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Short Communications

Proton Transfer in the 1,1-Dinitroethane/*n*-Dibutylamine Complex

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Abstract—The ^1H NMR spectra of 1,1-dinitroethane/*n*-dibutylamine solutions in CCl_4 have been investigated. It is shown that two types of complexes, the CH · · · N hydrogen bond complex and the ion pair are present in the solution simultaneously, with slow exchange through proton transfer between them. The exchange rates, activation energy and enthalpy of proton transfer are determined. It can be concluded that the act of proton transfer from carbon to nitrogen and back is kinetically determined.

STUDIES of the IR spectra of carboxylic acid–amine systems in inert solvents made it possible to establish the equilibrium between the molecular complex with an OH · · · N hydrogen bond and the ion pair formed in the proton transfer from the acid to the amine.[1–3] It is known that the CH acids which produce anions with a strongly delocalised charge upon ionisation differ considerably in chemical behaviour, specifically in the ionisation rate[4] from common hydroxy acids. Because of this, a study of the interaction in an inert solvent between 1,1-dinitroethane (p*K* 5·1) and *n*-dibutylamine was undertaken. ^1H NMR spectra of CCl_4 solutions, containing 1,1-dinitroethane and *n*-dibutylamine in the concentration range from 0·05 to 0·5 mol/l, were obtained. The spectra were registered on a Varian HR-100 high resolution instrument with hexamethyldisiloxane as the external standard. With the amine present, the proton quartet of the 1,1-dinitroethane CH group, which resonates in pure CCl_4 at $\delta = 6{\cdot}18$ ppm, is shifted towards lower field, its position depending on the solution concentration. As more amine is added, the signal position approaches the limiting value of $\delta = 7{\cdot}10$ ppm. This signal obviously belongs to an equilibrium mixture of free 1,1-dinitroethane and that forming the C—H · · · N hydrogen bond with the amine. The concentration dependence of the quartet position points to the fact that equilibrium is shifted towards the complex formation. At the same time, with amine present, the quartet intensity decreases and a broad signal belonging to the $[NH_2]^+$ group of the dibutylammonium cation appears, the signal position being strongly dependent upon concentration and temperature. This shows that the $[Bu_2NH_2]^+$ $[C(NO_2)_2CH_3]^-$ ion pairs formed by proton transfer from the CH group to the amine nitrogen atom are present in solution together with the molecular complexes. Simultaneous occurrence of the 1,1-dinitroethane methyl doublet, $\delta = 2{\cdot}08$ ppm, and of the anion singlet, $\delta = 2{\cdot}44$ ppm, in the spectrum is another indication of the presence of two types of complexes. The spectrum shape does not change as the 1,1-dinitroethane–dibutylamine equimolar mixture is diluted with an inert solvent over the concentration range from 0·5 to 0·05 mol/l. The total strength of all signals of the molecular forms increases reversibly with temperature at the cost of the ion pair signals.

The width of the CH quartet components and of the methyl doublet lines increase with temperature (as does the width of the methyl singlet for the ion pair) and eventually the multiplets change into a single broad line at about 70 °C. The signals at $\delta = 2{\cdot}08$ ppm and 2·44 ppm, belonging to the methyl groups of the molecular and ionic complexes, respectively, begin to coalesce with further increase in temperature. The spectra of this system were also recorded for tetrachloroethylene solutions over a temperature range from 30 to 120 °C. Spectra in both solutions (in CCl_4 and C_2Cl_4) practically coincided in the range from 30 to 70 °C. A rise in the temperature from 70 to 120 °C leads first to coalescence of the signals and then to a narrowing and shift of the singlet line formed, the latter caused by the temperature dependent relative quantities of the two forms of the complex present. The CH and $[NH_2]^+$ signals of the molecular form and the ion pair also begin to overlap, but are still well separated at 120 °C. The results show that proton exchange occurs between the two forms of complexes found in solution, and because the concentration of free molecules of 1,1-dinitroethane is negligibly small, the rate of exchange determined from the ^1H NMR spectra coincides with the rate of proton transfer over the barrier dividing the two minima at the potential energy surface of the system. Mean times between the two acts of proton transfer from a carbon atom to nitrogen and back, and hence the thermodynamic parameters of the direct and reverse monomolecular reactions, were determined in the slow exchange approximation from the methyl group doublet shape for the molecular complex, the methyl group singlet for the ion pair and the CH group quartet. With this approximation, the molecular state lifetime τ_1 can be determined both from the doublet and the quartet shapes. The ratio of signal intensities measured experimentally at a maximum and the central minimum was compared with that calculated by the procedure suggested by Loewenstein and Meiboom.[5,6] The values of τ_1 determined by the two methods coincide within the random error limits at all temperatures up to 72 °C. The ionic state lifetime τ_2 was determined from the halfwidth of the anion methyl group signal. The

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TABLE 1. PROTON TRANSFER RATE CONSTANTS IN THE 1,1-DINITROETHANE-*n*-DIBUTYLAMINE SYSTEM

t °C	$k_1(s^{-1})$	$k_{-1}(s^{-1})$	k_1/k_{-1}	K
20	2·5			7
30	4·0	1·0	4·0	4·5
40	6·6	2·5	2·6	2·5
45	10	4	2·5	
50	13	7	1·9	1·5
55	15	11	1·4	
60	18	20	0·9	1·0
65	25	28	0·9	
70	33	40	0·8	0·7
77	40	75	0·53	0·45

k_1 = rate constant of proton transfer from carbon to nitrogen, k_{-1} = rate constant of proton transfer from nitrogen to carbon, K = equilibrium constant of the proton transfer reaction.

$E_1{}^a = 10 \pm 1$ kcal/mol; $E_{-1}{}^a = 20 \pm 2$ kcal/mol.

linewidth with no exchange (T_2*) was determined at each temperature from the chloroform signal. The rate constants measured in this manner are listed in Table 1. The ratios of the rate constants for the direct and reverse reactions are in good agreement with the equilibrium constants determined from the relative signal intensities. The enthalpy difference of the two forms determined from the temperature dependence in the IR spectra ($\Delta H = 10 \pm 1$ kcal/mol) agrees within the experimental error limits with the difference in the activation energies of the direct and reverse reactions. This supports the assumption that the quantities measured pertain to the act of the proton transfer over the potential barrier. It is evident from our data that this is kinetically determined (as compared to a similar process for the hydroxy acids) and interaction with the solvent is likely to play a minor role in the reaction energetics.

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