The Mechanism of the Reaction of 2,3-Dimethoxy-1,4-naphthoquinone with Pyrrolidine in Ethanol–Water

Noemí Alvarado and José G. Santos *
Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 6177, Santiago, Chile

The reaction of 2,3-dimethoxy-1,4-naphthoquinone with pyrrolidine has been the object of a kinetic study in a wide range of ethanol–water solvent systems, at several temperatures. The effects of solvent composition and temperature have been discussed in terms of a mechanism with a tetrahedral intermediate. A change in the rate equation from first order in pyrrolidine at high water concentration of the solvent mixture to another more complex equation for lower water concentration has been found. Solvent effects are also discussed using the Koppel–Palm relationship.

We recently carried out an investigation[1] on the nucleophilic substitution reactions of 2,3-dimethoxy-1,4-naphthoquinone (**1**) with ethoxide, propoxide, butoxide, and isopropoxide ions with the respective alcohols as solvents, and the most important kinetic effects were attributed to the solvation and basicity of the alkoxide ion and also to the acidity of the alcohols used as the solvents.

Several studies to establish the mechanism of nucleophilic substitution of quinones[2–7] with halogen and alkoxy quinones have been described and showed different paths depending on the substrate, the solvent, and the nature of the nucleophile. In the alcoholysis reaction of (**1**) an ionic mechanism is proposed with tetrahedral intermediates that either lead to a product or revert to the initial reactants by the leaving of an alkoxide group.

If the mechanism in the aminolysis reaction were similar to that proposed for the alcoholysis reaction, it would be expected that a noticeable solvent effect would be observed due to the formation of charged intermediates. In this kinetic study the reaction of (**1**) with pyrrolidine to form 2-methoxy-3-pyrrolidino-1,4-naphthoquinone (**2**) was performed in different ethanol–water mixtures; the aim was to shed further light on the mechanism of the reaction.

Experimental

Visible spectra of different kinetic samples were recorded on a Pye-Unicam SP-1800 spectrophotometer, using 10 mm cuvettes. The pH values were measured with a Radiometer PHM-62 pH meter with Radiometer G 2040 (glass) and K 4040 (calomel) electrodes. The refractive indices (n_D) were measured using an Abbe refractometer and a sodium lamp.

The m.p. of compound (**2**) was determined in a Kofler hot-stage microscope apparatus and is uncorrected. The i.r. spectrum (KBr) was obtained on a Perkin–Elmer 567 spectrophotometer. The ^{1}H n.m.r. spectrum ($CDCl_3$) was obtained using a Varian XL-100 spectrometer with tetramethylsilane as an internal standard.

Materials.—2,3-Dimethoxy-1,4-naphthoquinone (**1**) was prepared as previously reported.[8] Merck supplied reagent grade ethanol which was used as purchased and pyrrolidine (Fluka A.G.) was distilled over KOH (b.p. 84–86 °C). 2-*Methoxy*-3-*pyrrolidino*-1,4-*naphthoquinone* (**2**). Pyrrolidine (0.05 cm^3, 0.6 mmol) in chloroform (25 cm^3) was added, at room temperature, to a solution of (**1**) (100 mg, 0.46 mmol) in chloroform (25 cm^3). After 2 h the excess of pyrrolidine was removed by washing with HCl solution (10%). The chloroform phase was washed with water until neutrality was reached, dried ($MgSO_4$), filtered on silica gel (70–230 mesh) with chloroform as the eluant and evaporated under reduced pressure. The crude product yield (**2**) (110 mg, 0.43 mmol, 93%), m.p. 65–67 °C, $\nu_{max.}$ 1 670 and 1 620 (C=O) and 1 440 cm^{-1} (C–N); δ_H 1.90 (m, 4 H, CH_2CH_2), 3.90 (s, 3 H, OCH_3), 3.90 (m, 4 H, CH_2NCH_2), 7.70 (m, 2 H, 6- and 7-H), and 8.80 (m, 2 H, 5- and 8-H) (Found: C, 69.7; H, 5.8%; M^+, 257. $C_{15}H_{15}NO_3$ requires C, 70.0; H, 5.8%; M, 257).

Kinetic Measurements.—Silica cells (1 cm; Hellma 100-OS) containing 2.5 cm^3 of a solution of pyrrolidine in the appropriate solvent mixture and ionic strength 0.05 mol dm^{-3} (maintained with LiCl) were placed in the thermostatted cell holder of the spectrophotometer. After thermal equilibration quinone stock solution (10 mm^3) was injected into the cell [the final concentration of (**1**) was 9.8×10^{-5} mol dm^{-3}]. The reaction was followed by monitoring the absorbance increase with time at 520 nm. For each ethanol–water mixture all equilibria spectra were identical and corresponded to the spectra of solutions prepared using (**2**). In some runs the ionic strength was modifed (0.4 mol dm^{-3} using KCl) but kinetic changes were not detected.

Pseudo-first-order rate constants (k_{obs}) were obtained in all cases and were determined as slopes of plots $\ln(A_\infty - A_t)$ *vs.* time, where A_∞ and A_t are the absorbance values at equilibrium and at time t, respectively. In some cases (see the Results) plots k_{obs} *vs.* [pyrrolidine] were linear and the second-order rate constants were determined from the slope. In other cases plots [pyrrolidine] k_{obs}^{-1} *vs.* [pyrrolidine]$^{-1}$ were linear, and from the slope and intercept the second-order rate constants were determined. The activation parameters were obtained from Eyring plots.

Determinations of pK_a.—These were carried out potentiometrically and spectrophotometrically under the same conditions as those of the kinetic measurements.

The potentiometric determinations (pyrrolidine in x_{EtOH} 0.430 and 0.856 ethanol–water solvent systems) involved the use of Radiometer titration equipment comprising a PHM-62 pH meter, ABU-11 autoburette, TTA-60 titration assembly, TTT-60 titrator, and REA-160 recorder. The electrodes were Radiometer G 2040 (glass) and K 4040 (calomel). Solutions (10 cm^3) containing 1×10^{-2} mol dm^{-3} of the protonated pyrrolidine in the aqueous ethanol mixture and ionic strength 0.05 mol dm^{-3} (maintained using LiCl) were thermostatted at 25 ± 0.1 °C and titrated with aqueous solutions of 0.5 mol dm^{-3} sodium hydroxide.

The spectrophotometric determinations (pyrrolidine in x_{EtOH} 0.033, 0.133, and 0.249 aqueous ethanol and in 'absolute'

Table 1. pK_a values of pyrrolidinium ion, determined in different ethanol–water mixtures at 25 °C and 0.05 mol dm^{-3} in LiCl.

x_{EtOH}[a]	0.033	0.113	0.249	0.430	0.856	1.0[b]
pK_a	10.8[c]	10.4[c]	10.4[c]	10.6[d]	9.7[d]	9.3[c]

[a] x_{EtOH} is the mole fraction of ethanol. [b] Absolute alcohol contains 300 ppm of water determined by the Karl–Fisher method. [c] Spectrophotometrically measured values. [d] Potentiometrically measured values.

ethanol) were carried out by measuring the absorbance (A) at 220 nm of solutions of pyrrolidine and its conjugate acid under the reaction conditions by means of a Pye–Unicam SP 1800 spectrophotometer. The measurements of pH were made using a Radiometer pHM-62 pH meter. The corresponding absorbance of the acid form (A_a) was determined in solution at pH 2 but the absorbance of the basic form (A_b) could not be measured because of changes in the spectra and was obtained by iterative fittings for the best straight line of $\ln[A_b - A)(A - A_a)^{-1}]$ *vs.* pH plots. The criteria used was the slope value (the slope must be 1.0 in these plots).

Data Treatment.—In the analysis of the effect of the aqueous ethanol composition on the nucleophilic rate constant the Koppel–Palm relationship was employed[9] [equation (1)].

$$A = A_0 + yY + p\alpha + eE + bB \qquad (1)$$

The solvent polarity (Y) in the ethanol–water mixtures were calculated from $Y = (\varepsilon_r - 1)(2\varepsilon_r + 1)^{-1}$ with the relative permittivity (ε_r) values from the literature.[10] The polarizability (α) values were determined for each mixture using $\alpha = (n_D^2 - 1)(n_D^2 + 2)^{-1}$ with the refractive index (n_D) taken from the literature[10] or measured experimentally. For the basicity parameter (B) we assumed that it would be additive and the values were calculated using $B = x_{EtOH}B_{EtOH} + x_{H_2O}B_{H_2O}$ where x is the mole fraction and B_{EtOH} and B_{H_2O} are the basicities of ethanol and water, respectively, obtained by Shorter.[11] The acidity (E) value for each mixture was estimated from the linear relation between E and the Reichard parameter $E_T(30)$ for alcoholic solvents and water.[9] The $E_T(30)$ values for the different ethanol–water mixtures were calculated from the Lanhals equation.[12] The E value for ethanol was obtained by Shorter.[11]

Results and Discussion

The spectrophotometric study (340–700 nm) of the reaction of (**1**) with pyrrolidine in different ethanol–water mixtures showed an increase in the absorption band at 520 nm and the presence of an isosbestic point at 410 nm. The increasing band corresponds to (**2**), assigned by comparison with the spectra of authentic samples in the same reaction media. In all cases the equilibria spectra were identical under different pyrrolidine concentrations.

Table 1 shows the pK_a values for the amine in the different ethanol–water mixtures. Although absolute ethanol may absorb some water it is not very important in this study since at the concentration used the pH values of solutions were greater than 11.3 and the pyrrolidine can be assumed to be completely free in this medium. However, neither pK_a nor pH values were corrected for each of the media because the aim was to find the free-amine concentration and there are no differences in this value between corrected and uncorrected (the correction is an additional value in both pK_a and pH).[13]

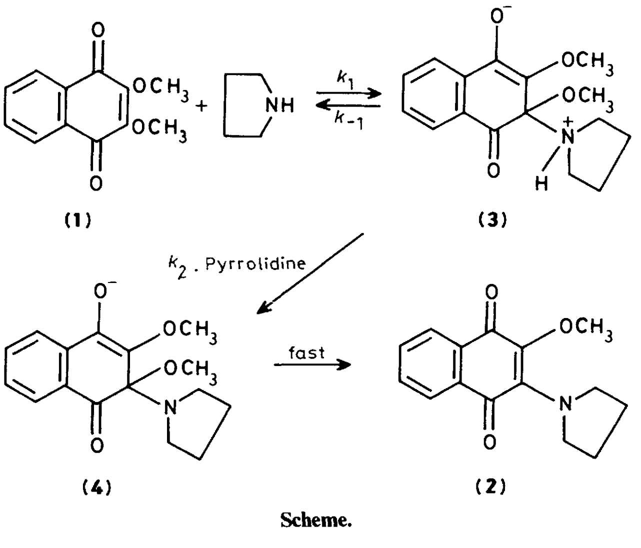
In order to obtain the dependence of the pseudo-first-order rate constant on the pH of the medium and ionic strength, the reaction was carried out at three free-amine fractions with ionic strength 0.4 mol dm^{-3} (maintained using KCl), and at one fraction with ionic strength 0.05 mol dm^{-3} (using LiCl), at 25 °C in ethanol–water x_{EtOH} 0.249. Table 2 shows the data of k_{obs} *vs.* free-pyrrolidine plots. These were linear in the four experiments with almost identical slope and intercept at the origin. When we represent k_{obs} *vs.* free amine for the four experiments in the same plot, one straight line can be obtained with deviation from linearity, $R = 0.994$. This result allows us to disregard both the effect of ionic strength and the protonated-pyrrolidine concentration on the reaction rate.

Table 3 shows the amine-concentration range used and the k_{obs} obtained for the reaction at different temperatures in different reaction media. For the reaction in solvent mixtures rich in water ($x_{EtOH} = 0.033$ and 0.113) k_{obs} *vs.* [pyrrolidine] plots were linear with intercepts at the origin; from the slopes of these plots the nucleophilic constants were obtained. For the other ethanol–water mixtures used, neither k_{obs}^{-1} *vs.* [pyrrolidine] nor *vs.* [pyrrolidine]^2 plots were linear, thus discounting both first- and second-order kinetics in the amine. The first-order plots deviate upwards and tend to be linear, and the second-order plots deviate downwards. [Pyrrolidine]k_{obs} *vs.* [pyrrolidine]$^{-1}$ plots were linear suggesting the empirical equation (2).

$$k_{obs} = k'[\text{pyrrolidine}]^2 (k'' + k'''[\text{pyrrolidine}])^{-1} \qquad (2)$$

An empirical equation such as equation (2) suggests that the overall reaction is a two-step reaction with a nucleophilic first step and a base-catalysed second step. If the first step is rate determining, $k'''[\text{pyrrolidine}] \gg k''$ and first-order kinetics in amine are observed (as seen for the water rich media mentioned above), and if $k'' \gg k'''[\text{pyrrolidine}]$ second-order kinetics are required; this condition probably fails in this study. However, as the pyrrolidine concentration increases, the denominators of equation (2) change, and at high concentrations first-order kinetics can be observed while at low concentration second-order kinetics are required. Effectively, the first-order plots in ethanol-rich media are linear for high pyrrolidine concentrations.

Considering these facts, as well as the structure of substrate and product, a pathway of reactions is proposed (see the Scheme). The (**4**) ⟶ (**3**) step was disregarded because, as mentioned above, no kinetic effects due to the protonated pyrrolidine were found and the protonation of (**4**) by the protonated pyrrolidine is a thermodynamically unfavourable step because of the decreasing basicity of the amine moiety relative to the free amine. The proton transfer from the nitrogen



Scheme.

Table 2. Pseudo-first-order rate constants (k_{obs}) for the reaction of (**1**) with pyrrolidine in ethanol–water ($x_{EtOH}{}^{a} = 0.249$) at 25 °C and at different free pyrrolidine fractions (F_N).[b]

$F_N = 0.25^{c}$		$F_N = 0.5^{c}$		$F_N = 0.75^{c}$		$F_N = 1.0^{d}$	
$N_L{}^{e}$/mol dm^{-3}	k_{obs}/10^{-3} s^{-1}	$N_L{}^{e}$/mol dm^{-3}	k_{obs}/10^{-3} s^{-1}	$N_L{}^{e}$/mol dm^{-3}	k_{obs}/10^{-3} s^{-1}	$N_L{}^{e}$/mol dm^{-3}	k_{obs}/10^{-3} s^{-1}
0.030	1.08	0.060	2.73	0.089	4.80	0.028	1.41
0.041	1.28	0.083	3.75	0.125	6.80	0.039	1.95
0.060	1.91	0.119	6.16	0.179	10.21	0.058	3.07
0.092	5.17	0.184	9.23	0.276	15.21	0.116	6.18
0.119	5.34	0.237	12.02	0.356	19.35	0.232	13.63
		0.297	14.75	0.445	23.01	0.463	26.74
		0.386	18.24	0.579	28.96	0.579	32.76

[a] x_{EtOH} is the mole fraction of ethanol. [b] F_N = [free amine]/[total amine]. [c] Ionic strength 0.4 mol dm^{-3} (KCl). [d] Ionic strength 0.05 mol dm^{-3} (LiCl). [e] N_L is the free-pyrrolidine concentration.

Table 3. Experimental conditions and rate constants obtained for the reaction of (**1**) with pyrrolidine.

x_{EtOH}	T/°C	n^{a}	$N_L{}^{b}$/ mol dm^{-3}	k_{obs}/ 10^{-3} s^{-1}	$k_1{}^{c}$/ 10^{-2} s^{-1} mol^{-1} dm^3	(k_2/k_{-1})/ mol^{-1} dm^3
1	25.4	6	0.12–0.59	0.66–5.20	1.09 (1.11)	7.97
	30.7	5	0.12–0.77	0.73–9.67	1.37 (1.56)	5.51
	34.7	7	0.12–0.77	0.82–10.9	1.56 (1.72)	5.58
	41.0	7	0.12–0.77	0.88–13.7	2.13 (2.31)	4.03
	45.2	6	0.12–0.77	0.92–16.3	2.69 (2.96)	2.99
0.856	25.0	8	0.0289–0.594	0.07–6.31	1.27 (1.46)	6.90
	30.3	7	0.0577–0.594	0.27–8.43	1.77 (1.96)	5.42
	35.4	6	0.0577–0.594	0.28–9.63	2.15 (2.12)	5.06
	40.5	6	0.0289–0.594	0.09–12.7	2.78 (2.90)	4.89
	45.7	7	0.16–0.747	2.71–22.2	3.38 (3.74)	5.05
0.430	30.9	8	0.0285–0.571	0.47–21.8	3.92 (3.94)	24.4
	35.7	9	0.0394–0.571	0.93–26.0	4.94 (4.65)	25.8
	40.6	10	0.0285–0.571	0.60–30.4	5.73 (5.78)	20.3
	45.2	8	0.0577–0.571	2.07–38.8	7.44 (7.25)	16.9
0.249	25.0	26	0.0282–0.579	1.41–32.8	5.41	—
	30.0	10	0.0282–0.579	1.46–41.0	7.27 (7.46)	78.8
	35.0	10	0.0282–0.579	1.69–52.8	9.14 (9.01)	62.7
	40.6	9	0.0282–0.579	1.87–64.8	11.4 (11.5)	42.9
	45.4	8	0.0282–0.579	2.21–74.8	13.4 (13.0)	56.0
0.113	15.6	10	0.0282–0.579	2.10–49.8	8.82	—
	20.1	5	0.116–0.463	14.0–53.3	11.2	—
	25.7	10	0.0282–0.579	3.29–83.0	14.3	—
	30.9	8	0.0282–0.579	3.57–99.9	17.7	—
	35.3	7	0.0282–0.357	5.91–74.6	21.1	—
0.033	15.7	10	0.024–0.513	3.52–96.0	18.4	—
	20.5	8	0.024–0.316	4.31–68.8	22.5	—
	25.2	9	0.024–0.410	6.33–116.4	28.8	—
	29.4	4	0.052–0.316	15.0–101.7	32.5	—

[a] Number of runs. [b] N_L is the free-pyrrolidine concentration. [c] Obtained from the linear portion of k_{obs} *vs.* [free pyrrolidine] plots. Values in parentheses correspond to the reciprocal of the intercepts for plots of equation (4).

atom of (**3**) to the vicinal oxygen atom of the methoxy group, with solvent assistance, was discounted as the rate-determining step because of the quadratic term in the empirical equation. The mechanism in the Scheme is in accord with that proposed by Jencks *et al.*[14] related to the aminolysis of esters.

Assuming the steady-state condition for intermediates (**3**) and (**4**), equation (3) can be derived. In ethanol-poor media deprotonation of (**3**) is probably faster than the departure of pyrrolidine (k_2[pyrrolidine] $\gg k_{-1}$) and first-order kinetics in pyrrolidine can be observed, with k_1 as the rate-determining step. In ethanol-rich solvent systems the terms in the denominators of equation (3) are comparable and there is no rate-determining step; at high pyrrolidine concentration k_2[pyrrolidine] $\gg k_{-1}$ probably holds and the k_{obs} against [pyrrolidine] plot is linear with k_1 as the slope.

$$k_{obs} = k_1k_2[\text{pyrrolidine}]^2\,(k_{-1} + k_2[\text{pyrrolidine}])^{-1} \quad (3)$$

Equation (3) can be rearranged to give equation (4) and [pyrrolidine]k_{obs}^{-1} against [pyrrolidine]$^{-1}$ plots are linear with intercept k_1^{-1} and slope k_{-1}/k_1k_2; from these, k_1 and k_2/k_{-1} values were obtained.

$$[\text{pyrrolidine}]k_{obs}^{-1} = k_1^{-1} + k_{-1}(k_1k_2[\text{pyrrolidine}])^{-1} \quad (4)$$

Table 3 shows the k_1 and k_2/k_{-1} values obtained at the different temperatures and solvents. As further evidence for the accuracy of the model, the k_1 values obtained from equation (4) should correspond to the k_1 values obtained in the same conditions from equation (3) (the slope of k_{obs} *vs.* [pyrrolidine] at high amine concentration); Table 3 also summarizes these values.

From Table 3 it can be seen that for the different solvents and temperatures, $k_2/k_{-1} > 1$. The possible transition-state structures for the first and second steps are (**5**) and (**6**), respectively, and it can be observed that (**6**) is more like (**3**) than (**5**), so fewer

Table 4. Solvent parameters[a] for the different ethanol–water mixtures.

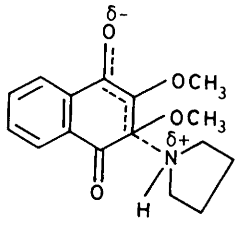
Parameter	x_{EtOH}[b]					
	1.0[c]	0.856	0.430	0.249	0.113	0.033
E	11.60[d]	12.26[e]	13.54[e]	14.09[e]	14.53[e]	14.81[e]
B	117.0[d]	113.0	101.6	96.7	93.1	90.9
Y(25)	0.4698	0.4722	0.4816	0.4856	0.4884	0.4899
Y(30)	0.4688	0.4714	0.4812	0.4852	0.4882	0.4897
Y(35)	0.4681	0.4702	0.4805	0.4848	0.4878	0.4896
Y(40)	0.4667	0.4696	0.4803	0.4844	0.4877	0.4885
Y(45)	0.4659	0.4689	0.4796	0.4839	0.4872	0.4888
α(25)	0.220 25	0.221 19	0.221 97	0.219 82	0.214 56	0.208 16
α(30)	0.218 38	0.219 49	0.220 09	0.217 33	0.212 67	0.206 70
α(35)	0.217 17	0.214 84	0.219 10	0.215 78	0.212 06	0.206 42
α(40)	0.216 23	0.217 44	0.218 11	0.215 62	0.211 67	0.206 03
α(45)	0.215 28	0.216 28	0.217 55	0.214 84	0.210 89	0.205 64

[a] The numbers in parentheses are the temperature values in °C. [b] x_{EtOH} is the mole fraction of ethanol. [c] 300 ppm water by Karl–Fisher titration. [d] Ref. 11. [e] From the linear relationship between E and $E_T(30)$ from ref. 9 and $E_T(30)$ from ref. 12.

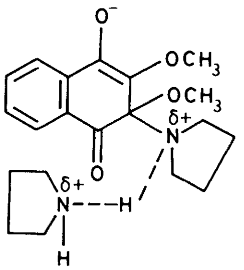
Table 5. Coefficients[a] for the equation $\ln k_1 = A + eE + p\alpha$ at different temperatures.

T/°C	A	e	p	R^2	F[b]
25	10 ± 2	0.66 ± 0.04	−100 ± 9	0.998	698
30	12 ± 2	0.64 ± 0.03	−106 ± 7	0.999	1 252
35	13 ± 2	0.63 ± 0.04	−113 ± 9	0.998	794
40	13 ± 2	0.64 ± 0.03	−114 ± 9	0.998	822
45	13 ± 2	0.65 ± 0.03	−114 ± 8	0.998	980

[a] Errors are standard errors. [b] Statistical F.



(5)



(6)

structural changes are required in forming the product than in reforming the reactants from (**3**); therefore, in accord with Hammond's principle[15] k_2 must be greater than k_{-1}, as found. Although the temperature effect is difficult to discuss, since there are two constants involved, it seems that in each medium the quotient decreases as temperature increases, suggesting a greater temperature effect on k_{-1} than k_2, also in accord with the above discussion on the similarity of (**6**) to (**3**).

At a given temperature k_2/k_{-1} increases as the water concentration increases; both transition states (**5**) and (**6**) are less polar than (**3**) and in a more polar medium (**3**) would probably be stabilized more than the transition states, therefore k_{-1} and k_2 must diminish as the water concentration increases. However, the pK_a of pyrrolidine (Table 1) varies with a change in solvent; the pK_a of intermediate (**3**) should also vary to the same extent as the pK_a of the amine, hence the proton transfer from (**3**) to the pyrrolidine would not be affected by the change in solvent. Taking this fact into account, and the fact that the rate constant for expulsion of pyrrolidine from (**3**) decreases with the increase in water concentration, the term k_2/k_{-1} must increase with increased water concentration, as was found.

In relation to the effect of the solvent composition on k_1 (Table 3), it is noteworthy that for all temperatures in the range studied, plots of ln k_1 against ε_r were linear (with the k_1 value interpolated from Eyring plots and relative permittivity obtained from literature[10]). In accord with Shorter[11] this result must be considered fortuitous and in principle inadmissible since the solvent between molecules of reactants does not behave in the same way as when it is between the plates of the capacitor used the determination of ε_r.

The use of the Koppel–Palm[9] relationship [equation (1)] to obtain the dependence of solvent on ln k_1 led us to conclude that the E, B, and Y parameters exhibit a remarkable co-linearity ($R^2 > 0.992$). Table 4 summarizes the solvent parameters at the different temperatures. Taking into account the proposed scheme and considering the possible structure for the first transition state (**5**), the acidity function E may explain more suitably the behaviour, because the acidity increase in the solvent stabilizes the transition state (**5**) more, due to the partial negative charge on the oxygen atom.

Equation (5) shows the dependence of ln k_1 at 25 °C on two variables. The polarizability α participation in the equations can be explained using the model because a polarizability increase of the solvent stabilizes reactants through the interaction between the permanent dipole of reactants and that induced in the solvent.

$$\ln k_1 = (10 \pm 2) + (0.66 \pm 0.04)E - (100 \pm 9)\alpha;\ (R^2 = 0.998) \quad (5)$$

Table 5 summarizes the parameters of equation (5) at different temperatures. Taking the values of E, α, and ln k_1, for five temperatures, equation (6) is obtained showing that, in practice the solvent effect is independent of temperature.

$$\ln k_1 = (16 \pm 2) + (0.60 \pm 0.03)E - (125 \pm 8)\alpha;\ (R^2 = 0.982) \quad (6)$$

Table 6 summarizes the activation parameters for the first step of the reaction in the different ethanol–water media. In all cases, $\Delta S^{\ddagger}$ is negative suggesting that solvation takes place during the formation of transition state (**5**) in accord with its greater polarity relative to reactants, which leads to a greater ordering of solvent molecules around the former. However, $\Delta H^{\ddagger}$ decreases with increased water concentration. This suggests a greater stabilization of the transition state (**5**) than of

Table 6. Activation parameters[a] for the nucleophilic attack of pyrrolidine to (**1**) in the different ethanol–water mixtures.

x_{EtOH}[b]	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
0.033	29 ± 2	-159 ± 7
0.113	30 ± 1	-160 ± 2
0.249	31 ± 2	-165 ± 5
0.430	32 ± 3	-165 ± 5
0.856	33 ± 2	-169 ± 7
1.0[c]	34 ± 2	-169 ± 7

[a] Errors are standard errors. [b] x_{EtOH} is the mole fraction of ethanol. [c] 300 ppm water by Karl–Fisher titration.

the reactants in a more polar solvent, it is also in accordance with the greater polarity of (**5**) than that of reactants.

Acknowledgements

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