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Reaction Path for the Proton Transfer NH_4^+/NH_3; An *ab initio* SCF-LCAO-MO Study

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Summary The proton jump from NH_4^+ to NH_3 is found to occur by a contraction of the associated species $NH_4^+ \ldots NH_3$, with a computed energy barrier of 2·5 kcal mol^{-1}.

PROTON transfer in solution from an acid AH to a base B is generally considered to occur in the three steps[1] shown in reaction (1). The rates of the first and third step (association to AH . . . B, and dissociation of A . . . HB) are

$$AH + B \rightarrow AH \cdots B \rightarrow A \cdots HB \rightarrow A + HB \qquad (1)$$

thought to be diffusion controlled, while the second step is the actual proton transfer reaction. The total rate constant k_1 may be measured by various methods.[2] For the title system, the transfer is essentially described according to reaction (2). The rate constant k_2 for reaction (2) is

$$NH_4^+ + NH_3 \rightarrow NH_4^+ \cdots NH_3 \rightarrow NH_3 \cdots NH_4^+ \rightarrow NH_3 + NH_4^+ \quad (2)$$

extremely large[3] either in aqueous solution ($k_2 \simeq 1{\cdot}2 \times 10^9 \text{M}^{-1}\,\text{s}^{-1}$ at 25 °C) or in non-aqueous solvents like dimethyl sulphoxide,[4] provided that the ammonium salt used to generate NH_4^+ is completely dissociated.[5] This shows that reaction (2) is intrinsically fast, and cannot be explained by the special properties of the hydrogen-bonded water structure.[6] We report the results of an *ab initio* SCF-LCAO-MO study of the reaction path for the above sequence. We used a basis set of eight *s*, four *p*, and one *d* Gaussian functions on nitrogen and three *s* and one *p* functions on hydrogen.[7] The energy curves for a given N · · · N distance *d* as a function of the abscissa *z* of the proton, relative to the middle O of N · · · N segment (Figure 1) are given in Figure 2. The N–H bond lengths and the angles α and β were first kept at 1·007 Å and 106·3° (optimum values for the ammonia molecule). The N–N distance was optimized to a value d_m = 2·587 Å by keeping the proton midway between the two nitrogens (z = 0). With this N–N distance, the minimum energy is obtained with the proton at z = 0·1835 Å from the origin O, and the depth of the well is 1·13 kcal mol^{-1} [curve (2)]. Then the N–N distance was varied together with the position of the proton, curves (1)—(7), so as to find the minimum energy of the system. This is achieved in curve (6) (points Q_0 and Q_1) with a N–N distance d_e = 2·778 Å, a proton at z = 0·316 Å from the origin, and an energy well of 6·1 kcal mol^{-1}. The angles α and β have been optimized for the maximum of curve (2) (α = β = 107·0°) and for the minimum of curve (6) (α = 108·7° and β = 106·0°). The small variations obtained in the values of α and β for these points indicate that the set of curves in Figure 2 should not be changed appreciably by the optimization of the angles.

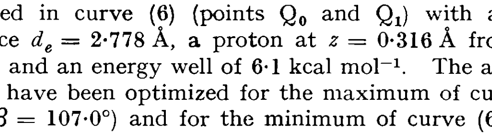

FIGURE 1.

The minimum energy geometry [minimum of curve (6)] has an equilibrium N–N distance of 2·778 Å and a binding energy relative to the systems NH_3 and NH_4^+ of 27·6 kcal mol^{-1}. No experimental values seem to be available. However, our computed N–N value is 0·7 Å shorter than the one (3·49 Å) computed for the ammonia dimer.[9,10] The binding energy of the H_3O^+–H_2O system has been computed as 32·2 kcal. mol^{-1},[9] to be compared with the 26·0 kcal mol^{-1} for the present system.

The reaction path may be visualized by a line C_0 joining the successive minima of curves (2)—(7), as the two particles NH_4^+ and NH_3 spontaneously approach each other up to the distance d_m (point P_0). In this situation, the top S of the double well is at a minimum, favouring a proton jump from NH_4^+ to NH_3, *i.e.* from P_0 to P_1. Thus the most favoured reaction path follows line C_0 (first step of equation (1) or (2): association), then the segment P_0 SP_1 of curve (2) (proton transfer), then the line C_1 symmetrical to C_0 (dissociation). The transition states at the top of curve (2) correspond to an N–N distance d_m shorter than d_e ($d_m/d_e = 0{\cdot}93$). A similar conclusion regarding the decrease of the energy barrier when decreasing the O–O separation has been reached recently for the $(HOHOH)^-$ system.[11] The energy barrier for the proton transfer is equal to the difference between the energies of the associated species AH · · · A and of the transition state; its value: 2·5 kcal mol^{-1}, or 872 cm^{-1}, is probably less than the first vibrational energy level of the "symmetrical" stretch A · · · H · · · A.[12] This may explain why the activation energy of this process has been found equal to zero in water by dynamic n.m.r. measurements.[3]

These results may provide a general method for the study of proton transfers. The three generally accepted steps: association, proton transfer and dissociation have been quantitatively studied and their energies obtained. The proton jump has been shown to occur through a contraction of the associated species obtained in the first step. This means that the symmetrical vibration of the associated species favours proton transfer, an assumption which has not previously been proved.

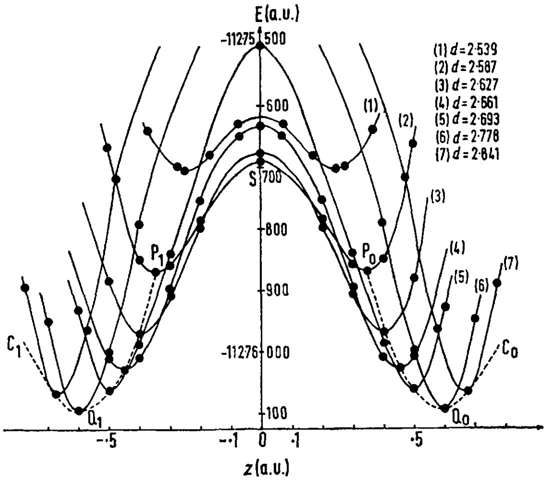

FIGURE 2. *Potential energy curve for the system* $NH_3 \cdots H \cdots NH_3$, *as a function of the position* **z** *(atomic units) of the exchanging proton for various* N–N *distances* **d**.

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