

# Solvent effects in the decomposition reaction of some products formed by the reaction of sorbic acid with sodium nitrite: 1,4-dinitro-2-methylpyrrole and ethylnitrolic acid

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A kinetic study of the decomposition reaction of 1,4-dinitro-2-methylpyrrole (NMP) and ethylnitrolic acid (ENA), both formed in the reaction between sorbic acid and sodium nitrite was performed in the 3.5–4.2 pH range in water/dioxane mixtures. Conclusions were drawn as follows: (i) The decomposition of NMP occurs through nucleophilic attack by OH<sup>-</sup> ions, the rate equation being:  $r = k_{dec}^{NMP} [OH^-][NMP]$ . (ii) The rate law for the decomposition of ENA is:  $r = k_{dec}^{ENA} [ENA]K_a/(K_a + [H^+])$ ,  $K_a$  being the ENA dissociation constant. (iii) The value of  $K_a$  decreases when the water/dioxane ratio decreases,  $\log K_a$  being proportional to the Onsager parameter  $(\epsilon - 1)/(2\epsilon + 1)$ . This permits the equilibrium between non-dissociated and the dissociated forms of ENA to be rationalized. (iv) No appreciable variation in the  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values with composition of the medium was observed, either in the NMP decomposition reaction, or in the ENA decomposition reaction. Copyright © 2008 John Wiley & Sons, Ltd.

**Keywords:** nitrite; sorbic acid; 1,4-dinitro-2-methylpyrrole; ethylnitrolic acid; solvent effect

## INTRODUCTION

Sorbic acid and its potassium and calcium salts are used as preservatives in a large number of foods, feeds, pharmaceuticals, and cosmetics<sup>[1,2]</sup> because of their inhibitory effects on yeasts, fungi, and bacteria.<sup>[3]</sup>

Sorbates are classified as 'Generally Recognized as Safe' (GRAS) additives by FDA,<sup>[4]</sup> and although, the most investigations have not revealed any mutagenic properties of sorbic acid and its salts, some reports have indicated a possible genotoxic potential of these compounds.<sup>[5–7]</sup> For this reason, the alkylating potential of the sorbic acid has been investigated previously.<sup>[8,9]</sup>

In the meat industry, sorbates are common inhibitors of mold growth in sausage casings while nitrites are used in meat products for curing, because of their effects on color as well as their antitubulinic activity.<sup>[10]</sup> It has been established that 2000–2600 ppm of potassium sorbate can be used in meat products in conjunction with 20–80 ppm of sodium nitrite for the purpose of lowering nitrite concentration to reduce carcinogenic N-nitrosamine formation, while maintaining meat color and controlling *Clostridium botulinum* growth and toxin production<sup>[11]</sup> (since the discovery in 1956 that nitrosamines are powerful carcinogens,<sup>[12]</sup> there has been a very large increase in studies of nitrosamine chemistry, particularly their formation and reactions).<sup>[13–15]</sup>

The induction of mutagenic activity by heating sorbic acid with sodium nitrite in aqueous medium has been reported by different

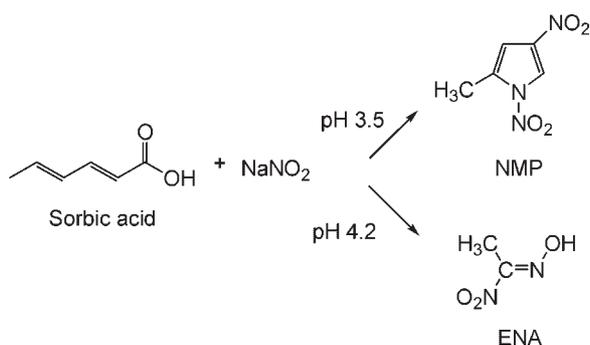
researchers.<sup>[16–20]</sup> In general, the literature concerning this subject stresses that the formation of products with mutagenic activity such as 1,4-dinitro-methylpyrrole (NMP) and ethylnitrolic acid (ENA) is optimal at a high nitrite/sorbate mole ratio of, ideally, 8:1, and mutagens are produced at a pH between 2 and 5, with a maximum in the 3.5–4.2 range<sup>[19,20]</sup> (Scheme 1).

In previous work, the decomposition reactions of NMP and ENA in aqueous solution were investigated.<sup>[21]</sup>

We are currently investigating the alkylating potential of NMP and ENA on the nucleophile 4-(*p*-nitrobenzyl)pyridine (NBP), a trap for alkylating agents with nucleophilic characteristics similar to those of DNA bases.<sup>[22,23]</sup> Because of the sparing solubility of NBP in water, it is necessary to work with aquo-organic mixtures in order to render the NBP soluble. For this reason, in this work a kinetic study of the stability of NMP and ENA in different water/dioxane media was performed.

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Scheme 1. Reaction of the nitrite ion with sorbic acid



Scheme 2. Decomposition of 1,4-dinitro-2-methylpyrrole

## RESULTS AND DISCUSSION

### Decomposition of 1,4-dinitro-2-methylpyrrole (NMP)

The decomposition reaction of NMP in 10:0, 8:2, 7:3, 6:4 and, 5:5 water/dioxane (v/v) media was investigated.

To monitor the NMP decomposition reaction, the absorbance at the wavelength of maximum absorption – which changes with the dioxane percentage in the reaction mixture – was followed.

Reactions were carried out in the 7.5–10.0 pH range. Phosphate and borate buffers were used to maintain pH constant.

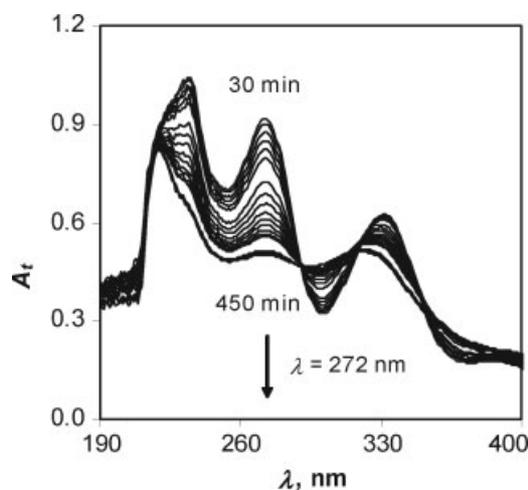
The decomposition reaction of NMP shows an inverse kinetic isotope effect and no significant variation in the  $k_{dec H_2O}^{NMP}/k_{dec D_2O}^{NMP}$  (Scheme 2) value with the dioxane percentage in the reaction mixture was observed (refer Table 1). This result was interpreted in terms of a nucleophilic attack of the OH<sup>-</sup> on the NMP molecule. Since OD<sup>-</sup> is a stronger nucleophile than OH<sup>-</sup>, the direct nucleophilic attack on the electrophilic carbon (Scheme 2) would be expected to proceed faster in D<sub>2</sub>O,<sup>[24]</sup> as was observed.

The presence of nitro groups on the pyrrole-ring may play a significant role in lowering the high  $\pi$ -electron density of the ring and in favoring the attack of the nucleophilic reagent.<sup>[18,25]</sup> This

**Table 1.** Kinetic isotope effect of the decomposition reaction of 1,4-dinitro-2-methylpyrrole in water/dioxane media;  $T = 37.5\text{ }^\circ\text{C}$

Water/ dioxane (v/v)	$k_{dec H_2O}^{NMP}$ (M <sup>-1</sup> s <sup>-1</sup> ) <sup>a</sup>	$k_{dec D_2O}^{NMP}$ (M <sup>-1</sup> s <sup>-1</sup> ) <sup>a</sup>	$k_{dec H_2O}^{NMP}/k_{dec D_2O}^{NMP}$
10:0	42.4 ± 1.0	60.8 ± 0.6	0.70 ± 0.03
8:2	25.8 ± 0.9	34.3 ± 0.8	0.75 ± 0.04
7:3	18.7 ± 0.6	30.3 ± 0.3	0.62 ± 0.03
5:5	6.3 ± 0.2	9.01 ± 0.1	0.70 ± 0.03

<sup>a</sup> Values are given within the 95% confidence interval.



**Figure 1.** Spectra showing the NMP decomposition over time in 7:3 water/dioxane medium.  $[NMP]_0 = 10^{-4}\text{ M}$ ;  $T = 37.5\text{ }^\circ\text{C}$ ; pH = 9.06 with borate buffer

explains the formation of the Meisenheimer-type adduct by the addition of OH<sup>-</sup> on the NMP molecule.

The NMP decomposition reaction obeys the following rate equation:

$$r = -\frac{d[NMP]}{dt} = k_{dec}^{NMP}[OH^-][NMP] = k_{obs}^{NMP}[NMP] \quad (1)$$

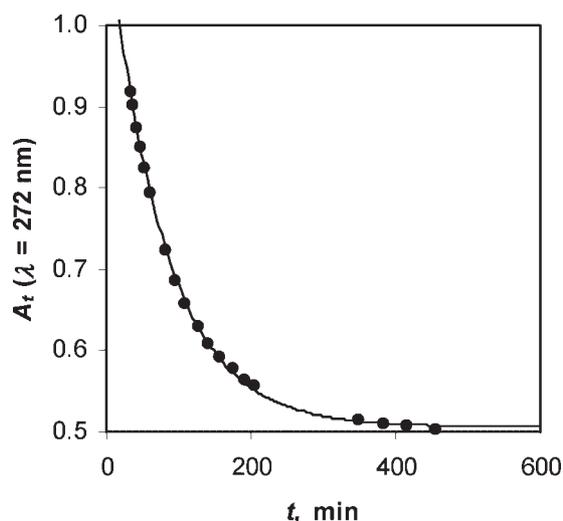
where  $k_{obs}^{NMP}$  is the pseudo-first-order rate constant, and [OH<sup>-</sup>] is kept constant with buffers

$$k_{obs}^{NMP} = k_{dec}^{NMP}[OH^-] \quad (2)$$

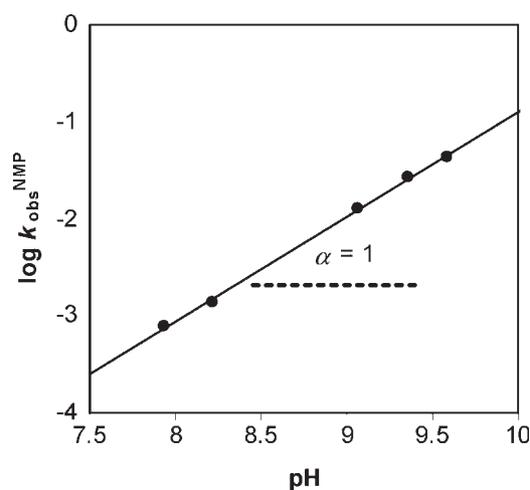
By designating the absorbance values of NMP as  $A_0$ ,  $A_t$ , and  $A_\infty$  at times, respectively, of zero,  $t$ , and infinity (end of reaction), the integration of Eqn (1) yields Eqn (3)

$$A_t = A_\infty + (A_0 - A_\infty)e^{-k_{obs}^{NMP}t} \quad (3)$$

Figure 1 depicts the variation in absorption of NMP with time. Figure 2 shows a typical kinetic run for the decomposition reaction of NMP in a 7:3 water/dioxane medium.



**Figure 2.** Determination of  $k_{obs}^{NMP}$  (Eqn (3)) in 7:3 water/dioxane medium.  $[NMP]_0 = 10^{-4}\text{ M}$ ;  $T = 37.5\text{ }^\circ\text{C}$ ; pH = 9.06 with borate buffer



**Figure 3.** Variation in the NMP decomposition rate constant with the acidity of the medium at  $T=37.5^\circ\text{C}$  in 7:3 water/dioxane medium.  $[\text{NMP}]_0 = 10^{-4}\text{ M}$ ; Phosphate and borate buffers

Experiments at different pH were performed (Fig. 3), the slope  $\alpha=1$  revealing first order with respect to the concentration of  $\text{OH}^-$  (Eqn (2)).

By fitting the absorbance values against those of time (Eqn (3)), the rate constant  $k_{\text{obs}}^{\text{NMP}}$  values were calculated. Using Eqn (2), knowledge of the  $k_{\text{dec}}^{\text{NMP}}$  values can be gained immediately (Table 3).

### Decomposition of ethylnitrolic acid

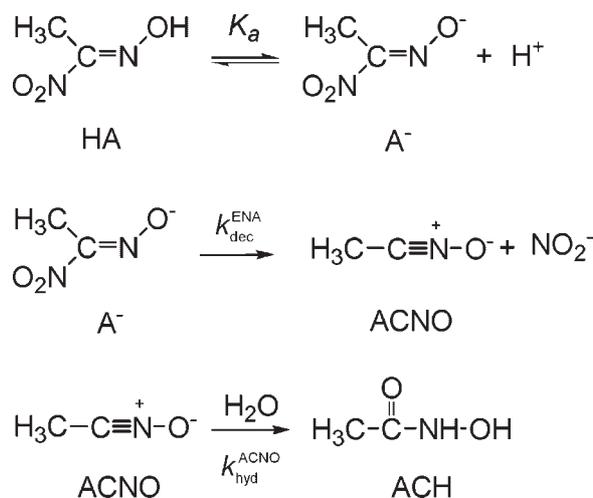
To monitor the ENA decomposition reaction, the absorbance at the wavelength of maximum absorption – which increases with increasing the dioxane percentage – was followed.

Reactions were carried out in the 7–10 pH range. Phosphate and borate buffers were used to maintain pH constant.

Since (i) the stability of ENA decreases with increasing pH, and (ii) the dissociated acid molecule undergoes  $\text{NO}_2^-$  loss, this being the limiting step,<sup>[26]</sup> the following mechanism for the decomposition of ENA was investigated (refer Scheme 3).

To determine  $k_{\text{dec}}^{\text{ENA}}$ , the value of the equilibrium constant  $K_a$  was obtained using spectrometric and titration methods.

Because (i) all the kinetic experiences were carried out in the pH = 7–10 range and (ii) the ACH  $\text{p}K_a = 9.31$ <sup>[27,28]</sup> (in water at



**Scheme 3.** Decomposition of ethylnitrolic acid (ENA) in its non-dissociated ( $\text{HA}$ ) and dissociated ( $\text{A}^-$ ) forms

$25^\circ\text{C}$ ), it can be assumed that all the ACH is protonated in the working acidity range.

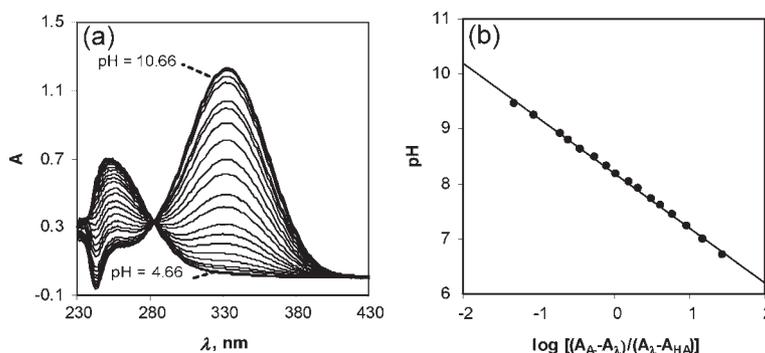
### Determination of the ethylnitrolic acid dissociation constant

#### Spectrometric method

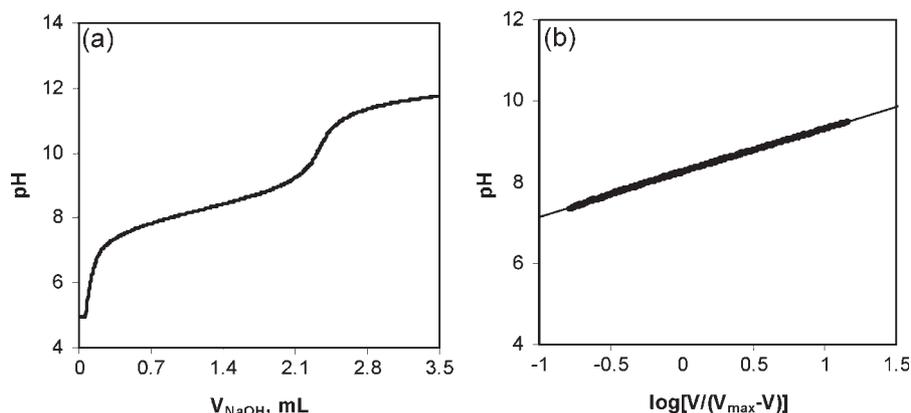
Figure 4a shows the UV–Vis absorption spectra for ENA at several pH in 7:3 water/dioxane media with a well defined isosbestic point at  $\lambda = 284\text{ nm}$ . It can be observed that the undissociated ( $\text{HA}$ ) and dissociated ( $\text{A}^-$ ) forms of ENA show maximum absorption at 255 and 335 nm, respectively. Since at  $\lambda = 360\text{ nm}$  the absorption of the anion is maximum and that of the neutral ENA is practically null, we studied the equilibrium at this wavelength. Spectra were obtained at pH 4–10 by adding increasing amount of NaOH, and absorbance/pH data were fitted using the Henderson–Hasselbalch equation.<sup>[29]</sup>

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = \text{p}K_a - \log \frac{A_{\text{A}^-} - A_\lambda}{A_\lambda - A_{\text{HA}}} \quad (4)$$

where  $A_{\text{HA}}$  and  $A_{\text{A}^-}$  represent, respectively, the absorbances of the non-dissociated ( $\lambda = 360\text{ nm}$ ,  $\text{pH} \approx 4$ ) and totally dissociated ( $\lambda = 360\text{ nm}$ ,  $\text{pH} \approx 10$ ) forms of ENA.  $A_\lambda$  represents the absorbance values at pHs between these boundary limits at  $\lambda = 360\text{ nm}$ .



**Figure 4.** (a) Absorption spectra of ENA at different pH in 7:3 water/dioxane medium and (b) determination of the  $\text{p}K_a$  of ENA at  $25.0^\circ\text{C}$  (Eqn (4)).  $[\text{ENA}]_0 = 1.5 \times 10^{-4}\text{ M}$ ;  $\lambda = 360\text{ nm}$



**Figure 5.** (a) Titration curve for ENA in 7:3 water/dioxane medium and (b) determination of the  $pK_a$  of ENA at 25.0 °C (Eqn (5)).  $[ENA]_0 = 2 \times 10^{-3}$  M;  $[NaOH] = 9.38 \times 10^{-2}$  M

Figure 4b shows the good fit of results to the Henderson–Hasselbalch equation.

#### Titrimetric method

By measuring the sodium hydroxide consumed for the titration of ENA at different pH values with a pH-Stat, the Henderson–Hasselbalch equation can be applied in the form,

$$pH = pK_a + \log \frac{V}{V_{max} - V} \quad (5)$$

where  $V_{max}$  represents the volume of NaOH at the endpoint and  $V$  is the volume of NaOH used at any other point during the titration.

Figures 5a and 5b show, respectively, the titration curve and the Henderson–Hasselbalch plot.

Table 2 shows the variation in  $K_a$  with the dielectric constant of the medium in different water/dioxane mixtures (the variation in  $K_a$  with temperature in the temperature range where the kinetic experiments were performed is smaller than the experimental error with which  $K_a$  was determined). Since the  $K_a$  values measured spectrophotometrically coincide in the range of experimental error with those determined by titration, the

**Table 2.** Equilibrium dissociation constants of ethylnitrolic acid in water/dioxane media at  $T = 25.0$  °C

Water/dioxane (v/v)	$10^8 K_a^a$ (M)	$\epsilon(T = 25.0$ °C) <sup>b</sup>
10:0	$4.0 \pm 0.8$	78.49
9:1	$2.5 \pm 0.5$	69.71
8:2	$1.6 \pm 0.3$	60.84
7:3	$1.0 \pm 0.2$	51.92
6:4	$0.4 \pm 0.1$	42.99
5:5	$0.10 \pm 0.02$	34.27

<sup>a</sup> Mean value.  
<sup>b</sup> Data from the literature<sup>[30,31]</sup> or calculated by linear interpolation against  $T$  of the data reported there.

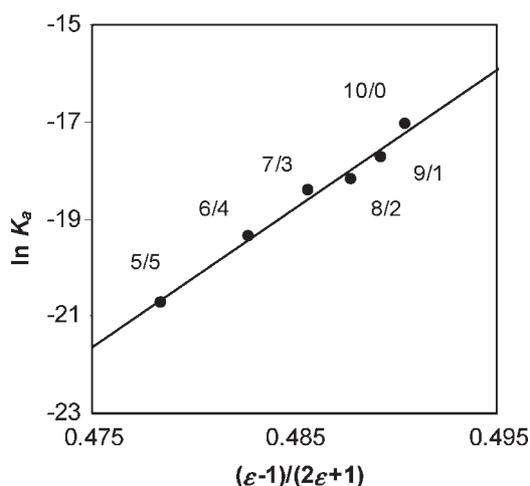
values resulting from the spectrophotometric method are reported in Table 2.

Attempts to relate the solvent dielectric constant to a number of mechanisms involving changes in dipole moment, such as the formation of quaternary ammonium ions,<sup>[32]</sup> solvolysis,<sup>[33]</sup> and proton transfer,<sup>[34,35]</sup> have related a parameter of the reaction to a

**Table 3.** Rate constants as a function of the composition of the media and the temperature for the decomposition reactions of 1,4-dinitro-2-methylpyrrole and ethylnitrolic acid

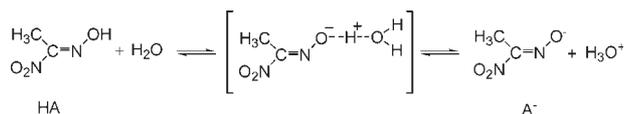
$T$ (°C)	10:0 <sup>a</sup>		8:2		7:3		6:4		5:5	
	$k_{dec}^{NMP}$ ( $M^{-1}s^{-1}$ ) <sup>b</sup>	$10^5 k_{dec}^{ENA}$ ( $s^{-1}$ )	$k_{dec}^{NMP}$ ( $M^{-1}s^{-1}$ )	$10^5 k_{dec}^{ENA}$ ( $s^{-1}$ )	$k_{dec}^{NMP}$ ( $M^{-1}s^{-1}$ )	$10^5 k_{dec}^{ENA}$ ( $s^{-1}$ )	$k_{dec}^{NMP}$ ( $M^{-1}s^{-1}$ )	$10^5 k_{dec}^{ENA}$ ( $s^{-1}$ )	$k_{dec}^{NMP}$ ( $M^{-1}s^{-1}$ )	$10^5 k_{dec}^{ENA}$ ( $s^{-1}$ )
25.0	$9.4 \pm 0.5$	$1.53 \pm 0.03$	$6.8 \pm 0.1$	$0.91 \pm 0.04$	$4.3 \pm 0.1$	$0.69 \pm 0.01$	$1.88 \pm 0.02$	$0.55 \pm 0.01$	$1.30 \pm 0.02$	$0.44 \pm 0.01$
27.5	$11.9 \pm 0.9$	$2.17 \pm 0.05$	$9.1 \pm 0.1$	$1.31 \pm 0.01$	$5.5 \pm 0.2$	$0.99 \pm 0.02$	$2.49 \pm 0.02$	$0.77 \pm 0.01$	$1.79 \pm 0.02$	$0.57 \pm 0.01$
30.0	$17.2 \pm 0.6$	$2.86 \pm 0.04$	$12.6 \pm 0.1$	$1.83 \pm 0.02$	$7.5 \pm 0.1$	$1.37 \pm 0.01$	$3.28 \pm 0.04$	$1.09 \pm 0.01$	$2.55 \pm 0.03$	$0.87 \pm 0.01$
32.5	$21.9 \pm 1.4$	$3.99 \pm 0.03$	$16.4 \pm 0.5$	$2.41 \pm 0.02$	$10.3 \pm 0.3$	$1.87 \pm 0.02$	$4.59 \pm 0.03$	$1.46 \pm 0.02$	$3.20 \pm 0.05$	$1.12 \pm 0.02$
35.0	$31.7 \pm 1.4$	$5.31 \pm 0.04$	$22.1 \pm 0.6$	$3.27 \pm 0.02$	$14.6 \pm 0.4$	$2.59 \pm 0.03$	$6.05 \pm 0.05$	$2.01 \pm 0.02$	$4.37 \pm 0.07$	$1.59 \pm 0.02$
37.5	$42.0 \pm 1.1$	$7.11 \pm 0.04$	$29.9 \pm 0.8$	$4.40 \pm 0.03$	$19.1 \pm 0.4$	$3.59 \pm 0.06$	$8.28 \pm 0.09$	$2.67 \pm 0.03$	$6.30 \pm 0.18$	$2.08 \pm 0.03$

<sup>a</sup> Reference 21.  
<sup>b</sup> Values are given within the 95% confidence interval.

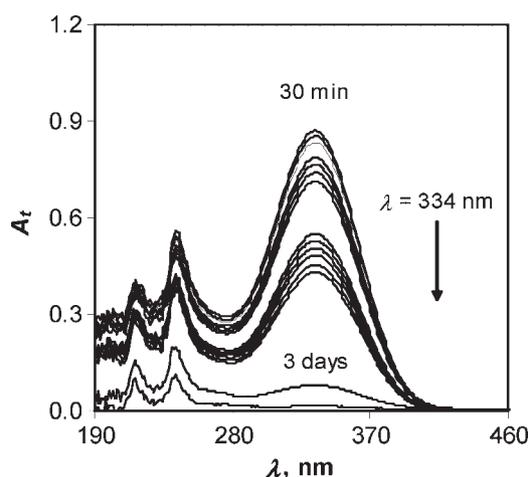


**Figure 6.** Plot showing the variation in ENA the equilibrium dissociation constant with Onsager coefficient in different water/dioxane media;  $T = 25.0\text{ }^{\circ}\text{C}$

number of functions of the dielectric constant, including the constant itself, the inverse of the constant, log of the constant, and the Onsager coefficient.<sup>[36]</sup> It has been shown<sup>[35]</sup> that in equilibria involving proton transfer, such as  $\text{OH} \cdots \text{N} \rightleftharpoons \text{O}^- \cdots \text{H}^+ \text{N}$  bonds, the equilibrium is shifted in favor of the polar structure in proportion to the Onsager<sup>[37]</sup> parameter  $(\epsilon - 1)/(2\epsilon + 1)$ . This result was rationalized<sup>[35]</sup> as being caused by the interaction of the dipole moment of the hydrogen bond with the reaction field arising from the polarization of the environment by the dipole. Since the current results (Fig. 6) show the variation of the ENA equilibrium dissociation constant with the Onsager coefficient,



**Scheme 4.** Formation of H<sup>+</sup>O bonds in ENA dissociation



**Figure 7.** Spectrograms showing the variation in ENA absorbance along time. 7:3 water/dioxane medium;  $[\text{ENA}]_0 = 1.3 \times 10^{-4}\text{ M}$ ;  $T = 37.5\text{ }^{\circ}\text{C}$ ; pH = 8.46 with borate buffer

this behavior has been considered to support the idea that the  $\text{HA} \rightleftharpoons \text{A}^- + \text{H}^+$  equilibrium (Scheme 3) occurs through the mechanism shown in Scheme 4.

#### Determination of the $k_{\text{dec}}^{\text{ENA}}$ rate constants

Since the ENA concentration  $[\text{ENA}]$  can be expressed as the sum of the concentration of non-dissociated ENA (HA) plus that present as anion ( $\text{A}^-$ )

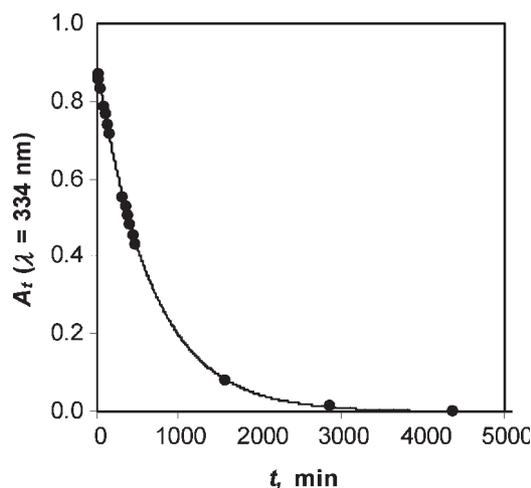
$$[\text{ENA}] = [\text{HA}] + [\text{A}^-] \quad (6)$$

and because  $K_a = ([\text{A}^-][\text{H}^+]/[\text{HA}])$ , Eqn (7) is easily deduced from Scheme 3

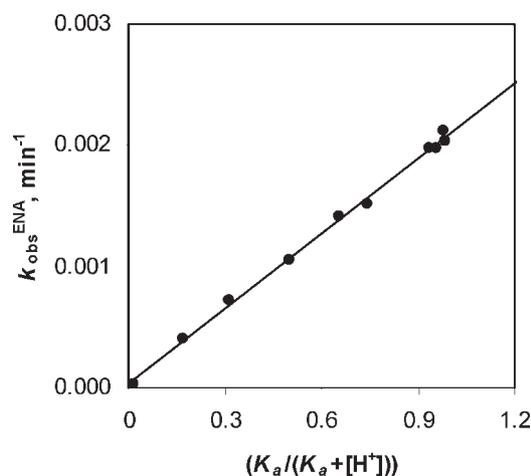
$$r = -\frac{d[\text{ENA}]}{dt} = k_{\text{dec}}^{\text{ENA}} \frac{K_a}{K_a + [\text{H}^+]} [\text{ENA}] = k_{\text{obs}}^{\text{ENA}} [\text{ENA}] \quad (7)$$

where  $k_{\text{obs}}^{\text{ENA}}$  is the pseudo-first-order rate constant

$$k_{\text{obs}}^{\text{ENA}} = k_{\text{dec}}^{\text{ENA}} \frac{K_a}{K_a + [\text{H}^+]} \quad (8)$$



**Figure 8.** Determination of  $k_{\text{obs}}^{\text{ENA}}$  (Eqn (8)) in 7:3 water/dioxane medium.  $[\text{ENA}]_0 = 1.3 \times 10^{-4}\text{ M}$ ;  $T = 37.5\text{ }^{\circ}\text{C}$ ; pH = 8.46 with borate buffer



**Figure 9.** Variation of  $k_{\text{obs}}^{\text{ENA}}$  with  $K_a/(K_a + [\text{H}^+])$  (Eqn (8)).  $[\text{ENA}]_0 = 10^{-4}\text{ M}$ ;  $T = 37.5\text{ }^{\circ}\text{C}$ ;  $K_a = 10^{-8}\text{ M}$

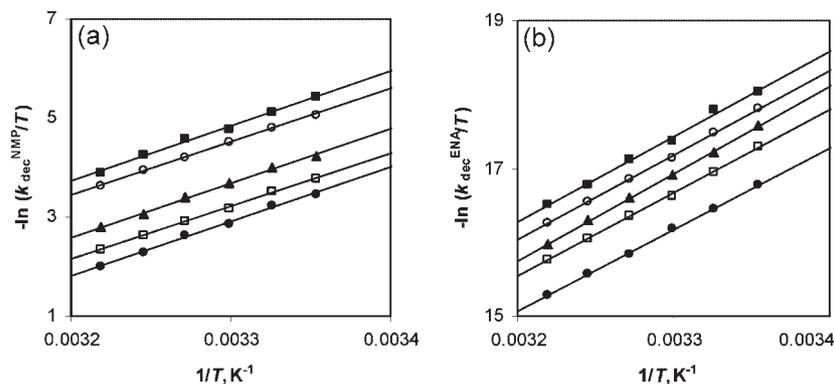


Figure 10. Eyring plots for (a) NMP and (b) ENA decomposition reactions in water/dioxane media. 10:0 (●), 8:2 (□), 7:3 (▲), 6:4 (○), and 5:5 (■)

By designating the absorbance values of ENA as  $A_0$ ,  $A_t$ , and  $A_\infty$  at times, respectively, of zero,  $t$ , and infinity (end of reaction) integration of Eqn (7) yields Eqn (9)

$$A_t = A_\infty + (A_0 - A_\infty)e^{-k_{obs}^{ENA}t} \quad (9)$$

Figure 7 shows the variation in the absorption of ENA with time.

Figure 8 represents a typical kinetic run for the decomposition reaction of ENA in 7:3 water/dioxane medium.

By fitting the absorbance values against those of time (Eqn (9)), the rate constant  $k_{obs}^{ENA}$  values were calculated. Using Eqn (8), knowledge of  $k_{dec}^{ENA}$  is immediate (Table 3).

With the previously determined  $K_a$  and  $k_{obs}^{ENA}$  values, Eqn (8) allows one to know the value of the decomposition rate constant,  $k_{dec}^{ENA}$  (refer Scheme 3). Figure 9 shows the good fit of the experimental results to that equation, the slope of the plot, being the value of  $k_{dec}^{ENA}$ .

The variation of  $k_{dec}^{NMP}$  and  $k_{dec}^{ENA}$  with temperature in different water/dioxane mixtures is reported in Table 3 (Fig. 10 shows the good fit of the results to the Eyring–Wynne–Jones equation). The decomposition rate constant values decrease when the water/dioxane ratio is decreased that is, when the dielectric constant of the medium decreases.

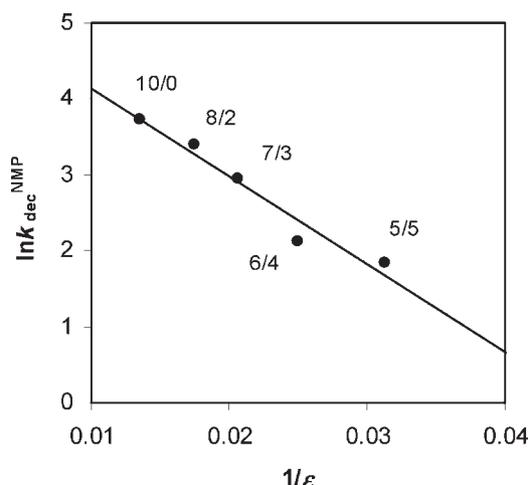


Figure 11. Variation of  $k_{dec}^{NMP}$  with the dielectric constant in water/dioxane mixtures;  $T = 37.5^\circ\text{C}$

In the proposed mechanism (Scheme 2), the decomposition reaction of NMP occurs through a nucleophilic attack by the hydroxide ion on the NMP molecule. Because in the second-order reactions of two polar molecules, two ions and one of each, the variation in the rate constant with the dielectric constant is such that a plot of the logarithm of the rate constant against the inverse of the dielectric constant of the solvent should be linear,<sup>[38]</sup> this behavior was checked. Figure 11 shows the linear relationship between  $\ln k_{dec}^{NMP}$  and the inverse of the dielectric constant of the medium in different water/dioxane mixtures. This supports the proposed mechanism.

With the values of  $k_{dec}^{NMP}$  and  $k_{dec}^{ENA}$  reported in Table 3, the activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were calculated. The results show no appreciable variation in these parameters with the composition of the medium, that is, the  $\Delta G^\ddagger$  value remains practically constant.

## CONCLUSIONS

- (I) The decomposition of NMP occurs through a nucleophilic attack by  $\text{OH}^-$  ions, the rate equation being  $r = k_{dec}^{NMP}[\text{OH}^-][\text{NMP}]$ . The observed linear correlation between  $\ln k_{dec}^{NMP}$  and the inverse of the dielectric constant of the medium in different water/dioxane mixtures support this mechanism.
- (II) The rate law for the decomposition of ENA is:  $r = k_{dec}^{ENA}[\text{ENA}]K_a/(K_a + [\text{H}^+])$ ,  $K_a$  being the ENA dissociation constant.
- (III) The value of  $K_a$  decreases when the water/dioxane ratio decreases,  $\log K_a$  being proportional to the Onsager<sup>[35]</sup> parameter  $(\epsilon - 1)/(2\epsilon + 1)$ . This permits the equilibrium between non-dissociated and dissociated forms of ENA, to be rationalized.
- (IV) No appreciable variation in the  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values with composition of the medium is observed, either in the NMP decomposition reaction, or in the ENA decomposition reaction.

## EXPERIMENTAL

### General remarks

A Shimadzu UV-2401-PC spectrophotometer with a thermoelectric six-cell holder temperature control system ( $\pm 0.1^\circ\text{C}$ ) was used.

A Crison Micro pH 2000 pH-meter was employed for pH measurements ( $\pm 0.01$ )

The reaction temperature was kept constant ( $\pm 0.05$  °C) with a Lauda Ecoline RE120 thermostat.

Titration was performed using a Metrohm 718 STAT Titrino pH-Stat, which releases NaOH, previously normalized with potassium hydrogen phthalate.

An QSTAR XLTOF-MS system (Applied Biosystems) was used for the determination of accurate masses. NMR proton spectra were obtained with a Varian spectrometer Mod. Mercury VS2000 (200 MHz).

Water was deionized with a MilliQ-Gradient (Millipore).

All kinetic runs were performed in triplicate.

Numerical treatment of the data was performed using the 7.1.44 Data Fit software.

### Procedures: synthesis of 1, 4-dinitro-2-methylpyrrole and ethylnitrolic acid

NMP was obtained from the reaction between sorbic acid and sodium nitrite in aqueous solution at pH = 3.5.<sup>[17,19]</sup>

A solution of sodium nitrite (11.0 g) was added to a partially suspended solution of sorbic acid (2.2 g) in distilled water (200 ml). Keeping the pH of the mixture constant at 3.5 with dilute H<sub>2</sub>SO<sub>4</sub>, the mixture was stirred at 60 °C for 2 h. The mixture was extracted with four 50 ml portions of CH<sub>2</sub>Cl<sub>2</sub>. The combined extracts were washed with water, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness *in vacuo* to give the residue. The residue was recrystallized in chloroform-ether.

UV  $\lambda_{\max}$  in nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 209 (11621  $\pm$  123), 229 (17428  $\pm$  135), 270 (13551  $\pm$  107), 329 (8764  $\pm$  66), 385 (1806  $\pm$  19). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  2.64 (s, 3H, CH<sub>3</sub>), 7.9 (d, 1H, CH—C—NO<sub>2</sub>), 8.8 (d, 1H, CH—N—NO<sub>2</sub>). Accurate mass calculated for C<sub>5</sub>H<sub>5</sub>N<sub>3</sub>O<sub>4</sub>Na (M<sup>+</sup>Na): 194.017227, found: 194.0187.

ENA was obtained from the nitrosation reaction of nitroethane in acidic aqueous solution.

Sodium nitrite (8.9 g) was added to a solution of nitroethane (8 ml) in aqueous sodium hydroxide (4.3 g in 100 ml) at 0 °C. Simultaneously to sodium nitrite addition, a solution of sulphuric acid (5 M) was added slowly to maintain the pH acidic in the reaction mixture. The aqueous solution was extracted with three 50 ml portions of ether and evaporated to dryness *in vacuo* to give the product. The product was recrystallized in dichloromethane-hexane. Because of its sparing thermal stability it was stored at 0 °C.

UV  $\lambda_{\max}$  in nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 240 (acid pH, 4341  $\pm$  29), 328 (alkaline pH, 8237  $\pm$  17). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  2.46 (s, 3H, CH<sub>3</sub>), 9.3 (broad, 1H, OH).

Sorbic acid, sodium nitrite, and dioxane were Panreac products. Nitroethane and D<sub>2</sub>O (98%) were supplied by Aldrich.

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