s^{-1}. For the other buffers quoted above, the $k^{\mathbf{B}}_{\mathbf{p}}[\mathrm{B}]$ terms were negligible, allowing $k^{\mathbf{BH}}_{-\mathrm{p}}$ to be determined readily from the slopes of the linear plots of $k_{\mathbf{obs.}}$ *vs.* [BH]. In these instances, eqn. (5) was used to calculate the corresponding $k^{\mathbf{B}}_{\mathbf{p}}$ values.

In chloroacetic acid buffers (pH 2.91–3.51) and dilute HCl solutions (5 × 10^{-4}–10^{-2} mol dm^{-3}), the reprotonation of **C-1** to **1** no longer followed the simple mechanism of eqn. (1). Instead, the interaction consisted of two steps with the initial and instantaneous formation of an intermediate species X which subsequently decomposed to **1**. The UV–VIS spectrum of X, whose formation is pH-dependent and essentially complete in 0.01 mol dm^{-3} HCl, could be recorded by stopped-flow spectrophotometry (Fig. 1). Based on the preferred resonance contributor for **C-1** and available features pertaining to nitronic acid formation from nitroalkanes and polynitrotoluene derivatives,[10,13,14] it will be shown in the discussion that X may be identified as the nitronic acid **C-1a,H** rather than the isomer **C-1b,H**. Thus, the most appropriate scheme for the conversion of **C-1** to **1** at low pH is as depicted in eqn. (7) where $K^{\mathbf{NOH}}_{\mathbf{a}}$ is the

$$\mathbf{C\text{-}1a,H} \overset{K^{\mathbf{NOH}}_{\mathbf{a}}}{\rightleftharpoons} \mathbf{C\text{-}1} \xrightarrow{k^{\mathbf{H}}_{-\mathrm{p}}[\mathrm{H}^+] + k^{\mathbf{BH}}_{-\mathrm{p}}[\mathrm{BH}] + k^{\mathbf{H_2O}}_{-\mathrm{p}}} \mathbf{1} \qquad (7)$$

acidity constant of the nitronic acid functionality of **C-1a,H**.

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† Supplementary material deposited at the British Library (SUPPL. No. 57259, 9 pp.). For details of the Supplementary Publications scheme see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, Issue 1, 1997.

Table 2 ^{13}C Chemical shifts for (4-nitrophenyl)nitromethane **1** and the related carbanion **C-1** in H_2O–Me_2SO mixtures and $(CD_3)_2SO$[a]

Solvent	Compound	$\delta(C^{\alpha})$	$\delta(C^1)$	$\delta(C^{2,6})$	$\delta(C^{3,5})$	$\delta(C^4)$	$J(C^{\alpha}H^{\alpha})$
$(CD_3)_2SO$	**1**	77.55	137.05	132.08	123.69	148.02	149.1
	C-1	109.76	143.26	121.87	123.90	140.09	180.11
	$\Delta\delta$	32.21	6.21	−10.21	0.21	−7.93	31.3
30:70 H_2O–Me_2SO	**1**	77.77	136.73	131.88	123.78	148.08	150.3
	C-1	111.62	141.63	124.26	123.89	142.53	180.4
	$\Delta\delta$	33.85	4.90	−7.62	0.11	−5.55	30.1
50:50 H_2O–Me_2SO	**1**	77.96	136.68	131.78	123.98	148.27	—
	C-1	113.27	140.44	125.41	123.94	143.74	—
	$\Delta\delta$	35.31	3.76	−6.37	−0.04	−4.53	—

[a] δ in ppm relative to internal reference $SiMe_4$; J in Hz.

Table 3 pK_a Values and tautomerization constants, K_T, for (4-nitrophenyl)nitromethane **1** and phenylnitromethane **2** in water, 50:50 H_2O–Me_2SO and in Me_2SO at 25 °C

Solvent	H_2O		50:50 H_2O–Me_2SO		Me_2SO	
Compound	**1**	**2**	**1**	**2**	**1**	**2**
pK_a^{CH}	5.89[a]	6.88[b] 6.77[c]	6.02	7.93[c]	8.62[d]	12.32[e]
pK_a^{NOH}	—	3.90[f] 3.64[c]	3.36	4.75[c]	—	—
K_T = [*aci*]/[nitro]	—	1.04×10^{-3} 7.41×10^{-4}	2.18×10^{-3}	6.61×10^{-4}[c]	—	—

[a] Ref. 3. [b] Ref. 2. [c] Ref. 10 at 20 °C. [d] Ref. 7. [e] F. G. Bordwell; cited in ref. 10. [f] Value at 25 °C reported in A. T. Nielsen, *The Chemistry of the Nitro and Nitroso groups*, ed. H. Feuer, Wiley, New York, 1969, Part 1, p. 349.

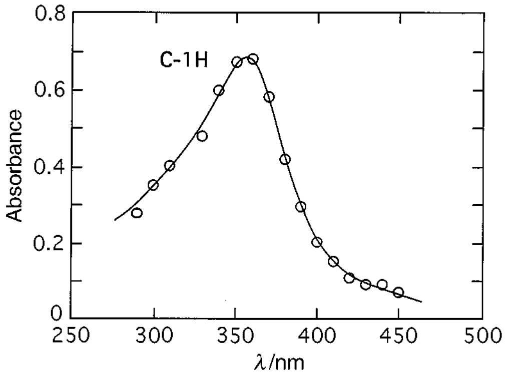
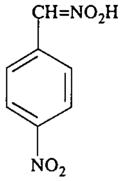
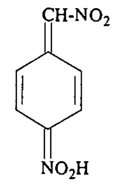


Fig. 1 UV–VIS absorption spectrum of the nitronic acid **C-1H** in 50:50 (v/v) H_2O–Me_2SO; $T = 25$ °C; $I = 0.5$ mol dm^{-3} (KCl); [**C-1H**] = 1×10^{-4} mol dm^{-3}



C-1a,H



C-1b,H

It follows that the measured $k_{obs.}$ values for the process (supplementary Tables S_3 and S_4) should obey eqn. (8) in

$$k_{obs.} = (k^{H}_{-p}[H^+] + k^{H_2O}_{-p})\frac{K_a^{NOH}}{K_a^{NOH} + [H^+]} + k^{BH}_{-p}[BH]\frac{K_a^{NOH}}{K_a^{NOH} + [H^+]} \quad (8)$$

chloroacetic acid buffer solutions and the reduced eqn. (9) in HCl solutions.

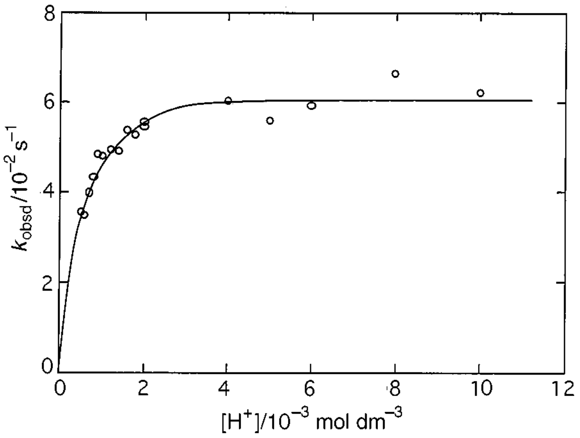


Fig. 2 Effect of HCl concentration on the observed rate of protonation of the carbanion **C-1** in 50:50 (v/v) H_2O–Me_2SO; $T = 25$ °C; $I = 0.5$ mol dm^{-3} (KCl)

$$k_{obs.} = (k^{H}_{-p}[H^+] + k^{H_2O}_{-p})\frac{K_a^{NOH}}{K_a^{NOH} + [H^+]} \quad (9)$$

In agreement with eqn. (9), a curved plot of $k_{obs.}$ *vs.* [H$^+$] was obtained from measurements in HCl solutions (Fig. 2). Since the solvent contribution ($k^{H_2O}_{-p}$) is negligible in the pH range at hand, eqn. (9) may be rewritten in the form of eqn. (10) which

$$\frac{1}{k_{obs.}} = \frac{1}{k^{H}_{-p}[H^+]} + \frac{1}{k^{H}_{-p}K_a^{NOH}} \quad (10)$$

predicts that one should obtain a satisfactory straight line on plotting $1/k_{obs.}$ *vs.* $1/[H^+]$. Fig. 3 confirms this expectation, leading to the following estimates of k^{H}_{-p} and $k^{H}_{-p}K_a^{NOH}$ from the slope and the intercept, respectively: $k^{H}_{-p} = 153$ dm^3 mol^{-1} s^{-1}; $k^{H}_{-p}K_a^{NOH} = 0.067$ s^{-1}. Combination of these two values afforded a pK_a^{NOH} value of 3.36 for the ionization of **C-1a,H**.

Table 4 Second-order rate constants for the ionization of **1** in 50 : 50 (v/v) H_2O–Me_2SO[a]

Buffer (BH)	pK_a	k_p^B/dm^3 mol^{-1} s^{-1}	k_{-p}^{BH}/dm^3 mol^{-1} s^{-1}
H_2O	17.34	14 250	7.97×10^{-8}[b]
4-Chlorophenol	10.18	957	0.08[c]
2-Bromophenol	9.52	375	0.14[c]
3,4-Dichlorophenol	9.10	368	0.18[c]
4-Cyanophenol	8.45	110	0.31[c]
2-Cyanophenol	7.97	56	0.54[c]
Butylamine	9.99	71.65	0.009[c]
2-(*N*-Methylamino)ethanol	9.39	56.65	0.03[c]
2-Methoxyethylamine	9.11	12.09	0.012[c]
Glycinamide	8.01	1.7	0.021[c]
Glycine ethyl ester	7.24	1.57	0.13
Acetic acid	5.84	1.05	1.91
Formic acid	4.45	0.12[c]	5.52
Chloroacetic acid	3.21	0.02[c]	13.69
Benzoic acid	5.13	0.49	4.59
3-Chlorobenzoic acid	4.63	0.25	7.38
2-Chlorobenzoic acid	4.21	0.20	15.31
H_3O^+	−1.44	5.29×10^{-6}[d]	153

[a] $I = 0.5$ mol dm^{-3} (KCl); $T = 25$ °C; experimental error in the rate constants: ±4% or better; calculated rate constants: ±12%; pK_a^{BH} values from refs. 12 and 43. [b] $k_{-p}^{H_2O}$ calculated from $k_p^{OH}K_s/K_a$ with p$K_s = 15.83$ at 25 °C (see text). [c] Calculated from k_p^B or k_{-p}^{BH} *via* eqn. (5). [d] $k_p^{OH}/27.6$ with $k_p^{H_2O}$ calculated from $K_a^{CH}k_{-p}^H$.

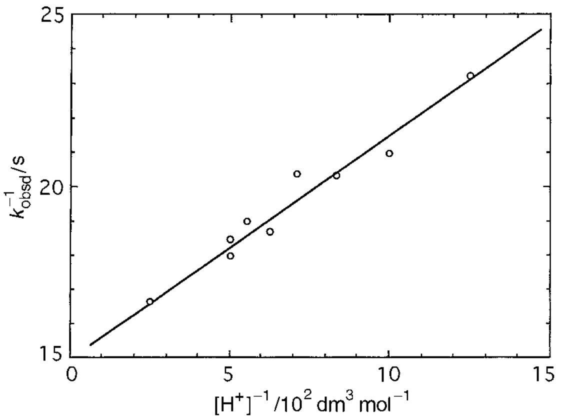


Fig. 3 Inversion plot according to eqn. (10) for protonation of the carbanion **C-1** in HCl solutions (8×10^{-4}–4×10^{-3} mol dm^{-3}) in 50 : 50 (v/v) H_2O–Me_2SO; $T = 25$ °C; $I = 0.5$ mol dm^{-3} (KCl)

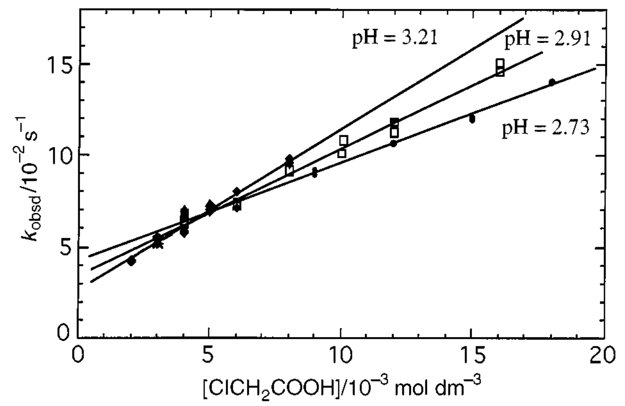


Fig. 4 Effect of buffer concentration and pH on the observed rate constant, $k_{obs.}$, for protonation of the carbanion **C-1** in chloroacetic buffers in 50 : 50 (v/v) H_2O–Me_2SO; $T = 25$ °C; $I = 0.5$ mol dm^{-3} (KCl); ● pH = 2.7; □ pH = 2.91; ◆ pH = 3.21

This pK_a^{NOH}value implies that the right hand term in eqn. (9) must become identical to $k_{-p}K_a^{NOH}$ in HCl solutions of pH ⩽ 2.3, a situation which accounts for the plateau observed in Fig. 2 and supplementary Table S_4 ($k_{-p}^H K_a^{NOH} = 0.063$ s^{-1}). From the k_{-p}^H value, the rate constant for deprotonation of **1** by the solvent was calculated as $k_p^{H_2O} = K_a^{CH}k_{-p}^H = 1.46 \times 10^{-4}$ s^{-1}.

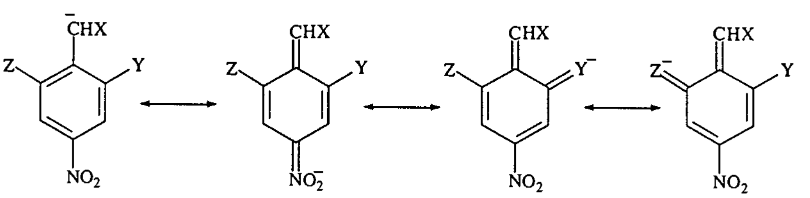
Regarding the reprotonation of **C-1** in chloroacetic buffers, eqn. (8) predicts that the $k_{obs.}$ values should depend linearly upon the BH concentration at constant pH, *i.e.* at a given buffer ratio, but that the slopes of these plots should decrease with increasing H^+ concentration. As shown in Fig. 4, the data obtained at the three pH values studied confirmed this expected relationship. After appropriate correction for the $K_a^{NOH}/(K_a^{NOH} + [H^+])$ terms, the slopes of the lines in Fig. 4 gave consistent values for k_{-p}^{BH}, allowing the calculation of the related k_p^B rate constant by means of eqn. (5).

All second-order rate constants for deprotonation of **1** (k_p^{OH}, k_p^B, $k_p^{H_2O}/27.6$) and reprotonation of **C-1** (k_{-p}^H, k_{-p}^{BH}, $k_{-p}^{H_2O}/27.6$) in 50 : 50 H_2O–Me_2SO are summarized in Table 4.

Discussion

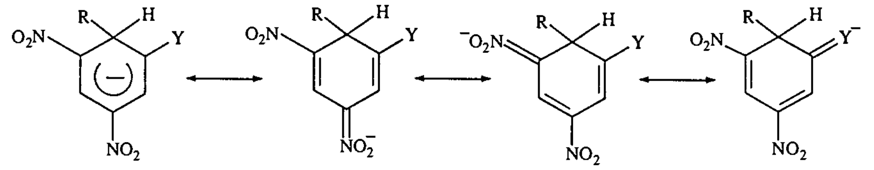
Structure of the carbanion C-1

Tables 1 and 2 show that the resonances of the exocyclic H^α and C^α atoms of **1** are subject to large downfield shifts upon ionization in 50 : 50 H_2O–Me_2SO : $\Delta\delta(H^\alpha) = 1.23$, $\Delta\delta(C^\alpha) = 35.31$ ppm. Inasmuch as such $\Delta\delta$ values are the reflection of two opposing effects, namely a high-field shift caused by increased electron density at C^α and a low-field shift caused by the $sp^3 \longrightarrow sp^2$ rehybridization of this carbon,[15–18] the large positive values associated with the ionization of **1** clearly show that the rehybridization factor is predominant. Also consistent with a strong olefinic character of C^α is the finding that the ionization induces large variations in $^1J(C^\alpha H^\alpha)$ ($\Delta J = 30.6$ Hz) together with the high values for this coupling constant for **C-1** [$^1J(C^\alpha H^\alpha)$ 180.9 Hz].[16] It follows from these results that a significant delocalization of the negative charge of the carbanion **C-1** must occur onto the exocyclic nitro group (structure **C-1a**) or through the nitrophenyl ring (structure **C-1b**). In this regard, it is noteworthy that the ionization of **1** induces relatively little change in the resonances of the protons and carbons of the phenyl ring. In general, an increased electron density at C^4 of a *p*-nitro substituted benzyl carbanionic structure or an anionic *p*-nitrocyclohexadienyl structure results in a significant shielding of this carbon.[13,19–24] Thus, $\Delta\delta(C^4)$ values in the range of −20 to −30 ppm have commonly been found for formation of carbanions of type **C-3** or σ-adducts of type **4**, in agreement with theoretical calculations which predict a predominance of the *para-*



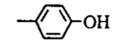
C-3 **C-3a** **C-3b** **C-3c**

X = $COCH_3$, Y=NO_2, Z=H
X = $COCH_3$, Y = Z = NO_2
X = COC_6H_5, Y = Z = NO_2

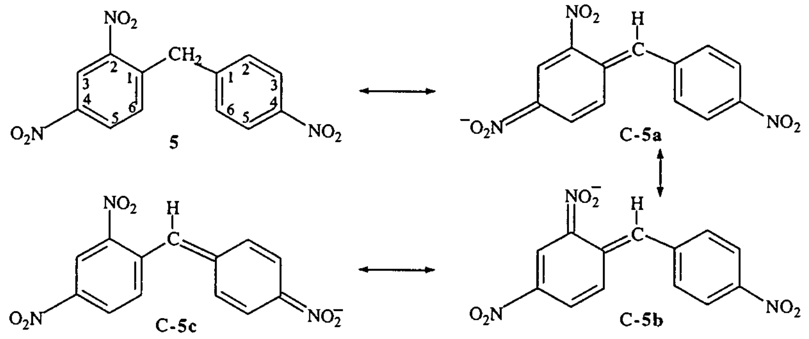


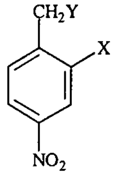
4 **4a** **4b** **4c**

R = OCH_3,
OC_6H_5,
CH_2COCH_3,

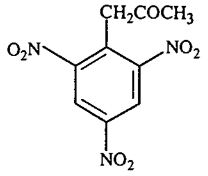


Y = H, NO_2





6a X=H, Y=CN
6b X=NO_2, Y=CN
6c X=NO_2, Y=H



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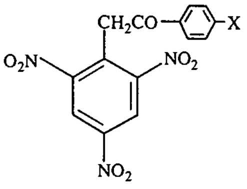


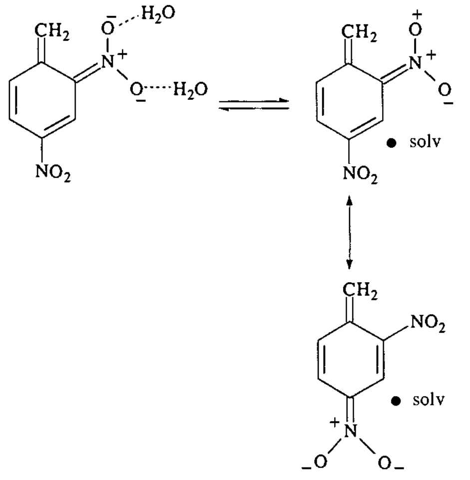
8a X=H
8b X=OMe

quinoid structures **C-3a** and **4a** in the delocalization of the negative charge of these species.[25–28] When Y and/or Z is also strongly electron-withdrawing, *e.g.* Y = NO_2, the role of the *ortho*-quinoid structures is not negligible and the $C^{2,6}$ carbons may also suffer a significant shielding [$\Delta\delta(C^{2,6}) \approx -10$ to -17 ppm]. In the case of the ionization of **1**, the $\Delta\delta(C^4)$ and $\Delta\delta(C^{2,6})$ values are comparatively small [$\Delta\delta(C^4) = -4.53$, $\Delta\delta(C^{2,6}) = -6.37$], suggesting that the nitrophenyl ring does not in fact contribute markedly to the delocalization of the negative charge of **C-1**. This situation may be usefully compared to that observed in the ionization of 2,4-dinitrophenyl(4-nitrophenyl)methane **5** to give the planar conjugate carbanion **C-5** whose stability derives for the most part from the resonance structures **C-5a** and **C-5b**.[15] In this instance, the process induces strong shieldings of the protons and carbons of the 2,4-dinitrosubstituted ring [$\Delta\delta(C^2) = -18.6$, $\Delta\delta(C^4) = -14.3$, $\Delta\delta(C^6) = -11.7$; $\Delta\delta(H^5) = -1.35$, $\Delta\delta(H^6) = -0.55$, $\Delta\delta(H^3) = -0.07$] but affects very little the resonances of the protons and carbons of the mononitrosubstituted ring [$\Delta\delta(C^{2',6'}) = -3.1$, $\Delta\delta(C^{4'}) = -4.4$, $\Delta\delta(H^{2',6'}) = -0.04$, $\Delta\delta(H^{3',5'}) = -0.17$]. Interestingly, the above $\Delta\delta(C^{4'})$ value is very similar to that for the ionization of **1**.

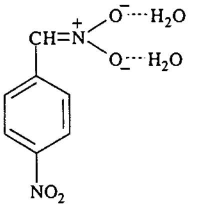
Going from 50:50 H_2O–Me_2SO to 30:70 H_2O–Me_2SO to pure Me_2SO does not change the $\Delta\delta$(C) and $\Delta\delta$(H) patterns to a sufficient extent to reverse the conclusion that the resonance structure **C-1a** is predominant in governing the stability of **C-1**. Nevertheless, a close inspection of Tables 1 and 2 shows that the change in solvent leads to an increase in the role of the resonance contributor **C-1b**. Thus, we note a regular increase in the shielding of C^4 on going from 50:50 Me_2SO–H_2O ($\Delta\delta = -4.53$) to Me_2SO ($\Delta\delta = -7.93$). Changes in the chemical shift of $C^{2,6}$ show a similar pattern. Concomitantly, the $C^{3,5}$ protons suffer some deshielding, in agreement with SCF MO calculations carried out on structures of type **C-3** or **4**.[25–28] Also noteworthy is an increased shielding of the $H^{3,5}$ protons ($\Delta\Delta\delta^{Me_2SO}_{50\%} = -0.15$) and the progressive disappearance of the deshielding of the $H^{2,6}$ protons ($\Delta\Delta\delta^{Me_2SO}_{50\%} = -0.21$).

Altogether, the above trends leave no doubt that the contribution of the nitrophenyl ring to the stabilization of **C-1** increases with increasing Me_2SO concentration, in agreement with the well-known solvating properties of this dipolar aprotic solvent.[29–31] However, as for many other anions in which the negative charge is highly localized on an electronegative atom, nitronate ions such as **C-1** and **C-2** may normally be expected to suffer significant loss of hydrogen bonding solvation and to be therefore strongly destabilized on going from aqueous to Me_2SO solutions.[31–34] That this situation holds in the case of **C-2** is evidenced by the finding that the solvent transfer is associated with a strongly positive free energy change ($\Delta G_T = 23.5$ kJ mol^{-1}) which goes along with a sharp increase in the basicity of this species ($pK_a^{H_2O} = 6.88$, $pK_a^{Me_2SO} = 12.32$).[7,10,32] A similar destabilization of the nitromethane anion has also been reported ($pK_a^{H_2O} = 10.28$, $pK_a^{Me_2SO} = 17.2$).[10,30] In contrast, Me_2SO is very prone to stabilize large and polarizable anions such as nitro-substituted benzyl carbanions **C-3** or **C-5** or nitrocyclohexadienyl anions **4**.[28,35] The free energies of transfer, ΔG_T, of these species from water to Me_2SO are negative while the pK_a values associated with their formation from the parent substrates decrease concomitantly to some extent.[36–38] Based on these contrasting solvent effects, an increase in the contribution of the *para*-quinoid resonance structure at the expense of the exocyclic nitronate one was to be expected on transfer of **1** from water to Me_2SO. In agreement with this idea, the solvent change is found to induce much less destabilization for the (4-nitrophenyl)nitromethane carbanion **C-1** than for the unsubstituted phenylnitromethane carbanion **C-2** or nitromethane anion: $\Delta pK = pK_a^{Me_2SO} - pK_a^{H_2O} = 2.73$, 5.44 and 6.92 for **1**, **2** and CH_3NO_2, respectively. The shift of λ_{max} to higher wavelengths and a concomitant increase in the extinction coefficient are also consistent with an increase in the contribution of the resonance structure **C-1b** with increasing Me_2SO concentration.[15] However, as evidenced by the observed increase in the pK_a^{CH} value of **1** ($\Delta pK = pK_a^{Me_2SO} - pK_a^{H_2O} = 2.73$), the change from **C-1a** to **C-1b** is not sufficient to avoid a notable destabilization of **C-1** on going from water to Me_2SO solutions. This indicates that the nitronate structure **C-1a** must remain largely predominant over the whole range of H_2O–Me_2SO mixtures and that protonation of **C-1** must afford the nitronic acid **C-1a,H** rather than the isomer **C-1b,H**. Interestingly, the UV–VIS spectrum recorded for the protonated species observed at low pH compares well with that reported for the *aci*-form of phenylnitromethane,[10] with a relatively low absorption maximum at λ 342 nm (ε 2400 dm^3 mol^{-1} cm^{-1}). In general, nitronic acids derived from nitrobenzyl carbanions or nitrocyclohexadienyl anions exhibit a strong absorption at $\lambda > 400$ nm.[13,14,39]

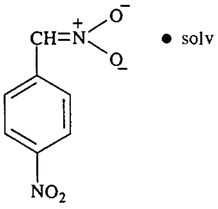
Regarding the changes in the absorption of **C-1** brought about by the transfer from water to Me_2SO or acetonitrile, it is of interest to emphasize that pronounced solvent effects on the absorption spectra of nitro carbanions have been encountered previously, for example in the case of the anion derived from 4-nitrophenylacetonitrile **6a** in H_2O–Me_2SO mixtures and the anion derived from 2,4-dinitrotoluene **6c** in H_2O–acetonitrile or –Me_2SO mixtures.[40–42] In these instances, the explanation which has been offered is that the anion can exist in two differently solvated forms, one where water molecules are tightly hydrogen bonded to the nitro group and a second non-specifically solvated form lacking this hydrogen bonding and which would be favoured in dipolar aprotic solvents.[40,41] Proposed structures by McClelland and Steenken for the 2,4-dinitrobenzyl carbanion are shown.[41]



Proposed structures for 2,4-dinitrobenzyl carbanion



A

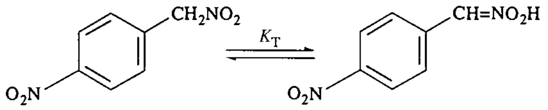


B

While such hydrogen bonding solvent effects have also been identified in the case of nitromethane and phenylnitromethane carbanions, they were not found to induce absorption changes of the same intensity as those found for **C-1**.[10] Even though it is clear that the delocalization of the negative charge onto the exocyclic nitro group is always largely predominant in the stabilization of **C-1**, it seems difficult to explain the changes in the spectra of this carbanion in terms of the existence of the two forms below, **A** and **B**. We therefore suggest that the very large solvent effect observed on the spectra of **C-1** is essentially interrelated with the increasing contribution of the 4-nitro group to the delocalization of the negative charge on going from water to Me_2SO. This trend is obviously favoured by the loss of hydrogen bonding solvation at the exocyclic NO_2 group consequent to this solvent transfer.

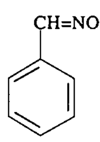
CH and NOH acidities of 1

The pK_a^{NOH} value for the ionization of **C-1a,H** is 3.36, as compared with a pK_a^{NOH} value of 4.75 for the nitronic acid **C-2a,H**.[10] This 20-fold increase in the acidity of the exocyclic NO_2H function reflects the expected acidifying effect of the *p*-nitrophenyl moiety of **C-1a,H**. To be noted is that the related increase in the pK_a^{CH} value is of the same order of magnitude: pK_a^{CH} (**1**) = 6.02; pK_a^{CH} (**2**) = 7.93 in 50:50 (v/v) H_2O–Me_2SO. From the pK_a^{CH} and pK_a^{NOH} values, the equilibrium constant K_T measuring the extent of the conversion of **1** into its *aci*-form **C-1a,H** [eqn. (11)] in 50:50 H_2O–Me_2SO can be calculated (Table 3).



(11)

1 **C-1aH**



C-2aH

As can be seen, K_T and hence the *aci*-content is very small, in agreement with the failure to detect the presence of **C-1a,H** in ^1H and ^{13}C NMR spectra recorded under common experimental conditions in this aqueous Me_2SO mixture.

Intrinsic reactivity of 1

Fig. 5 shows statistically corrected Brønsted plots for deprotonation of **1** by the various buffers employed. For a given $\Delta pK + \log (p/q)$ value, these figures exemplify the reactivity order $ArO^- > RCOO^- > ArCOO^- > RNH_2$. As has been discussed by many authors, this trend is considered to reflect the

Table 5 Brønsted coefficients and intrinsic reactivities for ionization of **1** and some representative carbon acids in 50:50 (v/v) H_2O–Me_2SO

Carbon acid	Base	β_B	log k_0
6a	ArO^-	—	$(4.50)^{b,c}$
	RR′NH	0.74	$3.70^{b,d}$
6b	ArO^-	—	$(3.50)^{b,c}$
	RR′NH	0.50	$2.70^{b,d}$
8b	ArO^-	0.44	$2.73^{a,e}$
7	ArO^-	0.41	$2.37^{a,f}$
8a	ArO^-	0.39	$2.25^{a,e}$
	$RCOO^-$	0.46	$1.55^{a,e}$
CH_3NO_2	ArO^-	—	$(1.5)^{b,c}$
	RR′NH	0.62	$0.73^{b,g}$
1	ArO^-	0.55	$0.60\ (0.57)^{a,h}$
	$RCOO^-$	0.65	0.11^{a}
	RNH_2	0.65	-1.08^{a}
2	ArO^-	—	$(0.20)^{b,c}$
	RR′NH	0.52	$-0.25^{b,g}$
	$RCOO^-$	~0.6	$-0.57^{b,g}$

[a] $T = 25$ °C. [b] $T = 20$ °C. [c] Values in parentheses estimated on the basis that log k_0 values for both $RCOO^-$ ions and secondary amines are generally lower than those for ArO^- ions by about 0.8 ± 0.3 log k unit. [d] Ref. 46. [e] Ref. 13(*b*). [f] Ref. 13(*a*). [g] Ref. 10. [h] Ref. 3.

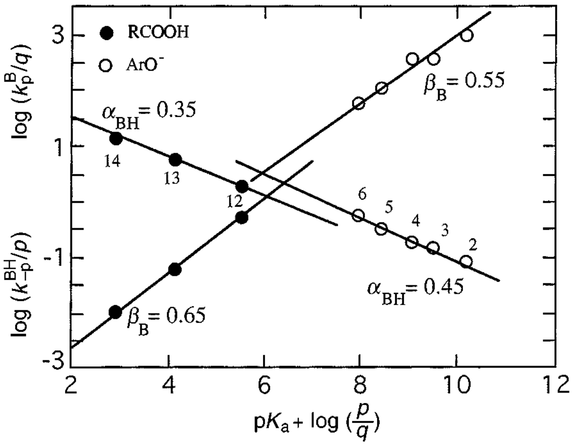


Fig. 5 Brønsted plots for deprotonation of **1** by various phenoxide and carboxylate ions and reprotonation of the carbanion **C-1** by the conjugate phenol and carboxylic acid catalysts in 50:50 (v/v) H_2O–Me_2SO; $T = 25$ °C; $I = 0.5$ mol dm^{-3} (KCl). The numbering of the catalysts is given in Table 4.

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.[3,8,10,12,33,34,37,38,43,44] On the other hand, all Brønsted β_B values reported in Table 5 lie in a range (0.55–0.65) commonly found for ionization of carbon acids, suggesting that proton transfer is about half-complete at the transition states of eqn. (1).[33,44] In particular, β_B values of the same order of magnitude have been reported for deprotonation of **1** by secondary amines and phenoxide ions in aqueous solutions as well as for deprotonation of phenylnitromethane **2** by secondary amines and carboxylate ions in various aqueous dimethyl sulfoxide mixtures.[3,10]

Extrapolation of the various Brønsted plots in Fig. 5 and supplementary figure S_1 to $pK_a^{BH} + \log(p/q) = pK_a^{CH}$ afforded the values of the intrinsic rate constants, k_0, for deprotonation of (4-nitrophenyl)nitromethane **1** by the various catalysts.[33,43] These k_0 values are compared in Table 5 with similar data available for some carbon acids, including **2**, known to exhibit either a nitroalkane behaviour or a nitrotoluene behaviour. The key feature in Table 5 is that the intrinsic reactivity of **1** is very low, comparing well with those of nitromethane and phenylnitromethane[3,10] but not with those of the two benzyl cyanides **6a** and **6b** or the three picryl ketones **7**, **8a** and **8b**.[13,45] Interestingly all these five compounds have been shown to ionize with formation of carbanions whose negative charge is essentially delocalized through the nitro substituted phenyl ring.[13] Based on intrinsic reactivity data, there is therefore no doubt that (4-nitrophenyl)nitromethane behaves essentially as a nitroalkane compound.

Experimental

Materials

Me_2SO was purified by fractional distillation from CaH_2 under reduced pressure and stored under nitrogen and over molecular sieves. Buffers (carboxylic acids, benzoic acids, phenols and primary amines) were all commercial products which were purified or distilled prior to use. (4-Nitrophenyl)nitromethane was obtained from the reaction of silver nitrate with 4-nitrobenzyl bromide, following the procedure of Kornblum;[47] **1**, mp 90–91 °C (lit.,[8,47] 90–91 °C). Solutions in 50:50 (v/v) H_2O–Me_2SO were made up as described previously.[12,13,18]

Rate and pK_a measurements

The pK_a^{CH} value of **1** was measured at 25 °C in 50:50 (v/v) H_2O–Me_2SO, using a conventional spectrophotometer and previously calibrated acetic and benzoic acid buffers.[48,49] The pK_a^{NOH} value of **1** was measured by means of a Durrum stopped-flow spectrophotometer, following the initial absorbance changes brought about by the protonation of the conjugate carbanion **C-1** in dilute HCl and chloroacetic acid buffer solutions. 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 supplementary Tables S_1–S_4 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 **1** up to at least 90% of the overall reaction.

Acknowledgements

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