Comparison of Proton Transfers in Cationic Heterodimers and Homodimers of NH₃ and OH₂

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Comparison of proton transfers in heterodimers and homodimers of NH₃ and OH₂

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Ab initio molecular orbital methods are used to study proton transfers in the cationic heterodimer (H₃NHOH₂)⁺ as well as the symmetric homodimers (H₂OHOH₂)⁺ and (H₃NHNH₃)⁺. All calculations are carried out at the Hartree-Fock level with a 4-31G basis set to ensure consistency. For proton transfers along a linear hydrogen bond in the heterodimer, asymmetric single-well potentials with a minimum corresponding to (NH₃)(OH₂)⁺ are obtained for R(NO) distances of less than 2.85 Å. Longer intermolecular separations lead to appearance of a second minimum in the potential (NH₃)(OH₂)⁺. The energy barrier between these two minima is much greater for transfer from N to O than for the reverse O to N. Transfer barriers in the two homodimers lie between these two extremes, with interoxygen transfer barriers somewhat higher than for the internitrogen process. Barriers for all systems are found to be sensitive to angular deformations as well as stretches of the H bond. Electronic redistributions occurring at various stages of proton transfer are monitored by means of density difference maps and population analyses. Greater amounts of charge transferred from the proton-accepting molecule to the donor are associated with more facile proton transfers. The calculated energies of the lone pair orbitals of the proton-accepting atom provide another accurate indicator of the height of the barrier to proton transfer. These observations are explained in terms of fundamental principles of electronegativity and orbital interactions.

I. INTRODUCTION

In addition to the well known importance of proton transfers in such fundamental chemical processes as acid–base equilibria and nucleophilic addition reactions, these transfers are a vital component in a surprising range of complex biological phenomena as well. Examples include photosynthesis, ATP synthesis and utilization, enzyme catalysis, and ionic transport across membranes. For this reason, proton transfer reactions have received a great deal of experimental attention. There are, however, various aspects of the problem for which experimental techniques are not well suited. For example, while equilibrium and rate constants may be determined, it is difficult to ascertain structural features of transient species such as the transition state.

Theoretical approaches are capable of supplying a great deal of information which nicely complements experimental data. For instance, the geometries of species involved in the proton transfer may be determined to good precision. Moreover, it is possible to "freeze" the proton at any desired stage of the transfer and study various properties such as the electronic distribution.

Since Clementi's ab initio study of the proton transfer between NH₃ and HCl in 1967, a number of theoretical treatments have appeared in the literature. However, rather than containing a complete body of consistent information, these papers report isolated studies of diverse individual systems and each generally involves a different quantum chemical technique. The present series of papers represents an attempt to study the proton transfer problem in a systematic fashion and to extract valid basic principles via comparisons of closely related systems using identical methods with each.

In order to study the fundamental properties of the proton transfer process it is desirable to minimize complicating effects from other chemical substituents. Systems involving transfers between simple hydrides of the type XH, offer the most attractive prototypes for detailed investigation. In particular, previous publications compared the energetics and charge redistributions in cationic homodimers of OH₂ and NH₃. The dimers studied, (H₂OHOH₂)⁺ and (H₃NHNH₃)⁺, are referred to here as homodimers because the central proton is being transferred between two identical molecules. It is expected however that some very important and interesting effects will be observed when the two molecules involved in the dimer are chemically distinct. Moreover, proton transfers between groups of somewhat different character are the rule rather than the exception in chemical and biological processes.

For these reasons, calculated results are presented here for the heterodimer (H₃NHOH₂)⁺ in which the hydrogen bond involves both NH₃ and OH₂. Previous ab initio study of proton transfer within this system is limited to a single paper. Delpuech et al. calculated the energetics of transfer for intermolecular R(NO) distances ranging from 2.66 to 3.16 Å. Only the fully linear hydrogen bond was considered with no examination of the effects of distortions of the bond upon the energetics. In addition, the authors focused their attention exclusively upon the energetics and made no attempt to study the electronic structure of the complex or to elucidate the underlying factors contributing to their results.

The present paper reports the energetics for proton transfer in the heterodimer (H₃NHOH₂)⁺ for a range of conformations including bends as well as stretches of the hydrogen bond. Rearrangements of the electron distribution accompanying the proton transfer are carefully monitored. Comparisons of results for (H₃NHOH₂)⁺ with those obtained for the homodimers lead to useful quantitative relationships and provide insights into the
manner in which the fundamental characteristics of the involved species manifest themselves in the proton transfer process.

II. CHOICE OF METHOD

Calculations of the (NOH)⁺ closed-shell system were carried out at the ab initio restricted Hartree–Fock level. Molecular orbitals were constructed as linear combinations of atomic orbitals using the GAUSSIAN-70 computer code.²⁵ The split valence-shell 4–31G basis set was used for a number of reasons. First, the same basis has been used previously to study (O₂H)⁺ and (N₂H)⁺. 4–31G calculations of (NOH)⁺ may thus be validly compared with results for these systems. Perhaps of greater importance, the 4–31G basis set has been demonstrated to provide an efficient and accurate means of studying proton transfer processes. Results for (O₂H)⁺, (N₂H)⁺, and (NOH)⁺ are in excellent agreement with those of much more sophisticated theoretical techniques including electron correlation.²¹–²⁴

In treating the transfer of a proton between two dissimilar molecules, as in the current study of the transfer between NH₃ and OH₂, it is crucial that the method of calculation accurately reflect the relative proton affinity of the two species involved. The proton affinities of XH₄⁺ defined as $\Delta A E$ for the reaction

$$XH_{\text{t}} + H^- \rightarrow (XH_{\text{n}})^+,$$

were calculated including full geometry optimizations of both XH₄ and (XH₄)^+. The proton affinities of NH₃ and OH₂ calculated at the Hartree–Fock level with the 4–31G basis set, were respectively 221.0 and 183.2 kcal/mol.³¹ This theoretical approach thus indicates a greater proton affinity of 37.8 kcal/mol for NH₃. Frisch et al.³² have recently reported calculated proton affinities for these two molecules using much larger basis sets and taking extensive account of electron correlation. Although their calculated proton affinities are slightly lower than those obtained with 4–31G (by 2 to 7 kcal/mol), the difference in affinity between NH₃ and OH₂, of greatest concern when treating proton transfers between the two molecules, is remarkably well reproduced by 4–31G at the Hartree–Fock level. For example, Frisch et al. found that, within the framework of a triple-zeta basis set with polarization functions on all centers, including two sets of $d$ orbitals on first-row atoms [6–311G**(2d)], the difference in proton affinity between NH₃ and OH₂ is 38.6 kcal/mol at second, third, and fourth order Moller–Plesset perturbation theory. This value compares quite well with the 4–31G difference of 37.8 kcal/mol.

Recent experimental work with both ion cyclotron resonance and high-pressure mass spectrometry techniques has established the proton affinity difference between NH₃ and OH₂ as 36.0 kcal/mol. When zero-point energy corrections are included, the theoretical difference is expected to be reduced by 1.1 kcal/mol,³³ bringing the 4–31G value down to 35.7, quite close to the experimental result. Because of its excellent agreement with both accurate theoretical and experimental approaches, the 4–31G basis set at the Hartree–Fock level appears to furnish an excellent theoretical tool for studying proton transfers between NH₃ and OH₂.

III. LINEAR HYDROGEN BONDS

In order to study the transfer of a proton between NH₃ and OH₂, the geometry of the (H₂NHOH)⁺ system was first fully optimized. This structure, illustrated in Fig. 1, contains an equilibrium $R(NO)$ separation of 2.664 Å. The NH₂ and OH₂ units, respectively, possess local $C_{2v}$ and $C_{2h}$ symmetry. The entire complex belongs to the $C_{2v}$ point group. Other details of the geometry are provided in the figure caption.

In the equilibrium structure, the central proton lies directly along the internuclear N–O axis at a distance $r$ of 1.049 Å from the nitrogen. Because this proton lies much closer to N than O, the equilibrium configuration may be characterized as (NH₄⁺)(OH₂). The energy increase resulting from motion of the central proton along the NO axis is illustrated by the lowest curve in Fig. 1. This curve has only a single minimum, corresponding to the equilibrium (NH₄⁺)OH₂ conformation. Approach of the central proton toward the oxygen does not lead to a stable (NH₄⁺)(OH₂) configuration as there is no energy barrier to motion of the proton back towards N and decay to (NH₄⁺)(OH₂).
Due to a variety of structural factors, very few NH–O hydrogen bonds in real chemical systems are free to adopt the optimal intermolecular arrangement. Surveys of a large number of systems indicate a range of $R(\text{NO})$ between about 2.6 and 3.2 Å. Hence, it is important to calculate proton transfer potentials for a series of intermolecular distances in this range. Such potentials for $R = 2.8, 2.95,$ and $3.1$ Å are presented in Fig. 1 along with that for the equilibrium $R = 2.66$ Å. The curves for $R = 2.8$ and $2.66$ Å are similar in that they are both of asymmetric single-well character. When $R(\text{NO})$ is increased to $2.95$ Å, on the other hand, the potential contains two distinct minima separated by an energy barrier. The right-hand minimum, representing $(\text{NH}_3)(\text{OH}_2)^+$, is some 26 kcal/mol higher in energy than the left-hand $(\text{NH}_4)^+(\text{OH})_2$ structure, reflecting the greater proton affinity of NH$_3$ than of OH$_2$. Nevertheless, the proton must cross a barrier of some 3 kcal/mol for $(\text{NH}_3)(\text{OH}_2)^+$ to decay back to $(\text{NH}_4)^+(\text{OH})_2$. When the NH$_3$ and OH$_2$ molecules are further separated to $R = 3.10$ Å, the barrier to conversion of $(\text{NH}_3)(\text{OH}_2)^+$ to $(\text{NH}_4)^+(\text{OH})_2$ has increased to 8 kcal/mol.

As the proton is moved along the NO axis, the remainder of the geometry of the complex is held fixed. This "rigid molecule approximation" has been demonstrated previously to be valid for $(\text{O}_2\text{H})^+$ and $(\text{N}_2\text{H})^+$ in that geometry optimizations at each stage of proton transfer did not lead to any significant changes in the calculated potentials. The same is true for the heterogeneous $(\text{H}_2\text{NH}OH_2)^+$ system. Geometry optimizations carried out for various positions of the central proton had only small effects on the potentials shown in Fig. 1. For example, the barrier to transfer of the proton to the left from O to N for $R = 2.95$ Å is increased by only 0.5 kcal/mol by geometry optimizations. Internal bondlengths in the NH$_3$ and OH$_2$ units change by less than 0.005 Å; bond angles by less than 4°. It is concluded that the rigid molecule approximation is valid for $(\text{NOH})^+$ as was the case also for the homogeneous $(\text{N}_2\text{H})^+$ and $(\text{O}_2\text{H})^+$ dimers.

The previous set of calculations of the $(\text{NOH})^+$ system by Delpuech et al. are in good agreement with the 4-31G results. Using a larger basis set including polarization functions, as well as the rigid molecule approximation, these workers obtained potentials quite similar to those depicted in Fig. 1. Delpuech et al. observed a single-well potential for $R = 2.79$ Å in agreement with the 4-31G result for $R = 2.80$ Å in Fig. 1. The 4-31G barrier for proton transfer from O$_2$H$_2$ to NH$_3$ with $R(\text{NO}) = 2.95$ Å is 2.7 kcal/mol, only slightly lower than the value of 3.1 obtained with the larger basis set. Moreover, recent CI calculations indicate that electron correlation contributions produce only small corrections upon the 4-31G results in Fig. 1. All the calculations further agree that the equilibrium structure of the complex is $(\text{NH}_3)^+(\text{OH})_2$ and that, with $R(\text{NO})$ allowed full relaxation, any $(\text{NH}_3)^+(\text{OH})_2$ configuration will spontaneously collapse back to the equilibrium structure with no energy barrier.

It is interesting to compare the energetics of proton transfer in the $(\text{NOH})^+$ system with the homogeneous $(\text{O}_2\text{H})^+$ and $(\text{N}_2\text{H})^+$ dimers. Figure 2 shows the calculated barriers to proton transfer $E'$ as a function of the distance $R$ between the two first-row atoms. OH–O refers to the transfer between the two oxygens in $(\text{O}_2\text{H})^+$; NH–N to $(\text{N}_2\text{H})^+$.

From Fig. 2 it is clear that for a given fixed intermolecular distance $R$, the highest barrier occurs for proton transfer from NH$_4$ to OH$_2$, followed by the two homogeneous OH–O and NH–N transfers, and finally by OH–N. For example, for $R = 2.95$ Å, the calculated barriers are 29.1, 16.9, 11.4, and 2.7 kcal/mol, respectively for these transfers. The high barrier for NH–O and low barrier for the reverse OH–N is reasonable in terms of the relative proton affinities of the NH$_3$ and OH$_2$ molecules. The much lower affinity of OH$_2$ makes it difficult for this molecule to pull the excess proton away from NH$_4^+$, resulting in the high barriers for NH–O. Similarly, the greater affinity of
NH₃ facilitates the OH−N transfer and leads to low barriers for this process. An intermediate situation arises for the homogeneous (Q₃H₃)⁺ and (N₃H₃)⁺ dimers wherein the two molecules have identical proton affinities. The internitrogen transfer is associated with a somewhat lower barrier than OH−O, due perhaps to the lesser electronegativity of nitrogen. Since the valence electrons of N are better shielded from the nucleus than are those of oxygen, the lone electron pairs of nitrogen are expected to be somewhat longer; i.e., extend farther from the nucleus. Therefore, a proton at the midpoint between two N atoms may interact more strongly with the N lone pairs than when midway between two O atoms with their shorter lone pairs. The net result is less destabilization of the N−H−N midpoint and hence a lower barrier to proton transfer. Other characteristics of the appropriate lone pairs are discussed in greater detail below.

The intersection of each curve in Fig. 2 with the horizontal axis provides the minimum value of R for which the proton transfer potential contains two distinct wells. For example, the potential for (H₂O+OH₂)⁺ is of double-well form for R greater than about 2.45 Å. For shorter interoxygen separations, the equilibrium position of the central proton is midway between the two oxygens and the potential contains a single symmetric well. The transition from single to double well occurs at the somewhat longer distance of 2.53 Å for (N₃H₃)⁺. This fact is again consistent with longer lone pairs for N than O. In the asymmetric (H₂N⁺NH₂)⁺ system, a second well makes its appearance only at intermolecular separations of 2.85 Å or greater. Since there is only one well (NH₃−OH₂) for shorter distances, and hence no barrier, neither the NH−O nor the OH−N curves extend to the left of R = 2.85 Å.

The curves in Fig. 2 may also be used to estimate the R(XY) distance corresponding to a given transfer barrier. Let us assume that the proper functioning of some chemical process requires an energy barrier of 5 kcal/mol for the proton transfer step. Figure 2 indicates that for a transfer between oxygen atoms, an R(00) distance of 2.69 Å would correspond to a barrier of this magnitude while the longer R(NN) distance of 2.78 Å would be needed for NH−N transfer. For OH−N transfer, a separation of R(ON) = 3.02 Å is required while the reverse NH−O transfer never has a barrier less than about 25 kcal/mol since single-well potentials are associated with R(NO) < 2.85 Å.

With regard to the absolute magnitudes of the barriers in Fig. 2, use may be made of results calculated with larger basis sets and including electron correlation. Comparisons are quite consistent from one system to the next. In every case examined, enlargement of the basis set beyond the 4-31G level leads to higher barriers. However, when the effects of electron correlation are included the barrier is reduced to values quite close to those calculated at the Hartree-Fock level with 4-31G. The net result is that all the barriers in Fig. 2 may be expected to be lowered a small amount when much more sophisticated theoretical treatments are used. However, these changes are relatively minor and certainly the qualitative conclusions concerning the relative properties of transfers in the various systems would remain unchanged.

IV. ELECTRON DENSITY REARRANGEMENTS

In order to better understand the various factors involved in the proton transfer process, it is informative to examine the redistributions of the electronic structure that accompany the motion of the proton. The electronic rearrangements associated with half-transfer of the central proton from its equilibrium position (H₄XH−−−−XH₄) to a point midway between the two first-row atoms (H₄X−H−XH₄) were reported in paper 4 for the homodimers (N₃H₃)⁺ and (O₂H₂)⁺. The analysis presented there furnished useful information about the fundamental properties of the proton transfer process as well as about basic differences between the nitrogen and oxygen atoms. However, the symmetry of these homodimers restricted the analysis to proton transfers between identical groups, thereby precluding the extraction of important information about transfers between unlike groups with different properties such as proton affinity and basicity.

For this reason, we turn here to investigation of the electronic redistributions accompanying the transfer of a proton between the NH₃ and OH₂ molecules in (H₃NHOH₂)⁺. In order to ensure consistency with the previously described (N₃H₃)⁺ and (O₂H₂)⁺ homodimers, and to negate discrepancies arising from different equilibrium intermolecular separations, the distance R between the N and O atoms was chosen as 2.75 Å. For this value of R, the equilibrium position of the central proton is along the N−O axis at a distance r from the nitrogen of 1.047 Å. Figure 3 illustrates the electronic redistributions accompanying the motion of the central proton from this position (H₃NH−−−−OH₂) to a point exactly midway between the N and O atoms (H₃N−H−OH₂). These two positions of the central proton are connected by the arrow in Fig. 3.

Specifically, the contours in Fig. 3 designate the difference between the electron density ρ of the midpoint configuration and that of the equilibrium structure: ρ(H₃N−H−OH₂)−p(H₃NH−−−−OH₂). Solid contours indicate greater density in the midpoint geometry while charge depletions upon half-transfer are represented by the dashed contours. As the numerical labels of each contour are equal to the negative of twice the logarithm of the density change occurring within the contour, smaller numbers are associated with greater changes in density.

Electronic redistributions occurring in the xz plane of (NOH₂)⁺ are shown in the upper half of Fig. 3 while the lower half contains the perpendicular yz plane. The central horizontal strip has been cleared of contours in order to accurately display the positions of the N, H, and O atoms lying along the x axis; the contours above and below this strip are in fact continuous. The other atoms explicitly shown in Fig. 3 are those H atoms lying in the half-planes contained in the figure. These include one hydrogen of NH₃ and one from OH₂ (see Fig. 1).

While Fig. 3 represents the half-transfer of the cen-
central proton from N to the N–O midpoint in (H₂NHOH₂)⁺, the reverse situation wherein O acts as proton donor is presented in Fig. 4. That is, this figure exhibits the difference in electron density between the (H₃N–H–OH₂) midpoint geometry and that in which the central proton is in close proximity to the oxygen (H₃N–HOH₂). For purposes of clarity and consistency, the entire complex has been rotated so that the proton-donating atom, here the oxygen, is on the left. The central arrow again indicates the motion of the proton from the proton-donating atom to the midpoint of the N–O bond.

It is noted that the (H₃N–HOH₂) configuration is not a minimum on the proton transfer potential curve for R(NO) = 2.75 Å; neither does the midpoint (H₃N–H–OH₂) represent an energy maximum for the heterodimer as it does for the homodimers (OH₂)₆ and (NH₃)₆. Nonetheless, the electronic rearrangements accompanying the half proton transfers in (H₃NHOH₂)⁺ are expected to provide a consistent base for comparison with half-transfers in the symmetric homodimer systems.

The shifts of electron density resulting from proton transfer are presented in a pictorial manner in Figs. 3 and 4. While this type of representation furnishes valuable insights into charge rearrangements in individual regions of space, examination of gross charge shifts from one chemical group to another is facilitated by collecting together electron density in the neighborhood of a given atomic center, thereby assigning a net charge to that atom. Mulliken population analyses have been used for this purpose extensively in the past and are applied here to study density shifts associated with proton transfers.

The charge transferred from the proton-accepting group to the remainder of the complex is analyzed in this fashion in Table I. The first row of the table contains the amount of charge reduction in the YH₂ unit of (H₃XHYH₂)⁺ as a result of half-transfer of the central proton from the proton-donating X to the accepting Y atom

\[
(H₃XH–YH₂)⁺ → (H₃X–H–YH₂)⁺. \tag{1}
\]

The half-transfer in Eq. (1) is also abbreviated as XH–Y in this paper. As an example, the first entry in the table indicates that the total charge assigned to the OH₂ group in (H₃NHOH₂)⁺ is decreased by 69 me when

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**FIG. 3.** Electron density difference map for half-transfer of the central proton from NH₃ to OH₂: \( \rho(\text{H}_3\text{N}-\text{H}-\text{OH}_2) - \rho(\text{H}_3\text{NH}-\text{OH}_2) \). Solid contours represent increases of density and broken contours decreases. The arrow extends from the equilibrium position of the central hydrogen to the N–O midpoint. Only atoms located in the xz (upper half of figure) and yz (lower half) planes are included. The density change occurring within each contour labeled by the number \( n \) is \( 10^{n/2} \text{e/Å}^3 \), \( R = 2.75 \text{Å} \).

**FIG. 4.** Contour map of proton half-transfer from OH₂ to NH₃: \( \rho(\text{OH}_2-\text{H}-\text{NH}_3) - \rho(\text{H}_2\text{OH}-\text{NH}_3) \). The OH distance in the H₂OH–NH₃ configuration is 1.05 Å. Conventions are the same as in Fig. 3.
The central proton is transferred halfway towards it from H₂NH⁺. The reverse half-transfer from H₂OH⁺ to the O–N midpoint is included as the last column of the table; the second and third columns, respectively, correspond to the homodimers (Q₃H)⁺ and (N₃H)⁺.

The charge loss in the proton-accepting (YH⁺) group may be broken down into depletions from the first-row Y and each of the H atoms. As indicated by the second and third rows of Table I, of the 69 me lost by OH₂ in (H₂NHOH₂)⁺, none is withdrawn from the oxygen, whereas each of the two hydrogens loses 35 me. It is possible to further partition the charge depletion of the first-row atom into contributions from each atomic orbital. In the same example, the populations of the 2s and 2pₓ orbitals of the proton-accepting oxygen are reduced by 15 and 33 me, respectively. These decreases are offset by an increment of 48 me in the 2pᵧ orbital. (Note that a negative sign in Table I refers to charge increase.) The 2pᵧ orbital undergoes no change in population.

It is well known that data obtained from population analyses of Mulliken or similar type, based upon an arbitrary scheme of assigning electron density to various atomic centers, are heavily basis-set dependent and subject to some ambiguity in interpretation. However, we are dealing in Table I not with the raw Mulliken populations themselves but instead with changes in these populations resulting from protonic motion. Moreover, these changes are calculated as differences between two similar molecular geometries, both of which are calculated with the same basis set. For these reasons, the data in Table I are expected to be relatively insensitive to basis set choice and to reflect real chemical phenomena. In addition, analysis of this data in conjunction with the completely objective information in Figs. 3 and 4 should serve as a further verification of its validity. In summary, the numerical atomic charge data in Table I are a valuable complement to the more detailed and less arbitrary density difference maps.

We begin our analysis with the charge transferred from the proton-accepting group YH⁺ to the donating molecule (HₓXH⁻) as a result of half proton transfer in the (HₓXHYHₓ⁻) complex. As may be easily seen from the first row of Table I, this quantity increases in the sequence

\[ \text{NH} \rightarrow \text{O} < \text{OH} \rightarrow \text{O} < \text{NH} \rightarrow \text{N} < \text{OH} \rightarrow \text{N}. \]  

(2)

The amount of charge transferred ranges from a minimum of 69 me shifted from the proton-accepting OH₂ to H₂NH in (H₂NHOH₂)⁺ up to a maximum of 132 me transferred from NH₂ to H₂OH for OH⁻–N. The order indicated above suggests that NH₂ releases more electron density as a proton is transferred towards it than does OH₂. This observation is quite reasonable since N is less electronegative than O and might be expected to release its charge more readily. The amount of charge transfer is affected also by the nature of the proton-donating species XH⁺. For either proton-accepting molecule, more charge is released to proton-donating H₂OH than to H₂NH. For example, NH₂ transfers 132 me to H₂OH (OH⁻–N) and only 106 me to H₂NH (NH⁻–N). Again, an explanation based upon the greater electronegativity of oxygen than nitrogen, and its greater attraction for electrons is satisfactory.

It is quite suggestive that the relative order of charge transfer in Eq. (2) is precisely opposite to the order of barrier energies described in Fig. 2. That is, those systems in which the greatest amount of charge is transferred from the proton-accepting group to the proton-donating unit also have associated with them the lowest energy barriers to transfer of the proton. It is therefore not unreasonable to conclude that the transfer of a proton in one direction is somewhat facilitated by shift of electron density in the other direction.

The pictorial representations of charge shifts in Figs. 3 and 4 bear out the conclusions based on Table I. The greater loss from the proton-accepting NH₂ group than from the OH₂ molecule is supported by the dashed contours surrounding the right-hand molecules in these figures. Specifically, a fairly extensive region of charge loss to the right of N in Fig. 4 may be noted; the analogous density difference maps of the homodimers, previously published as Fig. 2 of paper 4, show similar contours about the right-hand N and O atoms.

The greater propensity of a proton-donating O atom to withdraw charge from the proton-accepting group is also verified by the density difference maps. Specifically, the dashed contours in the vicinity of the right-hand NH₂ group in Fig. 4, where H₂OH acts as proton donor, encompass noticeably smaller areas when the proton donor is H₂NH (Fig. 2a of paper 4). A further indication of the lesser charge-withdrawing capability of H₂NH than of H₂OH is the fact that the “3” contour immediately to the left of the right-hand N atom in Fig. 4 is absent in Fig. 2(a) of paper 4. Since lower numerical labels on the contours indicate greater density change, charge depletion from this region is more severe when H₂OH acts as proton donor than when does H₂NH. Similar conclusions may be reached by comparison of Fig. 2(b) of paper 4 with Fig. 3 which represent the OH⁻—O and NH⁻—N proton transfers, respectively.
An interesting feature of the density difference maps is the set of solid contours about the proton-accepting atom, indicating a region of charge gain amidst a general trend toward density loss in the remainder of the molecule. As described in detail in paper 6, these contours are a result of H-Y polarization within the YH₄ molecules. Thus, charge is transmitted from the H atoms of the proton-accepting YH₄ molecule to the other molecule via the intermediacy of the Y atom. As a consequence of this source of density, the net charge lost by the Y atom is rather small, as indicated in the second sequence of this source of density, the net charge lost by density gained from polarization of the OH bonds, resulting in zero net change on the O atom. The H atoms, which may be thought of as the principal source of charge transferred, suffer a much more severe loss of electron density, as may be noted from the third row of the table.

Analogous polarizations, but in the opposite direction, are noted in the proton-donating group on the left in Figs. 3 and 4. Most of the additional charge accumulated by this molecule makes its way to the H atoms. The density retained by the first-row X atom is found, in large part, in the region "behind" it, i.e., to its left. Some increase is noted as well to the right of the proton-donating oxygen atom in the "lone pair" region; there is no charge gain to the right of the nitrogen (Fig. 3). This feature is consistent with the higher electronegativity of oxygen and the fact that greater charge transfer is observed when O is the proton-donating atom.

The lone pair region of the proton-donating atom is affected by the nature of the accepting atom as well. A solid "4" contour is noted to the right of O in Fig. 4, whereas this contour is absent in Fig. 2b of paper 4, where the proton-accepting N atom has been replaced by O. Again, this feature may be explained by the lesser electron-releasing ability of O than of N. Similar observations pertain to the NH-O (Fig. 3) and NH-N (Fig. 2a of paper 4) transfers.

Population changes in the individual atomic orbitals of the homodimers have been discussed in paper 4. It was noted there that the oxygen and nitrogen atoms exhibit distinct patterns which are characteristic of each atom. The 2s and 2pₓ orbitals of O undergo changes of the same sign while opposite behavior is observed in the corresponding N orbitals. Changes noted in the 2pₓ and 2pᵧ orbitals of N, equivalent in the local Cₛ₈ symmetry of NH₄, are identical to one another and of opposite sign to that of the pₓ orbital. For O, the pₓ orbital located in the OH₂ molecular plane behaves similarly to the pₓ and pᵧ orbitals of N while the O pₓ orbital, prohibited by symmetry from interacting with the hydrogens of OH₂, suffers no net change in population.

The orbital population changes in the heterodimers are qualitatively quite similar to those of the homodimers but do show some interesting quantitative differences. For either proton-accepting atom, the changes of the pₓ-orbital populations are accentuated when the proton-donating atom is changed from N to O. For example, the pₓ orbital of N loses 105 me when a proton is transferred to it from another nitrogen (NH-N) while the pₓ and pᵧ orbitals each gain 44 me. When the proton is donated instead by oxygen (OH-N) the respective values are 125 and 51, increases of roughly 18%. These increases may be explained as follows. Oxygen, as a stronger electron attractor, pulls more density from the pₓ orbital of the proton-accepting atom. This orbital serves as a primary source of charge transfer. The other source of this charge is the set of hydrogen atoms of the proton-accepting molecule. As described above, charge originating on these H atoms is relayed to the other molecule via polarization of the YH bonds. The greater electronegativity of the proton-donating oxygen causes increased polarization of these YH bonds and consequently a larger charge increase in the pₓ (and pᵧ for N) orbitals of Y.

By freezing the central proton at various points during its transfer from one molecule to the other, it is possible to obtain "still snapshots" of the electronic redistributions occurring as the proton moves. Figures 3 and 4 have frozen the action at that point where the proton is midway between the NH₃ and OH₂ molecules. Figure 5 depicts the electronic rearrangements accompanying full transfer:

\[ \text{H}_2\text{NH} \rightarrow \text{O}_2 \rightarrow \text{H}_2\text{N} \rightarrow \text{H}_2\text{O}_2 \]

The central arrow extends from the equilibrium position of the central proton [r(NH) = 1.047 Å] to a location only 1.05 Å from the oxygen atom [r(NH) = 1.70 Å].

Comparison of Figs. 3 and 5 clearly indicates the manner in which the electrons redistribute themselves during the second half of the proton transfer from NH₃ to OH₂. The general trend is that density rearrangements beginning during the first half of the transfer (Fig. 3) continue as the transfer is completed (Fig. 5). For example, the region of charge gain behind the proton-donating atom, indicated by the solid "5" contours to the left of N in Fig. 3, has grown considerably and by the time the proton transfer has completed (Fig. 5) includes the hydrogens of NH₃ in its continuous range as well as extending to domains above the nitrogen in the xz plane. Similarly, the region of density depletion to the right of the oxygen extends over a greater area in Fig. 5. The "4" and "5" dashed contours surrounding the right-most hydrogen in Fig. 3 have enlarged and extend directly behind the oxygen and even into the xz plane after full proton transfer.

The charge loss in the lone pair region directly to the left of the proton-accepting oxygen, begun in Fig. 3, is notably nonisotropic in Fig. 5. Whereas during the first half of the proton transfer, density is lost nearly equally from the xz and yz planes, completion of the transfer draws much more "lone pair" charge from the xz plane; i.e., that plane not containing the hydrogens of OH₂.

Examination of the lone pair region to the right of the proton-donating nitrogen yields another interesting observation. The first half of the proton transfer did not result in any increase of density in this region. In fact, the dashed contours in Fig. 3 indicate a charge loss at
the beginning of the transfer. However, the second half of the transfer reverses this trend as indicated by the solid contours in Fig. 5. Thus, the density increase in the lone pair of the proton-donating nitrogen resulting from full proton transfer is smaller in magnitude than the charge loss in the proton-accepting oxygen lone pairs and also occurs much later in the transfer process.

Comparison of the Mulliken population changes for full and half proton transfer confirms the conclusions derived from the density difference maps. The trends noted in Table I for the first half of the transfer persist in the second half as well. The charge transfer from the proton-accepting molecule to the remainder of the complex continues as the proton moves from the X–Y midpoint towards the Y atom. Indeed, the order of charge transfer listed in Eq. (2) above is unaltered by completion of the charge loss, the Y and H atoms share more equally to each other biomolecules where the native conformation arises from a complex combination of a large number of molecular interactions. Accordingly, the NH3 and OH2 units of (H3NHOHa)⁺ were twisted from their optimal arrangements as described in Fig. 6. α1 and α2 represent the angles made with the N–O axis by the C1 rotation axis of NH3 and the C2 axis of OH2, respectively. The internal geometries of the NH3 and OH2 molecules were otherwise held fixed in the optimum structure described above. Positive values for both α1 and α2 indicate twists of the two groups in the same direction as depicted in Fig. 6. Twists in opposite directions are represented by opposite signs for α1 and α2. For a given configuration of the hydrogen bond, represented by the two angles α1 and α2, the proton transfer potential was computed by moving the central proton from left to right in small steps. For each horizontal displacement, defined as the projection of the H position on the N–O axis, the perpendicular vertical distance from this axis was optimized.

First to be considered were bent configurations of the hydrogen bond for which the R(NO) distance is fixed at its optimum value of 2.66 Å. As noted above, the transfer potential contains only a single minimum, corresponding to (NH3)⁺(OH2), for a linear H bond at this intermolecular separation. Relatively small bends of the hydrogen bond do not alter this single-well character of the potential. In fact, a second shallow well, corresponding to (NH3)(OH2)⁺, appears only for bends of greater than approximately 40°. For example, when NH3 and OH2 are both twisted in the same direction, the transition from single to double well occurs at α1 = α2 = 40°. Even when the two molecules are twisted in opposite

![Figure 5](image-url)  
**FIG. 5.** Electronic rearrangements accompanying full proton transfer from NH3 to OH2. Contours represent the difference in electron density ρ(NH3—OH2)−ρ(NH3NH−OH2). The arrow indicates the two positions of the central proton. R(NO) = 2.75 Å.

![Figure 6](image-url)  
**FIG. 6.** Angular distortions of the hydrogen bond in (H3NHOH₂)⁺. α₁ and α₂ are both positive here.

V. HYDROGEN-BOND DEFORMATIONS

Up until this point, we have been dealing exclusively with linear hydrogen bonds. That is, the N–O axis is coincident with both the local C2 rotation axis of NH3 and the C2 axis of OH2 (see Fig. 1). Moreover, the central proton has been located along this axis as well. Thus, the proton transfer potentials displayed in Fig. 1 include stretches of the H bond; i.e., R(NO)>2.66 Å, but not "bends" wherein θ(NHO)<180°. Such bent configurations are the rule rather than the exception in a large variety of chemical systems including proteins and other biomolecules where the native conformation arises from a complex combination of a large number of molecular interactions. Indeed, H bonds deviating by 10° to 15° from linearity occur as frequently as more linear bonds and bends of even 40° are not uncommon.

It is therefore crucial to consider the effects of angular hydrogen bond deformations upon the energetics and electronic structure involved in proton transfer.
directions; i.e., \( \alpha_1 = -\alpha_2 \) bends of nearly 40\(^\circ\) are needed before the potential acquires double-well character.

As may be seen in Fig. 1, for an intermolecular separation of \( R(\text{NO}) = 2.95 \text{ Å} \), the potential curve for proton transfer contains two minima for a linear hydrogen bond. Table II contains information about the enlargement of the barrier separating the two minima, \( E' \), resulting from angular distortions of the hydrogen bond with \( R \) held fixed at 2.95 Å. Besides the forward (NH \(-\) N) and reverse (OH \(-\) N) transfers in \((\text{H}_2\text{NHOH})^+\), barriers are included also for the \((\text{N}_2\text{H}_2)^+\) and \((\text{O}_2\text{H}_2)^+\) homodimers, \(35\) also with intermolecular distances of 2.95 Å. The barriers contained in Table II are illustrated pictorially in Fig. 7. For each system, three modes of bending are explicitly considered. The first, represented by the solid curves, involves a bend \( (\alpha_2) \) of the proton acceptor while the donator molecule is held in its optimal orientation \( (\alpha_1 = 0\)\(^\circ\)\). Both molecules are twisted by equal amounts in the same direction \( (\alpha_1 = \alpha_2) \) in the mode designated by the dashed curves. Dotted curves indicate twists of the two molecules in opposite directions \( (\alpha_1 = -\alpha_2) \).

A number of salient rules are clearly indicated in Fig. 7. First is the observation that the height of the barrier to proton transfer is rather sensitive to angular distortions of the hydrogen bond; greater deformations result in substantially higher barriers. Secondly, for any given system, twisting the two molecules in opposite directions produces the highest barrier. Rotations of the molecules in the same direction \( (\alpha_1 = \alpha_2) \) results in a somewhat lower barrier while an even smaller barrier arises from twisting only the proton acceptor \( (\alpha_1 = 0\)\(^\circ\)\).

Also, as noted above for linear H bonds, the highest barriers are generally associated with the NH \(-\) O transfer, followed in order by OH \(-\) O, NH \(-\) N, and OH \(-\) N. It should be emphasized, however, that the above sequence is only a general one and is dependent upon the particular configuration adopted by the complex. For example, while 

\[
\begin{align*}
\text{NH-} N & \\
\text{OH-} O & \\
\text{NH-} N & \\
\text{OH-} N & \\
\end{align*}
\]

Comparison of Figs. 2 and 7 provides evidence that the effects of the angular orientation of the hydrogen bond upon the energetics of proton transfer can be as important as the intermolecular distance. For example, the barrier to OH \(-\) N transfer across a linear H bond rises from 2.7 kcal/mol to 8.1 when the \( R(\text{ON}) \) distance increases from 2.95 Å to 3.1 Å. If, on the other hand, the intermolecular separation is held constant at 2.95 Å, and the two molecules both rotated by 40\(^\circ\) in the same direction, the barrier rises to the even greater value of 11.4 kcal/mol.

It is an important conclusion of this study that the energetics of proton transfer are quite sensitive to the geometry of the hydrogen bond, viz. angular and linear deformations, as well as to the nature of the chemical groups involved.

The total SCF energies of the various bent conformations of the heterodimer and homodimer systems are listed in Table III. These energies pertain to the initial geometry \((\text{H}_2\text{XH-}Y\text{H}_2)^+\) in which the central proton is more closely associated with the proton-donating X atom. It is clear from the table that angular distortions of each hydrogen bond lead to weaker interactions between the \((\text{H}_2\text{XH})^+\) and \((\text{YH}_2^-)\) units of the complex. In fact, the patterns followed by these H-bond weaken-

<table>
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<tr>
<th>(\alpha_1, \alpha_2)</th>
<th>(\text{NH-} O)</th>
<th>(\text{OH-} O)</th>
<th>(\text{NH-} N)</th>
<th>(\text{OH-} N)</th>
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</thead>
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<td>11.4</td>
<td>2.7</td>
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<tr>
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<td>12.9</td>
<td>3.3</td>
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<tr>
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<td>23.4</td>
<td>16.0</td>
<td>7.1</td>
</tr>
<tr>
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<td>19.9</td>
<td>14.0</td>
<td>4.3</td>
</tr>
<tr>
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<td>43.8</td>
<td>30.2</td>
<td>24.0</td>
<td>11.4</td>
</tr>
<tr>
<td>(20, -20)</td>
<td>33.5</td>
<td>20.5</td>
<td>15.1</td>
<td>4.6</td>
</tr>
<tr>
<td>(40, -40)</td>
<td>52.2</td>
<td>37.2</td>
<td>33.9</td>
<td>16.9</td>
</tr>
</tbody>
</table>

| In kcal/mol. |
| In degrees. |
TABLE III. Total energies of \((H\_XH-\_YH\_m)^+\) complexes for \(R(XY)=2.95\ \text{Å}\).

<table>
<thead>
<tr>
<th>((\theta_1, \theta_2))</th>
<th>NH - O</th>
<th>OH - O</th>
<th>NH - N</th>
<th>OH - N</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0, 0)</td>
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<td>-152.1573</td>
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<tr>
<td>(0, 20)</td>
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<tr>
<td>(0, 40)</td>
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<td>-132.3494</td>
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<tr>
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<tr>
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<td>(4, -40)</td>
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<td>-152.1305</td>
<td>-112.5845</td>
<td>-132.3313</td>
</tr>
</tbody>
</table>

*aAll entries in hartrees.  
*bDegrees.

ings are similar to the increases of proton transfer barriers described in Table II.

The proton transfers between the NH\(_3\) and OH\(_2\) molecules may be considered as a shift of the proton from the lone electron pair of one first-row atom to that of the second. Consequently, it is not unreasonable to expect some fundamental relationship to exist between the energetics of proton transfer and various properties of the N or O lone pairs. Such a relationship has in fact been identified here and is illustrated in Fig. 8 which depicts the dependence of the energy barrier to proton transfer \(E_t\), upon the calculated orbital energy or eigenvalue \(\epsilon\) of the lone pairs of the proton-accepting atoms. Specifically, these orbital energies are extracted from the \(H\_XH-\_YH\_m\) structure, prior to proton transfer, in which the central hydrogen is much more closely associated with the proton-donating atom X. The orbitals whose energies are presented in Fig. 8 correspond to the lone pair or pairs of the proton-accepting atom Y. For example, when Y = N, the highest occupied molecular orbital (HOMO) of the \((H\_XH-\_NH\_3)^+\) system is a 2p*-like orbital, oriented along the local C\(_3\) rotation axis of NH\(_3\), with greater amplitude in the direction of the central proton. This "N HOMO", with eigenvalues ranging between -0.64 and -0.59 a.u. is designated the "lone pair" of N and is represented by the right-most curve in Fig. 8. The two lone pairs of the proton-accepting oxygen in \((H\_XH-\_OH\_2)^+\) correspond to the two highest occupied MOs of the cationic complex. The second highest (HOMO - 1) is quite similar to the N HOMO while the HOMO is composed exclusively of the 2p\(_x\) or \(\pi\) atomic orbital of oxygen.

The curves in Fig. 8 indicate a very nearly quadratic dependence of the proton transfer barrier upon the energy of the lone pair orbitals of the proton-accepting Y atom in the initial \((H\_XH-\_YH\_m)^+\) geometry. The curves were obtained by fitting the data to a second order polynomial via least squares analysis. In all cases the fit is quite good with a standard error of 3 kcal/mol or better for estimating \(E_t\) from \(\epsilon\).

This good correlation is notable for a number of reasons. First, each curve includes a wide range of H-bond geometries, with \(R(XY)\) distances varying between 2.55 Å and 3.15 Å, and angular deformations of up to 40° considered as well. Perhaps even more striking is the fact that, for each curve, two different proton-donating molecules are involved. For example, the N HOMO curve includes both NH-N and OH-N transfers. These observations point out the generality of the interdependence of transfer barriers and the orbital energies of the proton-acceptor lone pairs. This finding is of some fundamental importance and, in addition, may have great implications for predictions of transfer barrier energetics. Calculation of the latter quantity normally requires a number of time-consuming geometry optimizations, but use of the relationships in Fig. 8 may allow extraction of the barrier from a single point on the potential surface.

The general shapes of the curves in Fig. 8 are not

![Fig. 8. Relationship between proton transfer barriers and the eigenvalues of the lone pairs of the proton-accepting atoms.](https://jcp.aip.org/about/rights_and_permissions)
unreasonable. Since the proton-acceptor lone pairs are stabilized by interaction with the positively charged proton-donating molecule, distortions of the H bond such as stretches and bends may be expected to increase the eigenvalues of these MOs. Similarly, such distortions militate against a facile proton transfer, thus raising also the transfer barrier $E'$. The quadratic dependence of $E'$ upon $\epsilon$ indicates an increasing sensitivity of the energetics of proton transfer upon small changes in $\epsilon$ as the destabilization of the lone pairs progress further.

VI. CONCLUSIONS

Systematic comparison of proton transfers in ionic dimers involving NH$_3$ and OH$_2$ molecules presents us with a good deal of information about the fundamental nature of the process. The energetics are seen to be quite sensitive to the geometry of the hydrogen bond; stretches and angular distortions lead to substantial increases in the height of the energy barrier to transfer. The functional dependence of the barrier upon the geometry is rather consistent from one system to the next. For similar geometrical arrangements, proton transfer from N to O is associated with the highest energy barrier while the reverse transfer from oxygen to nitrogen is the most facile. Intermediate between these two extremes are the symmetric transfers between identical molecules with OH-O corresponding to somewhat greater barriers than NH-N.

The relative order of ease of proton transfer may be simply explained on the basis of electronegativities of the N and O atoms. This description is further supported by examination of the electronic rearrangements that accompany the proton transfer process. The transfer of a proton appears to be facilitated by a net shift of electron density in the reverse direction from proton-acceptor to donor. The nitrogen atom is capable of releasing more density than is oxygen and hence serves as a more efficient proton-acceptor atom. Analogously, OH$_2$ is superior to NH$_3$ as a proton donor since the more electronegative oxygen may better attract electron density away from the other molecule.

Density shifts in various regions of space at chosen stages of proton transfer may be monitored by electron density difference maps. The lone pairs of the proton-accepting atom suffer a loss of density as the proton is transferred; the donor lone pairs generally accumulate additional charge. While the latter density increase occurs uniformly throughout the proton transfer for oxygen, the first half of the transfer from nitrogen is characterized by a density loss. It is only during the second half of the transfer that the trend is reversed and the N lone pair picks up additional charge. Along the same line, during the first half of the transfer, the primary source of charge being transferred from the proton-accepting to donating group is the set of H atoms of YH$_4$. The first-row Y atom shares more equally in the density loss during the second half.

The lone pairs of the proton-accepting atoms appear to play a dominant role in the transfer process as indicated by the strong correlation between the energies of these orbitals and the barriers to proton transfer. The stabilization of these orbitals via interaction with the proton-donating species leads to a marked enhancement of the ease of proton transfer.

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