Intramolecular Electron Exchange with Solvent Participation: Electron Spin Resonance Study of the Radical-Anion of Benzene-1,3-dicarbaldehyde in Propan-2-ol–Water Mixtures

M. Cândida B. L. Shohoji,* Bernardo J. Herold, and Horácio M. Novais
Instituto Superior Técnico, Química Orgânica, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal
Steen Steenken
Max-Planck Institut für Strahlenchemie, Stiftstrasse 34—36, 4330 Mülheim an der Ruhr, Federal Republic of Germany

The short-lived radical anion of benzene-1,3-dicarbaldehyde was generated by *in situ* photolysis of the parent compound in pure ethanol, propan-2-ol, and propan-2-ol–water mixtures at pH >7 and identified by e.s.r. In one of the three detected rotamers (*Z,E*) an alternating linewidth effect was observed at temperatures between 252 and 315 K. This phenomenon was studied in terms of a two-jump model involving two asymmetrically solvated radical anions. Rates of interconversion between these two in propan-2-ol were found to be in the range 0.5—1.25 × 10^9 s^{-1}. Variation of the water content in mixtures of propan-2-ol and water mainly affects the coupling constants. The 3-formyl-α-hydroxybenzyl radical (the conjugate acid of the radical anion) has also been generated by photolysis of benzene-1,3-dicarbaldehyde in pure propan-2-ol at pH 4—7 and has been studied by e.s.r.

The radical anions of benzene-1,2-[1,2] and -1,4-dicarbaldehyde[1,3] have been shown to exhibit rotational isomerism: Stone and Maki[1] reduced both dialdehydes electrolytically and analysed the e.s.r. spectra of the resulting solutions. That from benzene-1,2-dicarbaldehyde showed only the spectrum of the *Z,E*-isomer (also referred to as *cis-trans* or *meso*) and that from benzene-1,4-dicarbaldehyde exhibited two overlapping spectra due to the *Z,Z*-(*cis*-) and *Z,E*-(*trans*-) isomers of the radical anion. More recently Herold *et al.*[2] and Lunazzi *et al.*[3] generated the same radical anions by photolysis and confirmed the results of Stone and Maki.

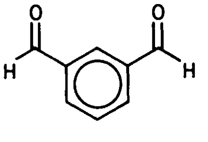
We report here a study of the short-lived radical anion of benzene-1,3-dicarbaldehyde (3BDC), for which three rotamers (**1**)—(**3**) can exist. Its e.s.r. spectrum shows a pronounced alternating linewidth effect, which was not detected in the spectra of the 1,2- and 1,4-isomers. We hoped to discover whether this effect is caused by rotational isomerism or by intramolecular electron exchange.

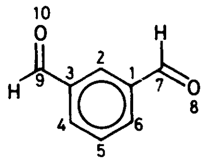
Experimental

Radicals were generated by *in situ* photolysis of flowing solutions.[4] The photolytic device included a Canrad-Hanovia 1000 W xenon lamp and an optical system for focussing the light on the e.s.r. cell.[5] 3BDC was obtained from EGA Chemie. Anhydrous ethanol and propan-2-ol as well as propan-2-ol–water mixtures and water were used as solvents. Low concentrations of carbaldehyde (5 × 10^{-4} M) were chosen to avoid intermolecular electron transfer, detectable at higher concentrations.

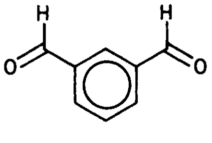
Deaeration was accomplished by bubbling argon through the solutions. Flow rates of 6—10 ml min^{-1} were used. The pH of the solutions was adjusted by adding small amounts of perchloric acid, sodium hydroxide, sodium alkoxide, or concentrated aqueous ammonia.

E.s.r. spectra were recorded with Varian E-9 (Mülheim) and Bruker 200D (Lisbon) spectrometers. Spectra at temperatures below 298 K were obtained from solutions passed through a heat exchanger cooled by circulating ethanol from a cryostat. Temperatures inside the flat sample cell were measured with a Pyrex-coated platinum thermometer placed in the upward solution stream immediately above the flat cell.


Z,Z
(**1**)



Z,E
(**2**)


E,E
(**3**)

Results and Discussion

Identification of Radical Rotamers and Assignment of Coupling Constants.—It is well established that at room temperatures 3BDC exists as a mixture of three planar rotamers: *Z,Z* (also referred to as *cis-cis* or *endo*) (**1**), *Z,E* (*cis-trans* or *meso*) (**2**) and *E,E* (*trans-trans* or *exo*) (**3**). Their relative abundances have been measured by analysis of dipole moments[6] and Kerr effects[7] and also have been estimated by *ab initio* molecular orbital calculations.[8]

In this work we have detected three rotamers of the radical anion $(3BDC)^{-\bullet}$. Figure 1 shows their overlapping e.s.r. spectra in ethanol in the presence of added base. The existence of contact ion pairs is ruled out, not only because polar solvents were used throughout these studies, but also because identical e.s.r. spectra were obtained in the presence of cations other than NH_4^+ (Na^+, K^+).

By double integrating graphically the representative lines of each rotamer of the radical anion, we obtained relative abundances of 60:26:14 respectively for $(Z,E)^{-\bullet}$, $(E,E)^{-\bullet}$, and $(Z,Z)^{-\bullet}$ which do not differ significantly from the values found by Mirarchi *et al.*[7] for the parent aldehyde, *viz.* 56:26:18, respectively, for rotamers (**2**), (**3**), and (**1**).

We were able to interpret the e.s.r. spectra of the two most abundant radical rotamers [$(Z,E)^{-\bullet}$ and $(E,E)^{-\bullet}$]. From the third isomer, $(Z,Z)^{-\bullet}$, only a few e.s.r. lines are visible, insufficient for a full interpretation of the spectrum.

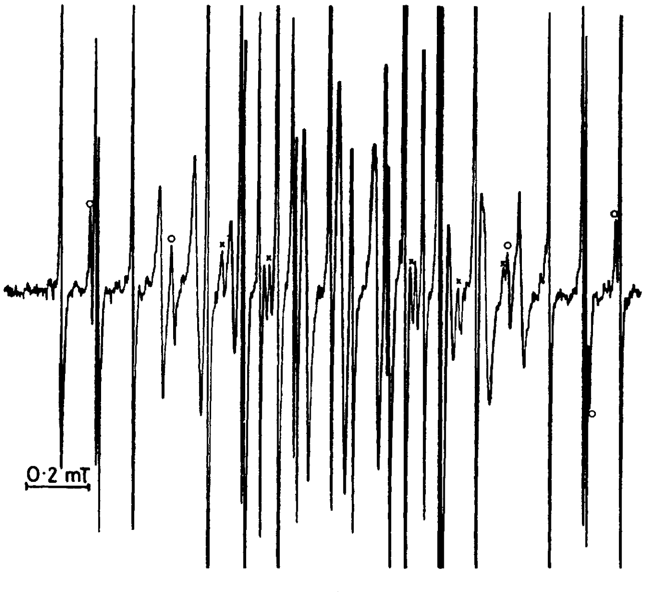
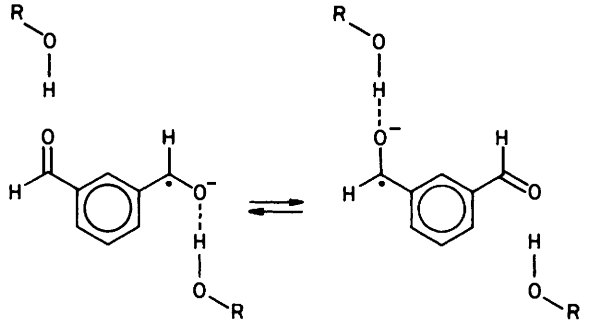


Figure 1. Spectrum of the radical anion of benzene-1,3-dicarbaldehyde in ethanol at 278 K: ○, $(E,E)^{-\bullet}$; ×, $(Z,Z)^{-\bullet}$ [unmarked lines $(Z,E)^{-\bullet}$]



(A) (B)

Table 1. Observed and calculated hyperfine coupling constants (mT) for $(3BDC)^{-\bullet}$ in ethanol at 278 K

Rotamer		Positions					
		2	4	5	6	7	9
$(Z,E)^{-\bullet}$	exp.	0.190	0.740	0.175	0.740	0.505	0.505
	calc.	0.030	0.763	0.195	0.710	0.503	0.493
$(E,E)^{-\bullet}$	exp.	0.140	0.690	0.180	0.690	0.550	0.550
	calc.	0.133	0.673	0.178	0.673	0.530	0.530

Table 2. Observed hyperfine coupling constants (mT) for $(Z,E)^{-\bullet}$ in propan-2-ol–water at 292 K

Solvent	Positions					
	2	4	5	6	7	9
Propan-2-ol	0.129	0.780	0.173	0.780	0.457	0.457
Propan-2-ol–water (0.7 mol fract. H_2O)	0.175	0.765	0.175	0.765	0.505	0.505
Water	0.205	0.740	0.175	0.740	0.530	0.530

The hyperfine coupling constants of the *Z,E*- and *E,E*-rotamers were assigned by comparison with the results of Hückel–McLachlan calculations using $\lambda = 1.2$. For these calculations we assumed that one of the two oxygen atoms is more strongly solvated than the other. This is justifiable in view of the observed alternating linewidth effect, which was studied in more detail for $(Z,E)^{-\bullet}$ in propan-2-ol, water, and their mixtures and which, as will be discussed later, leads to the conclusion that $(Z,E)^{-\bullet}$ exists as two rapidly interconverting structures (A) and (B). For $(E,E)^{-\bullet}$ an analogous equilibrium between two complexes is shown by an alternating linewidth effect in ethanol solution. The effect of the asymmetric solvation thus assumed was included in the way suggested by Freed and Fraenkel.[9] In this model the Coulomb integral of the oxygen atom which is more strongly solvated is adjusted by varying δ_O in the equation $\alpha_O = \alpha_C + \delta_O\beta_{CC}$. Calculations were carried out by varying either $\delta_{O(8)}$ or $\delta_{O(10)}$ between 1.7 and 2.9. The other parameters used were: $\beta_{CO} = 1.6\beta_{CC}$, $\beta_{1,7} = \beta_{3,9} = 0.9\beta_{CC}$ for both carbonyl substituents and $\alpha_O = \alpha_C + 1.7\beta_{CC}$ for the less solvated oxygen atom. Geometrical differences between rotamers of $(3BDC)^{-\bullet}$ were modelled in the calculations by using the α-method,[1] in which the Coulomb integral α_C' of the ring carbon atoms close to the two carbonyl oxygens [2 and 6 in $(Z,E)^{-\bullet}$; 4 and 6 in $(E,E)^{-\bullet}$] was varied.

Calculated spin densities at the 4- and 6-position and the 7- and 9-position change significantly in going from complex (A) to (B) [$(Z,E)^{-\bullet}$]; however, spin densities at the 2- and 5-position are very similar in both complexes, as expected. For the two corresponding complexes of $(E,E)^{-\bullet}$ the same applies, but of course in this case spin densities at the 2- and 5-position are identical for the two complexes. Spin densities were converted into splitting constants by using $Q_{CH}^{H} = -2.5$ mT in the McConnel equation. The most satisfactory results were obtained by using $\alpha_C' = \alpha_C - 0.1\beta_{CC}$ and $\delta_{O(8)} = 2.3$, $\delta_{O(10)} = 1.7$ for complex (A), and $\delta_{O(10)} = 2.3$, $\delta_{O(8)} = 1.7$ for complex (B).

The averaged experimental splitting constants in ethanol at 278 K and the calculated values are reported in Table 1.

Determination of Electron Exchange Rates for $(Z,E)^{-\bullet}$.—A solution of benzene-1,3-dicarbaldehyde (3BDC) in propan-2-ol with added base (ammonia) was irradiated between 292 and 266 K at 5 K intervals. Figure 2 shows the spectrum at 292 K and the amplified low-field wings of the spectra at 292 and 266 K. The e.s.r. spectra show predominantly one of the three rotamers of $(3BDC)^{-\bullet}$, other lines being much weaker. By comparison with the spectrum in ethanol (Figure 1) one can easily conclude that this rotamer is $(Z,E)^{-\bullet}$. An alternating temperature-dependent linewidth effect is clearly visible in the lines of the second quartet on the low-field side, which in the absence of broadening would have twice the height of the first quartet. In ethanol this effect is visible for $(Z,E)^{-\bullet}$ as well as for $(E,E)^{-\bullet}$, but because in the latter case an insufficient number of lines can be seen, no detailed study of the alternating linewidth effect was possible. For $(Z,E)^{-\bullet}$ in propan-2-ol, water, and their mixtures the experimental values of the couplings are reported in Table 2.

The alternating linewidth effect is interpreted in terms of a two-jump model, like that proposed by Freed and Fraenkel[9] for the radical anion of 1,3-dinitrobenzene in *N,N*-dimethylformamide. According to these authors the alternation in linewidths is produced by an out-of-phase modulation of the hyperfine coupling constants due to an asymmetric solvation mechanism, such that only one nitro group at a time interacts strongly with the solvent to form one of two possible solvent complexes, which are in dynamic equilibrium.

With 1,3-dinitrobenzene the linewidth alternation effect increases markedly in protic solvents; this was explained[10] in terms of hydrogen bonding between a negatively charged oxygen atom and the solvent. Such a model adapted to our

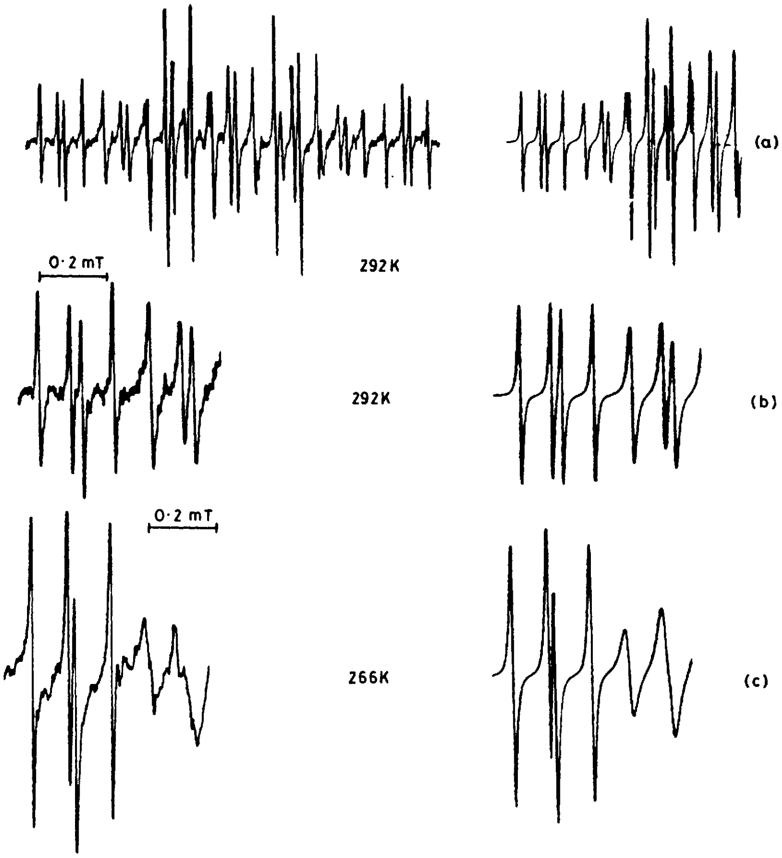


Figure 2. (a) Experimental (left-hand) and simulated (right-hand) spectra of radical anion of benzene-1,3-dicarbaldehyde in propan-2-ol at 292 K; (b), (c) amplified low-field wings of the experimental (left-hand) and simulated (right-hand) spectra at 292 and 266 K

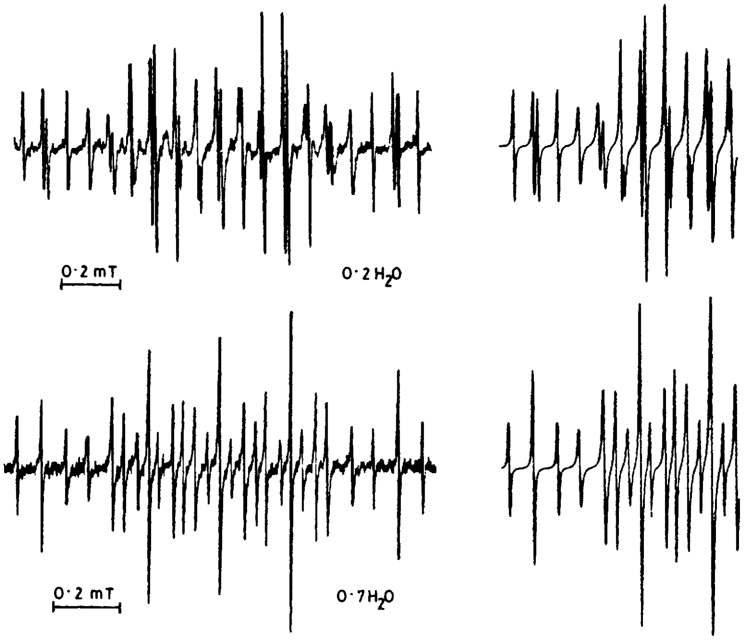


Figure 3. Experimental (left-hand) and simulated (right-hand) spectra of the radical anion of benzene-1,3-dicarbaldehyde in propan-2-ol–water mixtures (mole fractions of water: 0.2 and 0.7) at 292 K

case is shown [$(A) \rightleftharpoons (B)$] for $(Z,E)^{-\cdot}$. If the exchange is rapid, only time-averaged values of hyperfine coupling constants are observed. This mechanism also accounts for the absence of linewidth effects in the e.s.r. spectrum of the radical anion of benzene-1,4-dicarbaldehyde, being due to lower sensitivity of the hyperfine coupling constants of the 1,4-isomers to unsymmetrical perturbations.[9,11]

Experimental spectra of solutions in propan-2-ol were simulated applying the density matrix formalism to a two-jump model close to the limit of fast exchange, as reviewed by

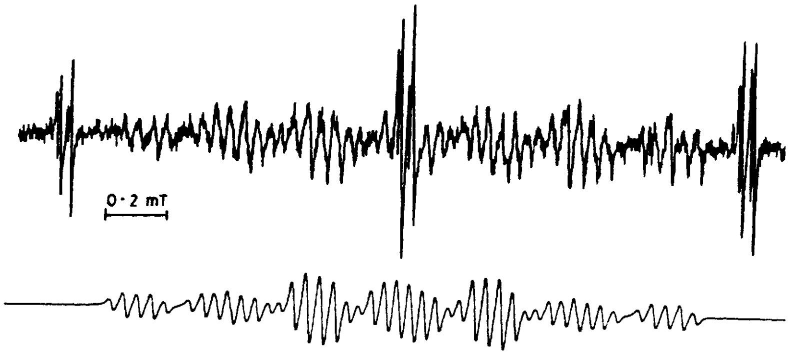


Figure 4. Experimental (top) and simulated (bottom) spectrum of 3-formyl-α-hydroxybenzyl radical in propan-2-ol at 298 K; the groups of narrow lines are from $(CH_3)_2\dot{C}OH$

Atherton.[12] Concentrations and lifetimes of complexes (A) and (B) were considered equal. Although it was not possible to obtain a spectrum corresponding to the slow exchange limit, from which all coupling constants could be measured, matching of the computed with the observed spectra was carried out by changing $(\Delta\omega)^2\tau$ (where $\Delta\omega$ is the variation in line position as a result of hyperfine splitting fluctuations and τ is the mean lifetime of each complex of the radical anion with the solvent). Also the averaged splitting constants $\langle a_4 \rangle = \langle a_6 \rangle$, $\langle a_7 \rangle = \langle a_9 \rangle$, $\langle a_2 \rangle$, and $\langle a_5 \rangle$ were adjusted to account for their slight temperature dependence. The very small fluctuation of the hyperfine splittings of protons at the 2- and 5-position between complexes (A) and (B) was included in the basic linewidth. The value of $(\Delta\omega)^2\tau$ changes from 0.46×10^{-16} T^2 s at 292 K to 1.14×10^{-16} T^2 s at 266 K for the lines of protons at the 4- and 6-position and from 2.85×10^{-16} T^2 s at 292 K to 7.10×10^{-16} T^2 s at 266 K for the lines corresponding to the aldehyde protons. Representative computed spectra are included in Figure 2.

As all our e.s.r. spectra are in the fast-exchange range, only the product $(\Delta\omega)^2\tau$ is accurately known. Measurements of dynamic frequency shifts, in order to calculate $\Delta\omega$, as carried out by Faber and Fraenkel[11] for the radical anion of 1,3-dinitrobenzene, cannot be performed in the same way for splittings of protons.[13] However, if we assume that the fluctuation in the hyperfine splitting constants of aldehydic protons is 0.6 mT, as indicated by McLachlan calculations of spin densities, we obtain τ in the range 0.79—1.97×10^{-9} s. This value compares well with those found for 1,3-dinitrobenzene, 3,5-dinitrophenolate, and 3,5-dinitromesitylene radical anions.[9,11] Thus it seems acceptable to use the foregoing values of τ to estimate the activation parameters.

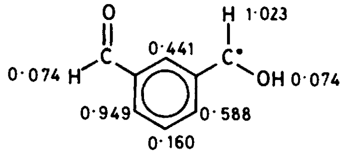
An Arrhenius plot of ln$k$ *vs.* $1/T$ gives an estimate of $E_a = 22.3 \pm 2.0$ kJ mol^{-1} and $\ln(A/s^{-1}) = 30.2 \pm 0.9$. These values allow a calculation of the activation parameters at 292 K: $\Delta H^{\ddagger} = (19.9 \pm 2.0)$ kJ mol^{-1}, $\Delta S^{\ddagger} = (-2.0 \pm 7.0)$ J mol^{-1} K^{-1}, and $\Delta G^{\ddagger} = (19.3 \pm 2.8)$ kJ mol^{-1}. The value of $\Delta H^{\ddagger}$ is in the range found for similar processes.[14] The small value for $\Delta S^{\ddagger}$ is also not surprising. The transition state of the electron-exchange process studied in this work is a symmetrically solvated radical anion, whereas the complexes (A) and (B) are asymmetrically solvated. Nevertheless in (A) and (B) both oxygen atoms interact with the solvent, although one of them more strongly. Therefore the geometry of the transition state is very similar to that of either complex, (A) or (B). Indeed MO calculations show that the carbonyl bond order changes only between 1.616 and 1.752 from one complex to another, which corresponds to a variation of bond length between 1.29 and 1.23 Å.[15] This shows that the degree of asymmetry responsible for the alternating linewidth effect is small.

Influence of Solvent on the Spectrum of $(Z,E)^{-\bullet}$.—E.s.r. spectra of the radical anion of 3BDC were also studied in water and propan-2-ol–water mixtures. Figure 3 shows spectra obtained at 292 K in mixtures with 0.2 and 0.7 mole fraction of water, and their computer simulations.

The splitting constants in Table 2 show a clear change in going from propan-2-ol to water, except for $\langle a_5 \rangle$ which does not change with solvent composition. The variation of the couplings and the constancy of $\langle a_5 \rangle$ can be accounted for by varying the correcting parameter δ_O of the Coulomb integral of the negatively charged oxygen from 2.2 (pure propan-2-ol) to 2.4 (pure water).

At 292 K, the spectra in propan-2-ol–water mixtures were satisfactorily simulated (Figure 3) using a constant extent of broadening for several compositions of the mixture. An explanation for this may be seen in the fact that an expected increase of the mean lifetime (τ) of either complex (A) and (B) in water, is compensated by a decrease of $\Delta\omega$. This is reasonable in terms of a more effective solvation of both oxygen atoms by the water molecules as compared with propan-2-ol, resulting in a less asymmetric distribution of charge and spin. Indeed McLachlan calculations of spin densities account for the observed variation in hyperfine splitting constants if an increase in the Coulomb integral of both oxygen atoms is considered.

Spectra in equimolar mixtures of propan-2-ol and water were studied at several temperatures between 315 and 252 K. An Arrhenius plot gives $E_a = 23.7 \pm 1.0$ kJ mol^{-1}, only slightly higher than in propan-2-ol.



(4)

3-*Formyl-α-hydroxybenzyl Radical.*—Photolysis of solutions of 3BDC in propan-2-ol was also carried out at pH 4—7. Under these conditions a radical was observed with the e.s.r. spectrum shown in Figure 4 [superimposed lines of the radical $(CH_3)_2\dot{C}OH$ are also observed]. This spectrum can be assigned to the neutral radical 3-formyl-α-hydroxybenzyl (**4**), the conjugate acid of the radical anion $(3BDC)^{-\bullet}$, and was satisfactorily simulated with the coupling constants shown in structure (**4**). The coupling constants were assigned to the various positions by comparison with the α-hydroxybenzyl radical.[16]

Conclusions

Interconversions of the three rotamers $(Z,Z)^{-\bullet}$, $(Z,E)^{-\bullet}$, and $(E,E)^{-\bullet}$ are too slow to lead to any observable line-broadening in the e.s.r. spectrum. The intramolecular electron exchange between the isomeric solvation complexes (A) and (B) of $(Z,E)^{-\bullet}$ has a rate in the range 0.50—1.25 × 10^9 s^{-1}. Lowering the temperature does not cause the system to approach the slow exchange limit. Transition-state theory reveals that $\Delta S^{\ddagger}$ is practically negligible, as a consequence of the very slight change in geometry along the reaction path. The variation of the exchange rate with the composition of the propan-2-ol–water mixture is slight enough for us to conclude that the value of the rate is determined essentially by the possibility of hydrogen bonding in both solvents, and bears little relation to dipolar solute–solvent interactions.

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