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REVERSIBLE PROTON TRANSFER IN THE 2,3,5,6-TETRACHLOROPHENOL-*N,N*-DIMETHYLANILINE HYDROGEN-BONDED COMPLEX STUDIED BY LOW-TEMPERATURE ^{1}H NMR SPECTROSCOPY*

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ABSTRACT

Low temperature ^{1}H NMR studies of the bridging OHN signal in the hydrogen-bonded complex formed between 2,3,5,6-tetrachlorophenol and *N,N*-dimethylaniline in C_2H_5Cl solution have shown that separate signals for the molecular and ion-pair forms of the complex can be observed below $-135\,^\circ$C (138 K). Analyses of the observed lineshapes have yielded values for the thermodynamic quantities ΔH°, ΔS° as well as for the activation quantities $\Delta H^\ddagger$, $\Delta S^\ddagger$.

INTRODUCTION

The proton transfer process (transfer of unit positive charge) along the hydrogen bond is one of the most interesting phenomena in molecular science. It plays an important role in chemistry, physics and biology since it determines the specific properties of hydrogen-bonded molecular systems and solids [1-3]. Therefore it is of fundamental importance to understand more deeply the mechanism of the process. In principle, one can visualize two different mechanisms which depend on the nature of the potential energy profile of the hydrogen bond

1. The proton occupies two states in a double-minimum potential well which results in the tautomeric equilibrium

$$\mathrm{X{-}H\cdots Y \rightleftharpoons X^-\cdots H{-}Y^+}$$

2. The proton occupies only one state in a single-minimum potential well

$$\mathrm{X\cdots H\cdots Y}$$

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*Dedicated to Professor W.J. Orville-Thomas.

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i.e. there is no potential barrier to proton exchange.

It has been shown experimentally that both of these mechanisms are possible. The tautomeric equilibrium (1) has been observed in hydrogen-bonded systems of the type O–H···N and C–H···Y both in solution and in the solid phase [1,4–8]. The second mechanism (2) of proton transfer has so far only been observed in hydrogen halide/base complexes in low-temperature matrices [9–14]. However, it is not yet clear to what extent the electronic structure of the bridged atoms and to what extent the nature of the environment influences the mechanism of proton transfer.

We have recently shown [15] that low-temperature ^{1}H NMR studies of the tautomeric equilibrium which exists in the 1:1 hydrogen-bonded complex formed between 2,4-dichlorophenol and triethylamine have enabled an estimate of the size of the potential barrier to proton transfer to be obtained for the first time for such systems in solution. We now report the results of a similar study of the tautomeric equilibrium in the closely related 1:1 hydrogen-bonded complex formed between 2,3,5,6-tetrachlorophenol and *N,N*-dimethylaniline (NNDMA). The latter base has a mixed aliphatic/aromatic nature and proton transfer may be favoured because the charge on nitrogen can be delocalized onto the aromatic ring. It is of interest to discover to what extent this influences the size of the potential barrier to proton exchange.

EXPERIMENTAL

2,3,5,6-Tetrachlorophenol (Aldrich) was purified by sublimation and stored over silica gel. The solvent C_2H_5Cl (Ferlak, Berlin) was vacuum distilled and stored over P_2O_5. *N,N*-Dimethylaniline (P.O. Chem.) was purified by fractional distillation and stored over molecular sieve 4A.

The NMR samples were prepared in a nitrogen-filled dry-box and the solvent was added by vacuum-line techniques. There was no direct contact between the chemicals and air. ^{1}H NMR spectra were obtained at 100 MHz using a Jeol JNM-PFT-100 spectrometer. The sample temperature was determined to an accuracy of ± 1 K by means of a platinum resistor.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the chemical shift of the bridging OHN proton signal for a sample which was 0.1 M in tetrachlorophenol and 0.5 M in NNDMA. Decoalescence into separate signals occurred at $T_c = -135\,^\circ C$ (138 K) and the limiting chemical shifts of the two tautomers were δ_A(molecular form) = 13.1 ppm and δ_B(ion-pair) = 14.1 ppm.

In the slow-exchange regime below T_c the intensities of the two signals are a direct measure of the fractional populations p_A and p_B of the tautomers. In the fast-exchange regime above T_c the observed chemical shift is given by

$$\delta^{\text{obs}} = p_A \delta_A + p_B \delta_B$$
$$= p_A \delta_A + (1 - p_A)\delta_B$$

so that again p_A and p_B may be evaluated. Thus the temperature dependence of ln $K_{\text{equil.}} = \ln(p_B/p_A)$ could be determined and their inverse linear dependence yielded the thermodynamic values $\Delta H° = -3.3 \pm 0.2$ kJ mol^{-1} and $\Delta S° = -27.5 \pm 2$ J K^{-1} mol^{-1} which are similar to those determined for the 2,4-dichlorophenol/triethylamine system. These results were reproducible for samples having compositions [tetrachlorophenol] = 0.1 M and [NNDMA] = 0.3–0.7 M. The excess of base is a necessity, otherwise decoalescence is not observed. We attribute this to the fact that the base acts as a donor which stabilizes the ion-pair, thus accounting for the large negative $\Delta S°$ value.

An estimate of the forward and backward rate constants k_{AB} and k_{BA} for the proton exchange process at the coalescence temperature T_c was obtained by the method of Shanan-Atidi and Bar-Eli [16] as described before [15]. The values of $k_{AB} = 130$ s^{-1} and $k_{BA} = 203$ s^{-1} so obtained are approximately one third of those found in the 2,4-dichlorophenol/triethylamine system. However, since the separation of the signals in the slow-exchange limit has also been reduced by one third, then T_c remains approximately the same for both systems.

In order to establish the activation parameters $\Delta H^‡$ and $\Delta S^‡$ for the proton exchange process, an analysis of the changes in lineshape as a function of temperature in the slow-exchange regime is required. Vold and Correa have derived [17] the closed form of the lineshape function for a spin $I = 1/2$ nucleus exchanging between two sites A and B where in site B it is scalar coupled to a

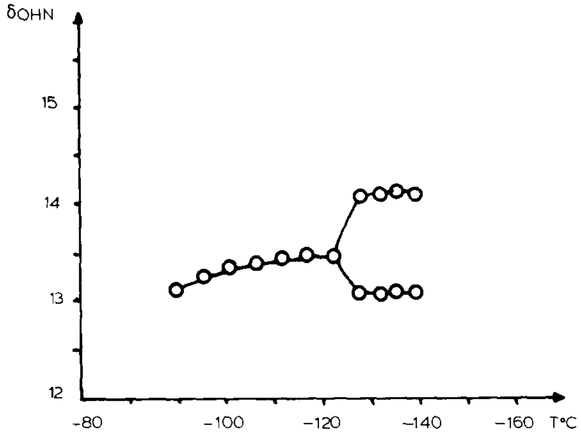

Fig. 1. Temperature dependence of the chemical shift of the hydrogen bridge proton signal for a sample which was 0.1 M in 2,3,5,6-tetrachlorophenol and 0.5 M in NNDMA in C_2H_5Cl solution.

TABLE 1

Rate constants for chemical exchange determined from lineshape analysis

T (K)	k_{AB} (s^{-1})	k_{BA} (s^{-1})
162.1	650.0	1538.3
156.7	624.0	1359.9
151.4	480.0	959.4
146.0	352.0	640.0
140.6	165.0	270.9
138.2	130.0	203.5
127.8	48.0	59.8

quadrupolar nucleus of spin $I=1$ as is the case here. The required shape function parameters were assigned as follows.

(i) The populations p_A and p_B were taken from the thermodynamic data evaluated earlier.

(ii) The chemical shifts in the absence of exchange were δ_A and δ_B.

(iii) The relaxation rate R_2° in the absence of both chemical exchange and quadrupolar effects was calculated from the linewidth (12.6 Hz) of the A signal in the lowest temperature spectra where these effects were frozen out.

(iv) The scalar coupling constant $J(^{14}N–H)=54.5$ Hz determined for protonated aniline [18] was used.

(v) Fast quadrupolar relaxation was assumed since in no case was a resolved triplet structure observed for signal B. Since the rate of quadrupolar relaxation R_1 and the rate constant k_s (which describes exchange of the spin $I=1/2$ nucleus among the three B subsites) appear as a sum, they may be treated together. Thus k_s was arbitrarily set to zero and R_1 was chosen to yield the experimental linewidth (14.7 Hz) of the B signal when the chemical exchange was frozen out.

With the above assumptions, the lineshape could be calculated on a point by point basis for any values of the forward and reverse rate constants k_{AB} and k_{BA} bearing in mind that these are related by the principle of microscopic reversibility $p_A k_{AB}=p_B k_{BA}$. The values of the rate constants assigned to the observed lineshapes at each temperature by visual matching of the computed lineshapes are given in Table 1. They yield the activation parameters $\Delta H_{AB}{}^{\ddagger}=12.8\pm1$ kJ mol^{-1} and $\Delta S_{AB}{}^{\ddagger}=-104\pm8$ J K^{-1} mol^{-1} for the forward process and $\Delta H_{BA}{}^{\ddagger}=16.1\pm1$ kJ mol^{-1} and $\Delta S_{BA}{}^{\ddagger}=-77\pm8$ J K^{-1} mol^{-1} for the reverse process.

CONCLUSIONS

Although the lineshape analyses must be regarded as approximations and the determination of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ spans a small temperature range, there is a satisfying internal consistency between the estimated enthalpy changes in that $\Delta H_{AB}^{\ddagger} - \Delta H_{BA}^{\ddagger} = \Delta H^{\circ}$. The small ΔH° value provides strong evidence that the potential energy profile for reversible proton transfer in the OHN hydrogen-bonded system is very nearly symmetric with a double minimum. The free energies of activation $\Delta G^{\ddagger}$ derived from these values are virtually the same as those found earlier for the 2,4-dichlorophenol/triethylamine system [15] thus showing that the nature of the base is unimportant.

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