also to any system in which the two nitrogen nuclei are held stationary via some external constraint as might occur if the nitrogens were part of a macromolecular structure.) The barriers obtained by each quantum mechanical technique via the latter mechanism are denoted $E_a^\dagger$ in Table IV. These barriers were obtained by estimating the functional value of each curve in Figure 2 at the corresponding distance R_0 in Table IV. For example, on the basis of the RHF/DZP curve in Figure 2, the barrier expected for $R_0 = 2.84$ Å is 9.6 kcal/mol. The smaller 4-31G basis set predicts a much lower barrier of only 3.8 kcal/mol. The large difference between DZP and 4-31G RHF barriers arises from two factors. The 4-31G basis set yields smaller barriers than does DZP at any given value of R and, in addition, predicts a smaller value of R_0. A similar combination of effects also results in a POL-CI barrier much smaller than the RHF/DZP value. Interestingly, the RHF/4-31G barrier is quite similar to the POL-CI/DZP result. This near agreement is a result of the smaller 4-31G value of R_0 coupled with its inherently larger barriers when compared with POL-CI. The GVB barrier is substantially larger than any other, being nearly 5 times greater than the POL-CI barrier.

A second mechanism whereby the proton might be transferred allows relaxation of the R(NN) distance at each stage of transfer. Optimization of R(NN) for the midpoint structure (top of the barrier) yields R_b (see Table IV). The difference in energy between this geometry and the optimized end point structure with $R = R_0$ yields the barrier denoted as $E_b^\dagger$ in Table IV. These barriers are substantially lower than $E_a^\dagger$ obtained by the first mechanism involving fixed values of R(NN). For example, the POL-CI barrier of 3.5 kcal/mol obtained for fixed $R_0 = 2.80$ Å is lowered to 1.5 kcal/mol by allowing the two nitrogens to move closer together by 0.12 Å in the midpoint geometry. As was found for the previous mechanism, the Hartree-Fock procedures overestimate the barrier height with 4-31G predicting a value closer to POL-CI than does the DZP basis set. Previous calculations[25,26] which did not include correlation contributions have also resulted in barriers to proton transfer appreciably higher than the value of 1.5 kcal/mol calculated here with the use of POL-CI. Delpuech et al.[26] obtained a barrier of 2.5 kcal/mol using a basis set of essentially DZP quality whereas a smaller basis excluding polarization functions led to a value of 1.9 kcal/mol.[25] These results fit the general conclusion that at the Hartree-Fock level, increasing the size of the basis set leads to higher barriers whereas inclusion of correlation effects produces a substantial lowering.

There is no currently available experimental information concerning the barrier to proton transfer in $(N_2H_7)^+$ in the gas phase although NMR work[37] indicates the barrier is quite small in aqueous solution. This observation appears to be in good agreement with the theoretical results reported here. The difference between the equilibrium and barrier energies was found by POL-CI to be only 1.5 kcal/mol. Consideration of the ground vibrational energy may be expected to lead to a barrier to proton transfer somewhat less than the latter value.

As a final point it should be noted that although the POL-CI method has not been applied previously to proton-transfer reactions, results achieved for other reactions have been quite good. For example, the activation barrier calculated for the abstraction of an H atom from CH_4 by $O(^3P)$ was within the range of experimental values.[33b]

Conclusions

All the methods investigated, which include different basis set sizes and inclusion of varying amounts of correlation effects, predict the same qualitative increase in barrier height with larger intermolecular separations. The magnitudes of these barriers, however, differ significantly from method to method. At the Hartree-Fock level, the smaller 4-31G basis set yields smaller barriers than does DZP. Inclusion of configuration interaction with POL-CI greatly decreases the barriers while intrapair correlations alone (GVB) produce a slight increase. Extensive configuration interaction would thus appear to be necessary in order to obtain reliable values for the height of the barrier at each distance.

Similar trends were noted also for proton-transfer energetics at the optimized intermolecular distances and for hydrogen-bond energies in that decrease of basis set size at the Hartree-Fock level and inclusion of configuration interaction produce similar effects, opposite to those predicted by GVB. The results indicate that intrapair correlations in the nitrogen lone pairs, although of considerable magnitude, follow opposite trends, as a function of molecular geometry, to more complete treatments of electron correlation which are necessary for accurate calculation of transfer energetics.

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Gas-Phase Proton Affinities for H_2O, C_2H_4, and C_2H_6

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Abstract: Rate and equilibrium constant measurements are reported which provide proton affinities for H_2O, C_2H_4, and C_2H_6 and heats of formation for the corresponding protonated species at 298 K, on the basis of the well-established proton affinity of CO. The values recommended for the proton affinities are 165.3 ± 1.8, 163.0 ± 1.7, and 142.1 ± 1.2 kcal mol^{-1} for H_2O, C_2H_4, and C_2H_6, respectively. The proton affinity obtained for H_2O is lower than accepted values. The results obtained for C_2H_4 agree almost exactly with those obtained in a very recent photoionization (PIPECO) study by Baer. The measurements with C_2H_6 provide a new accurate determination of its proton affinity.

Recent photoionization studies of the formation of $C_2H_5^+$ and $C_3H_7^+$ from C_2H_5I and C_3H_7I, respectively, have provided important new heats of formation for these ions.[1] A significant discrepancy with previously accepted values was evident for the

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Table I. Proton Affinities and Standard Heats of Formation (in kcal mol^{-1}) at 298 ± 2 K

X	PA(X)	$\Delta H_f{}^\circ{}_{298}(XH^+)^a$	ref value
CO	141.4 ± 0.4^b	199.4 ± 0.4	
C_2H_6	142.1 ± 1.2	204.8 ± 1.3	220 ± 1^c
C_2H_4	163.0 ± 1.7	216.6 ± 1.7	$216.8 \pm 1.0,^d$ $220.5,^e$ 220.7 ± 1.0^f
H_2O	164.4 ± 2.9	145.0 ± 2.9	$138.9 \pm 3,^g$ $140.1,^h$ $139.1,^i$ 143.0 ± 2.4^j

[a] The heats of formation of X and $\Delta H_f{}^\circ{}_{298}(H^+) = 367.186$ kcal mol^{-1} were taken from the JANAF tables.[7] The electron is treated as a conventional element. [b] Reference value, ref 8. [c] Reference 9. [d] Reference 1. [e] Reference 10. [f] Reference 11. [g] Reference 7. [h] Reference 4. [i] Reference 12. [j] Reference 13.

heat of formation of $C_2H_5^+$ and thus the proton affinity (PA) of C_2H_4.[2] We report here results of equilibrium measurements which support the new heat of formation of $C_2H_5^+$. Previous equilibrium measurements[3] for the dissociation of $C_2H_7^+$

$$C_2H_7^+ = C_2H_5^+ + H_2 \qquad (1)$$

are combined with equilibrium measurements for the proton-transfer reaction

$$HCO^+ + C_2H_6 = C_2H_7^+ + CO \qquad (2)$$

to derive a value for $PA(C_2H_4)$ from the well-established value for PA(CO). The latter equilibrium measurements also provide accurate values for $PA(C_2H_6)$ and $\Delta H_f{}^\circ(C_2H_7^+)$ which have not been well established in the past. Furthermore, the high proton affinity of C_2H_4 allowed access to $PA(H_2O)$ through a determination of the equilibrium constant for the reaction

$$C_2H_5^+ + H_2O = H_3O^+ + C_2H_4 \qquad (3)$$

This has long been a goal in proton affinity studies, since it bridges the gap between molecules of relatively high and low proton affinities and permits reference to be made to an absolute proton affinity, e.g., PA(CO), which is much more certain than those employed previously, e.g., $PA(i\text{-}C_4H_8)$.[4]

Experimental Section

The experiments were carried out using both the flowing afterglow (FA) and the selected ion flow tube (SIFT) techniques for which details of construction, methods of operation, data analyses, and sources of error have been described elsewhere.[5,6] All measurements were carried out at room temperature, 298 ± 2 K.

Results and Discussion

The thermodynamic information derived from the rate and equilibrium constant measurements are summarized in Table I. Flowing afterglow measurements for reaction 2 proceeding at room temperature in hydrogen buffer provided an equilibrium constant of 11.2 ± 2.1 which corresponds to a standard free-energy change of −1.43 ± 0.11 kcal mol^{-1}.[14] The standard entropy change is estimated[15] to be +2.3 ± 2.2 cal mol^{-1} K^{-1} so that the standard enthalpy change becomes −0.74 ± 0.77 kcal mol^{-1}. The latter is a measure of the difference in the proton affinities of CO and C_2H_6. On the basis of a systematic equilibrium study involving molecules having low proton affinities reported elsewhere,[8] we were able to recommend an accurate absolute value of 141.4 ± 0.4 kcal mol^{-1} for the proton affinity of CO based on the appearance potential of HCO^+ from H_2CO reported by Guyon et al.[17] With PA(CO) = 141.4 ± 0.4 kcal mol^{-1}, $PA(C_2H_6)$ becomes 142.1 ± 1.2 kcal mol^{-1}. This result is consistent with the limiting values $136 < PA(C_2H_6) < 159$ kcal mol^{-1} which we obtained from bracketing measurements[18] but exceeds the value obtained previously from mass spectrometer ion-source measurements[9] of the equilibrium constant for the protonation of C_2H_6 by CH_5^+. Accepted heats of formation for ethane[16] and the proton[7] led to a heat of formation for $C_2H_7^+$ of 204.8 ± 1.3 kcal mol^{-1}.

The previous equilibrium measurements carried out for reaction 1 with a high-pressure ion-source mass spectrometer by Hiraoka and Kebarle[3] have provided a standard enthalpy change of 11.8 ± 0.4 kcal mol^{-1}. $PA(C_2H_4)$ is related to this enthalpy change and $PA(C_2H_6)$ by the equation

$$PA(C_2H_4) = PA(C_2H_6) + \Delta H_f{}^\circ(C_2H_4) - \Delta H_f{}^\circ(C_2H_6) - \Delta H_1{}^\circ \qquad (4)$$

The accepted values for the heats of formation of ethylene and ethane[16] lead to a value for $PA(C_2H_4) = 163.0 \pm 1.7$ kcal mol^{-1}. Also the heat of formation for $C_2H_7^+$ determined above leads to a heat of formation for $C_2H_5^+$ of 216.6 ± 1.7 kcal mol^{-1}. Most of the previous values for the heat of formation of $C_2H_5^+$ are somewhat higher (see Table I). They have been based almost exclusively on nonequilibrium studies of the appearance of this ion by dissociative ionization and the ionization of the ethyl radical. Baer[1] has drawn attention to the shortcomings of these two methods in his report of a photoionization and photoion–photoelectron coincidence (PIPECO) study of the appearance of $C_2H_5^+$ from C_2H_5I. His improvements in technique have led to a room-temperature heat of formation for $C_2H_5^+$ of 216.8 ± 1.0 kcal mol^{-1} which is in excellent agreement with the value obtained from our equilibrium studies.[19]

The high proton affinity of C_2H_4 could be coupled to that of H_2O via reaction 3. This was accomplished with separate studies of the forward and reverse reactions to provide the individual rate constants. Secondary reactions, particularly the fast reaction of $C_2H_5^+$ with C_2H_4, prevented the measurement of the equilibrium constant of reaction 3 in our usual manner from equilibrium concentrations established in the flowing afterglow.

The forward direction of reaction 3 was investigated with the conventional flowing afterglow with additions of C_2H_4 sufficiently small to prevent significant back reaction, as well as in the complete absence of C_2H_4. In the former case C_2H_4 acted as the parent neutral of $C_2H_5^+$ which was formed by the protonation reaction

$$H_3^+ + C_2H_4 \rightarrow C_2H_5^+ + H_2 \qquad (5)$$

In the latter case the $C_2H_5^+$ ion was derived from C_2H_6 by the dissociative proton-transfer reaction:[14]

$$H_3^+ + C_2H_6 \rightarrow C_2H_5^+ + 2H_2 \qquad (6)$$

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(15) The standard entropy of $C_2H_7^+$ was estimated to be 58 ± 2 cal mol^{-1} K^{-1} at 298 K from a comparison with the entropies of the isoelectronic species CH_3NH_2 and CH_3OH and ethane itself given in ref 16. $S^\circ{}_{298}(HCO^+)$ has been calculated by Bruna: Bruna, P. J. *Astrophys. Lett.* **1975**, *16*, 107.

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(19) We treat the electron as a conventional element as in ref 7. Account has been taken of the stationary electron convention adopted by Baer who reported a value for $\Delta H_f{}^\circ{}_{298}(C_2H_5^+)$ of 215.3 ± 1.0 kcal mol^{-1}.

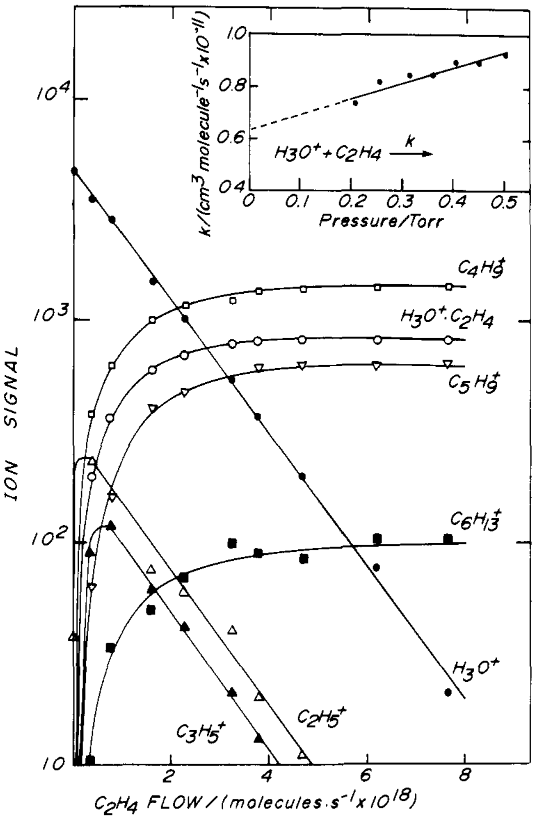

Figure 1. Variation in ion signals recorded with the addition of ethylene into the reaction region of a flowing afterglow in the SIFT configuration with H_3O^+ as the selected ion. Buffer gas = H_2, $P = 0.255$ torr, $T = 296$ K, $\bar{v} = 7.3 \times 10^3$ cm s^{-1}, and $L = 45$ cm. The insert shows the observed variation of the apparent two-body rate constant with total pressure in the reaction region.

The measured rate constant was found to be independent of the source of $C_2H_5^+$ within the precision of the measurements and to have a value of (1.4 ± 0.4) × 10^{-9} cm^3 molecule^{-1} s^{-1}.

The reverse direction of reaction 3 was investigated with the apparatus in the SIFT configuration[6] with hydrogen as the buffer gas. Results are shown in Figure 1. It was interesting to observe that the proton-transfer channel competed with three-body association in this case:

$$H_3O^+ + C_2H_4 \rightarrow C_2H_5^+ + H_2O \tag{7a}$$

$$H_3O^+ + C_2H_4 \xrightarrow{H_2} H_3O^+{\cdot}C_2H_4 \tag{7b}$$

Experimentally this was manifested, in part, by a pressure dependence in the rate constant for the total loss of H_3O^+ as is indicated in the insert in figure 1. Extrapolation of the observed pressure dependence to zero pressure provided a value for k_{7a} = (6.3 ± 1.6) × 10^{-11} cm^3 molecule^{-1} s^{-1}. This result is consistent with the branching ratio for the two product channels which is obtained when the observed $C_4H_9^+$, $C_5H_9^+$, and $C_6H_{13}^+$ ions are taken to be the "signature ions" for $C_2H_5^+$ and account is taken of mass discrimination. $C_2H_5^+$ is known[20,21] to react rapidly with C_2H_4 in the following manner:

$$C_2H_5^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_4 \tag{8a}$$

$$C_2H_5^+ + C_2H_4 \xrightarrow{M} C_4H_9^+ \tag{8b}$$

with the subsequent addition of ethylene

$$C_3H_5^+ + C_2H_4 \xrightarrow{M} C_5H_9^+ \tag{9}$$

$$C_4H_9^+ + C_2H_4 \xrightarrow{M} C_6H_{13}^+ \tag{10}$$

where the third body M is H_2 in our experiments.

The two individual rate constants determined in this study provide a value for $K_3 = k_3/k_{7a} = 22 \pm 7$. This result implies a standard free-energy change of −1.8 ± 0.2 kcal mol^{-1} and leads to a standard enthalpy change of only −1.4 ± 1.2 kcal mol^{-1} with an estimated standard entropy change of +2.3 ± 4.5 cal mol^{-1} K^{-1}.[22] With PA(C_2H_4) = 163.0 ± 1.7 kcal mol^{-1}, PA(H_2O) then becomes 164.4 ± 2.9 kcal mol^{-1}. This value agrees within experimental uncertainty with our earlier determination of PA(H_2O) = 166.4 ± 2.4 kcal mol^{-1} which was referenced to PA(CH_2O).[13] It is somewhat lower than the value of 167.3 ± 1.8 kcal mol^{-1} (corrected to 298 K) derived from the measured photoionization appearance potential of H_3O^+ from the water dimer[23] and significantly lower than the currently accepted value of 170 kcal mol^{-1}.[4,7,12] The heat of formation of H_3O^+ becomes 145.0 ± 2.9 kcal mol^{-1} and is higher than accepted values as shown in the summary given in Table I. On the basis of the results reported here and our earlier determination,[13] we recommend the weighted mean values of 165.3 ± 1.8 and 144.1 ± 1.8 kcal mol^{-1} for PA(H_2O) and $\Delta H_f{}^\circ{}_{298}(H_3O^+)$, respectively.

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