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Isomeric Forms of the Products of the Collisional Associations of CH_3^+ with CH_3OH and H_3O^+ with C_2H_4

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A selected ion flow tube has been used to study the reactions of $C_2H_7O^+$ generated by the collisional associations of CH_3^+ with CH_3OH and H_3O^+ with C_2H_4. Reactions with C_2H_5OCHO, $(CH_3)_2CHOH$, CH_3CO_2H, $CH_3C_6H_5$, CH_3CHO, H_2CCCH_2 (allene), CH_3OH, *c*-C_3H_6, H_2O, and C_2H_6 were studied to give information on the isomeric forms of the $C_2H_7O^+$ ions. The data were compared with previous data on the reactivity of other isomeric forms, $(CH_3)_2OH^+$ and $C_2H_5OH_2^+$, with the same reactant neutrals. The rate coefficient data show a very strong correlation between the reactivities of $(CH_3)_2OH^+$ and the associated ion CH_3^+/CH_3OH and between $C_2H_5OH_2^+$ and H_3O^+/C_2H_4, indicating that the associated ions are similar in form to these strongly bonded species. This is consistent with conclusions based on potential energy surfaces calculated in the accompanying paper. The agreement between the product ion distributions is not so conclusive. Generally, where proton transfer is exothermic for the strongly bonded species, it occurs rapidly for the associated ions. Where this proton transfer is very endothermic, association occurs for the associated ions as it does for the strongly bonded species. In intermediate cases, the associated ions show some additional products that are either endothermic for the strongly bonded species in their ground vibrational state or that can be construed as ligand switching, indicating that the associated ions have access to the weak ligand bonded form. The conclusion is that the associated ions are higher energy forms of protonated $(CH_3)_2O$ and C_2H_5OH with access to the weak ligand bonded form. The data imply that the reactions of the two types of isomers are controlled by an early barrier giving a set of rate coefficients that are independent of whether the isomer is the strongly bonded form or produced in the association reaction, but that the products are more controlled by the energy in the isomer and by the dominant structural conformation of that isomer.

Introduction

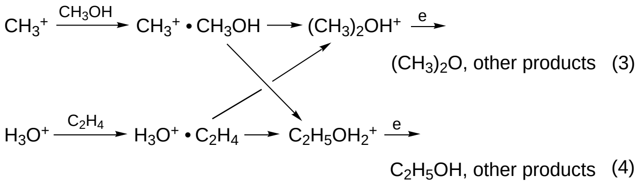
As ions become more complex, there is an increasing possibility of isomeric forms having varying stabilities.[1] The potential surfaces connecting these forms have been calculated for several cases (see, for example, ref 2). A particularly interesting and important case is $C_2H_7O^+$, the potential surface of which has been estimated by Jarrold et al.,[3] partially calculated by Herbst,[4] by Radom,[2] and by Audier et al.,[5] and more recently calculated by Fairley et al.[6] in the accompanying paper. Experimentally, this surface can be probed by producing the $C_2H_7O^+$ complex from different reactants and studying the further reactivity of the complex to obtain information concerning its structure. In a previous study,[7] we generated the $C_2H_7O^+$ isomers, $C_2H_5OH_2^+$ and $(CH_3)_2OH^+$, in high-pressure discharges in C_2H_5OH and $(CH_3)_2O$ via the reactions

$$C_2H_5OH^+ + C_2H_5OH \rightarrow C_2H_5OH_2^+ + C_2H_5O \qquad (1)$$

$$(CH_3)_2O^+ + (CH_3)_2O \rightarrow (CH_3)_2OH^+ + CH_3OCH_2 \qquad (2)$$

and studied their reactivity with C_2H_5OCHO, $(CH_3)_2CHOH$, CH_3CO_2H, $CH_3C_6H_5$, CH_3CHO, H_2CCCH_2 (allene), CH_3OH, *c*-C_3H_6, H_2O, and C_2H_6 (listed in order of decreasing proton affinity). Here, we have approached the $C_2H_7O^+$ surface via the collisional associations of CH_3^+ with CH_3OH and H_3O^+ with C_2H_4 and probed the reactivity of the associated ions (designated CH_3^+/CH_3OH and H_3O^+/C_2H_4), again with the above series of neutrals. Such studies provide information on the isomeric forms and on the isomerization between those forms. Complementary to this, Fairley et al.[6] probed the structural forms H_3O^+/C_2H_4, $C_2H_5OH_2^+$, and $(CH_3)_2OH^+$ by their reactivity with C_7H_7F and CH_2CHCN.

These CH_3^+ and H_3O^+ association reactions are of additional importance since they are implicated in the production of the C_2H_5OH and $(CH_3)_2O$ observed in interstellar clouds.[8] These interstellar species are believed to be produced via the reaction sequences



of radiative association (stabilized by photon emission) followed by dissociative ion recombination with electrons.[4,9,10] Note that the dissociative recombinations may generate other products in addition to those shown. Little information is available on the products of recombination;[11,12] however, recently a complete product distribution has been obtained for the relatively simple ion, H_3O^+, in which the ejection of an H-atom and the production of H_2O only occurs in a small fraction (∼5%) of the recombinations, and in ∼60% of the cases two atoms and a diatomic are produced.[13]

In a previous study,[3] Jarrold et al. produced $C_2H_7O^+$ which "almost certainly arises from an association between H_3O^+ and C_2H_4" and what they "believe to be $C_2H_7O^+$ generated by an association reaction between CH_3^+ and CH_3OH", using collision-induced dissociation (CID) to show that the dissociation spectra were appropriate to $C_2H_5OH_2^+$ and predominantly $(CH_3)_2OH^+$ respectively. The present observations, together

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with our previous studies of $C_2H_5OH_2^+$ and $(CH_3)_2OH^+$ reactions, test these suggestions and provide data on the reactivity of all of these isomeric species.

Experimental Section

These studies were conducted in a selected ion flow tube (SIFT) similar to that described previously,[14,15] and thus the present instrument will only be described briefly, emphasizing the features unique to this study. CH_3^+ ions were produced in a low-pressure ion source containing CH_4 and the H_3O^+ in a microwave discharge ion source containing about 0.2 Torr of H_2O. The ions were then mass selected by a quadrupole mass filter and focused with an electrostatic lens though a 1 mm orifice into the flow tube. The ions were constrained to flow in He carrier gas at a pressure of 0.5 Torr to a downstream quadrupole mass spectrometer sampling system. To produce the associated ionic forms of $C_2H_7O^+$, CH_3OH and C_2H_4 were added to the CH_3^+ and H_3O^+ ion swarms respectively, causing the collisionally stabilized association reactions, 5a and 6a

$$CH_3^+ + CH_3OH \xrightarrow{He} C_2H_7O^+ + He \tag{5a}$$

$$\rightarrow CH_3O^+ + CH_4 \tag{5b}$$

$$H_3O^+ + C_2H_4 \xrightarrow{He} C_2H_7O^+ + He \tag{6a}$$

$$\rightarrow C_2H_5^+ + H_2O \tag{6b}$$

to occur. Other gases and vapors were then added further downstream to probe the reactivity of the $C_2H_7O^+$. These were added through upstream-facing ring ports,[15] and the rate coefficients and product ion distributions were determined in the usual way.[16,17] Reactant vapors were obtained directly from liquids that had undergone several freeze, pump, thaw cycles, and all measurements were made at 300 K.

The decays of the injected ion signals with CH_3OH and C_2H_4 flows are shown in Figure 1a,b. It can be seen that there is excellent linearity in the ion decays and these yield rate coefficients of 2.6(−9) and 7.8(−11) cm^3 s^{-1} for CH_3^+ and H_3O^+ respectively, consistent with previous determinations (2.9(−9) for CH_3^+ [18] and 9(−11) cm^3 s^{-1} for H_3O^+ in an H_2 carrier gas at 0.5 Torr[19]). The product ion distribution for the CH_3^+ reaction is $C_2H_7O^+$ 10% and CH_3O^+ 90% (consistent with the previously determined distribution, $C_2H_7O^+$ ~22%; CH_3O^+ ~78% at 0.5 Torr[18]), and that for the H_3O^+ reaction is $C_2H_7O^+$ 35% and $C_2H_5^+$ 65% (previously $C_2H_7O^+$ 40% and $C_2H_5^+$ 60%, again in a H_2 carrier gas[19]). Note that some of the primary reaction products react further giving $CH_3OH_2^+$, $C_2H_9O_2^+$, and $C_3H_{11}O_2^+$ for the CH_3^+ reaction and $C_3H_5^+$, $C_4H_9^+$, and $C_5H_9^+$ for the H_3O^+ reaction. In order to best study the further reactions of the $C_2H_7O^+$ ions, CH_3OH and C_2H_4 flows were chosen, for the reaction distance to the reactant gas addition port, at which the $C_2H_7O^+$ is maximized, while minimizing complications due to the presence of the other ions in the flow tube. The presence of these other ions and CH_3OH or C_2H_4 did not of course influence the determination of the rate coefficients for the $C_2H_7O^+$ reactions but did complicate the determination of the product ion distributions. To obtain the best conditions, a relatively small flow of CH_3OH was used to minimize secondary products, such that the extent of reaction at the reactant gas inlet port was approximately as shown by the vertical dashed line in Figure 1a. To optimize the situation for the H_3O^+ reaction, a much larger C_2H_4 flow was used (see the dashed line in Figure 1b) at which H_3O^+ was destroyed and the primary products, other than $C_2H_7O^+$, were converted to secondary products.

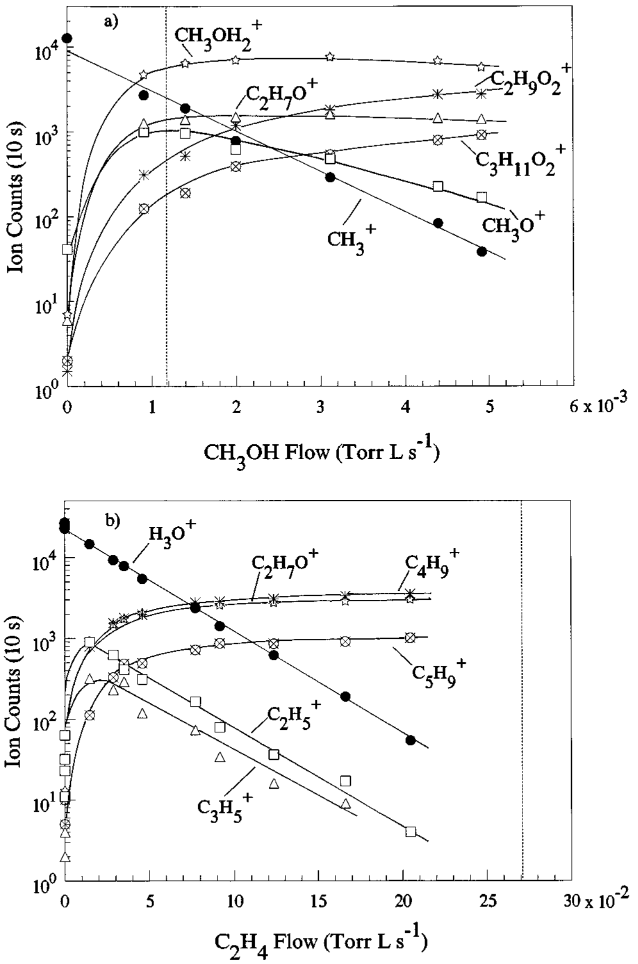

Figure 1. Data illustrating the formation of the $C_2H_7O^+$ isomers by the association of (a) CH_3^+ with CH_3OH and (b) H_3O^+ with C_2H_4. Note the linearity of the reactant ion decays over 2 orders of magnitude. In (a) $C_2H_7O^+$ and CH_3O^+ are primary products with the latter ion reacting rapidly to give $CH_3OH_2^+$ as the major ion in the spectrum. $C_2H_9O_2^+$ and $C_3H_{11}O_2^+$ (perhaps $CH_3OH_2^+ \cdot CH_3OH$ and $C_2H_7O^+ \cdot CH_3OH$ respectively) result from further reactions of these ions. (b) $C_2H_7O^+$ and $C_2H_5^+$ are primary products with $C_3H_5^+$, $C_4H_9^+$, and $C_5H_9^+$ being secondary. The data were obtained with a reaction length of 70 cm. The vertical dashed lines represent the ion composition of the flowing ion swarm at the port (a reaction length of 30 cm) where reactant gases were added for studies of the further reactivity of $C_2H_7O^+$ (for the flows of CH_3OH and C_2H_4 used in these studies). These data are uncorrected for mass discrimination.

The rate coefficients and product ion distributions for the reactions of the associated ions CH_3^+/CH_3OH and H_3O^+/C_2H_4 are given in Table 1. Where there is an association product, the equivalent binary rate coefficient at 0.5 Torr has been given for direct comparison with the other product channels. Since many of the association channels are very efficient, it is likely that the association is pressure saturated,[20] and thus only a lower limit to the ternary rate coeffficient could be obtained. For situations where this is the only channel, studies as a function of pressure would provide information on the degree of saturation. Where there are also binary channels or where association is slow, pressure studies could provide information on the competition between the product channels and a better value for the ternary association rate coefficient respectively. Such studies planned for the most appropriate reactions.

Also included in Table 1 for comparison are the rate coefficients and product ion distributions for the reactions of protonated C_2H_5OH and $(CH_3)_2O$ (obtained previously[7]) with

TABLE 1: Rate Coefficients ($cm^3\ s^{-1}$) and Product Ion Distributions (%) for the Reactions of the Isomeric Forms of $C_2H_7O^+$ with the Reactant Neutrals Indicated[a]

reactant neutral	proton affinity (kcal mol^{-1})	CH_3^+/CH_3OH	$(CH_3)_2OH^+$ 192.1	H_3O^+/C_2H_4	$C_2H_5OH_2^+$ 188.3	transition state theory
C_2H_5OCHO	193.1	1.9(−9) $C_2H_7O^+\cdot C_2H_5OCHO$ 100%	2.2(−9) $C_2H_7O^+\cdot C_2H_5OCHO$ 75% $C_2H_5OCHOH^+$ ≤25%	2.3(−9) $C_2H_7O^+\cdot C_2H_5OCHO$ 10% $C_2H_5OCHOH^+$ 90%	2.6(−9) $C_2H_5OCHOH^+$ 100%	2.16(−9)
$(CH_3)_2CHOH$	191.2	1.5(−9) $C_2H_7O^+\cdot(CH_3)_2CHOH$ 70% $CH_3^+\cdot(CH_3)_2CHOH$ 30%	2.1(−9) $C_2H_7O^+\cdot(CH_3)_2CHOH$ 100%	1.8(−9) $C_2H_7O^+\cdot(CH_3)_2CHOH$ 35% $(CH_3)_2CHOH_2^+$ 55% $(CH_3)_2CHO^+$ 10%	2.1(−9) $(CH_3)_2CHOH_2^+$ 75% $(CH_3)_2CHOH_2^+\cdot C_2H_4$ 25%	2.24(−9)
CH_3CO_2H	190.2	1.8(−9) $C_2H_7O^+\cdot CH_3CO_2H$ 60% $CH_3^+\cdot CH_3CO_2H$ 40%	1.2(−9) $C_2H_7O^+\cdot CH_3CO_2H$ 100%	1.9(−9) $C_2H_7O^+\cdot CH_3CO_2H$ 45% $CH_3CO_2H_2^+$ 55%	2.1(−9) $C_2H_7O^+\cdot CH_3CO_2H$ 40% $CH_3CO_2H_2^+$ 30% $CH_3CO_2H_2^+\cdot C_2H_4$ 30%	1.95(−9)
$CH_3C_6H_5$	189.8	6.9(−10) $CH_3C_6H_5H^+$ 100%	6.9(−10) $C_2H_7O^+\cdot CH_3C_6H_5$ ≤35% $CH_3C_6H_5H^+$ ≥65%	1.7(−9) $CH_3C_6H_5H^+$ 100%	1.7(−9) $CH_3C_6H_5H^+$ 100%	1.54(−9)
CH_3CHO	186.6	1.3(−9) $C_2H_7O^+\cdot CH_3CHO$ 100%	1.0(−9) $C_2H_7O^+\cdot CH_3CHO$ 100%	1.6(−9) $C_2H_7O^+\cdot CH_3CHO$ 95% CH_3CHOH^+ 5%	1.6(−9) $C_2H_7O^+\cdot CH_3CHO$ 100%	2.83(−9)
H_2CCCH_2[b]	186.3	6.8(−12) $C_2H_7O^+\cdot C_3H_4$ 50% $C_3H_7^+$ 50%	5.8(−12) $C_2H_7O^+\cdot C_3H_4$ 95% $C_3H_7^+$ ≤5%	3.0(−10) $C_2H_7O^+\cdot C_3H_4$ 10% $C_3H_7O^+$ 90%	4.8(−10) $C_3H_7O^+$ 100%	1.22(−9)
CH_3OH	181.9	4.8(−10) $C_2H_7O^+\cdot CH_3OH$ 100%	4.3(−10) $C_2H_7O^+\cdot CH_3OH$ 100%	8.1(−10) $C_2H_7O^+\cdot CH_3OH$ 100%	6.8(−10) $C_2H_7O^+\cdot CH_3OH$ 100%	2.11(−9)
c-C_3H_6	179.8	9.9(−12) $C_2H_7O^+\cdot C_3H_6$ 25% $C_3H_7^+$ 35% $C_4H_9^+$ 40%	6.4(−12) $C_2H_7O^+\cdot C_3H_6$ 100%	2.4(−10) $C_2H_7O^+\cdot C_3H_6$ 100%	2.4(−10) $C_2H_7O^+\cdot C_3H_6$ 40% $C_3H_7^+$ 60%	1.18(−9)
H_2O	166.5	5.4(−11) $C_2H_7O^+\cdot H_2O$ 100%	5.8(−11) $C_2H_7O^+\cdot H_2O$ 100%	8.1(−11) $C_2H_7O^+\cdot H_2O$ 100%	8.1(−11) $C_2H_7O^+\cdot H_2O$ 100%	2.47(−9)
C_2H_6	143.6	<1(−13)	<1(−13)	<1(−13)	<1(−13)	1.15(−9)

[a] These isomeric forms are $(CH_3)_2OH^+$, $C_2H_5OH_2^+$ (from a previous study[7]), and the unknown forms generated in the collisional associations $CH_3^+ + CH_3OH$ and $H_3O^+ + C_2H_4$. The proton affinities of the neutral reactants and those of $(CH_3)_2OH$ and C_2H_5OH (written below the reactant ion)[24] are given, as are the collisional rate coefficients deduced from variational transition state theory.[22] In cases where there is an association product, the equivalent binary rate coefficient at 0.5 Torr is quoted. Where products are quoted in a generic form, e.g., $C_2H_7O^+$, it is not necessarily meant to imply that they all have the same structure (see text for more detailed information). [b] Allene.

the same species and collisional rate coefficients calculated using variational transition state theory.[22] Mass discrimination in the detection system was determined by obtaining discrimination factors using the method described by Bohme et al.[21] when a reactant ion producing only one unique product could be distinguished. In the majority of cases, where this was not possible, the factors were determined by assuming that the total ionization density in all ions was independent of reactant gas flow and generating an algebraic equation for each flow by equating the count rates for each ion multiplied by the (unknown) mass discrimination factor to the total counts. The discrimination factors could then be obtained by multiple least-squares fitting. Such methods for determining discrimination factors will be accurate provided that there are no significant differences in the diffusion coefficients of the ions (such differences are not expected in the present case but are detectable as curvature in the H_3^+/N_2H^+ example given by Bohme et al.[21]) and that all the ion concentrations vary relative to each other at some point in the data. Using these techniques, mass discrimination factors, relative to the primary ions, of the order of 1.5−4 were determined depending on mass. These factors are, of course, also dependent on the mass spectrometer resolution and on the focusing conditions in the ion detection system.

Because the effects of other ions had to be accounted for in the product distributions for the associated ions, these distributions are less accurate than normal, being ±10 in the percentage (±5 for $C_2H_5OH_2^+$ and $(CH_3)_2OH^+$ reactant ions as usual). Only in one case was an apparent primary product seen that could be due to the reaction of CH_3OH or C_2H_4 with an actual primary product (in the H_3O^+/C_2H_4 reaction with allene, see below). The lack of such products was presumably because only a very small flow of CH_3OH was used and because C_2H_4 was unreactive. The equivalent data for the separate reactions of other coexisting ions are to be published elsewhere. The accuracy of the rate coefficients is normal at ±20% for permanent gases and ±30% for sticky vapors. Note that the rate coefficients for the CH_3CO_2H reactions had to be corrected for the presence in the flow measurement systems of dimers, which are known to dissociate before entering the flow tube.[23]

Results and Discussion

By inspection of the data in Table 1, it is very evident that the rate coefficients and product ions are similar for CH_3^+/CH_3OH and $(CH_3)_2OH^+$ and for H_3O^+/C_2H_4 and $C_2H_5OH_2^+$ for all of the reactant neutrals, but that there are very definite differences between the two cases. This suggests that CH_3^+/CH_3OH and $(CH_3)_2OH^+$ are closely related and similarly for H_3O^+/C_2H_4 and $C_2H_5OH_2^+$. This is consistent with the deductions of Jarrold et al.[3] from CID measurements and in the latter case with the conclusions of Fairley et al.[6] in the accompanying paper from reactions with C_7H_7F (2-fluorotoluene) and CH_2CHCN. That in the present data the rate coefficients for proton transfer reactions agree is not surprising or conclusive since this type of reaction usually proceeds at the collisional rate. However, there is also excellent agreement for the slower reactions, for example, the allene reactions with CH_3^+/CH_3OH:$(CH_3)_2OH^+$ being 6.8(−12):5.8(−12) $cm^3\ s^{-1}$ and H_3O^+/C_2H_4:$C_2H_5OH_2^+$ being 3.0(−10):4.8(−10) $cm^3\ s^{-1}$. Also, for the cyclopropane reactions the values are 9.9(−12):6.4(−12) and 2.4(−10):2.4(−10) $cm^3\ s^{-1}$ respectively. The potential surface of Fairley et al.[6] shows that, in both associations, there are stable weakly bound isomers, $CH_3^+{\cdot}CH_3OH$ and $H_3O^+{\cdot}C_2H_4$, with similar binding energies (∼18 kcal mol^{-1}) and with similar barriers (∼7 kcal mol^{-1}) to the formation of the strongly bonded isomers $(CH_3)_2OH^+$ and $C_2H_5OH_2^+$ respectively. Note that in the case of $(CH_3)_2OH^+$ the well from the separated reactants is 2.5 times deeper than that of $C_2H_5OH_2^+$. In agreement with this, Audier, et al. calculated that there is a stable $CH_3^+{\cdot}CH_3OH$ isomer.[5] They also provide experimental evidence for this from ^{13}C and deuterium labeling in reaction 5b. These theoretical and experimental studies suggest, consistent with our experiments, that the $CH_3^+ + CH_3OH$ association should produce $(CH_3)_2OH^+$ and $H_3O^+ + C_2H_4$ should produce $C_2H_5OH_2^+$. However, although our experimental data suggest a strong correlation between CH_3^+/CH_3OH and $(CH_3)_2OH^+$ and between H_3O^+/C_2H_4 and $C_2H_5OH_2^+$, there is not complete agreement, especially in the product ion distributions. This requires further discussion.

CH_3^+/CH_3OH and $(CH_3)_2OH^+$. When CH_3^+ associates with CH_3OH, if $(CH_3)_2OH^+$ is formed it contains ∼80 kcal mol^{-1} of internal energy.[6] After a few collisions with the He carrier gas, this ion will be sufficiently stabilized that it cannot unimolecularly decompose back to the reactants, but it will still be highly excited. If it is to react in the same way as the protonated $(CH_3)_2O$ produced in the ion source, then this energy needs to have been dissipated before further reaction. Under our experimental conditions, there are about 10^4 collisions with He and a few with CH_3OH to internally relax the ion before we reactively probe it. If, however there is a small well to $CH_3^+{\cdot}CH_3OH$, then a proportion of the CH_3^+/CH_3OH could be stabilized into that form. Thus, there could be two reactive forms of CH_3^+/CH_3OH in our experiments. However, if this occurred, the decay curves might be expected to be nonlinear, due to the two forms having different reactivities. These reactivities could be similar for the fast reactions, but no such deviations were observed even for the slow reactions where this type of effect would be expected to be most evident. It was concluded that only one structural isomer was present. What is observed is that there are somewhat different products for CH_3^+/CH_3OH and $(CH_3)_2OH^+$ in the case of some of the reactants. The reactions with C_2H_6, H_2O, CH_3OH, CH_3CHO, and C_2H_5OCHO gave essentially identical results, but there are differences for the other reactants (see Table 1). These latter reactions are now treated individually.

c-C_3H_6. With $(CH_3)_2OH^+$, only association is observed, but CH_3^+/CH_3OH additionally gives 35% $C_3H_7^+$, which is endothermic by 11.5 or 4 kcal mol^{-1} for ground vibrational state $(CH_3)_2OH^+$ depending on whether the product ion is protonated cyclopropane or propylene respectively (an endothermicity of 4 kcal mol^{-1} is consistent with the rate coefficient for this channel assuming an Arrhenius type behavior). CH_3^+/CH_3OH also gives 40% $C_4H_9^+$, which is exothermic for both protonated $(CH_3)_2C{=}CH_2$ and $CH_3CH{=}CHCH_3$ (by 25 and 8 kcal mol^{-1} respectively). Note that there may be barriers to ring opening. All information for calculating energetics has been obtained from Lias et al.[24] However, if $C_4H_9^+$ is the cluster ion $CH_3^+{\cdot}C_3H_6$, this channel may be ligand switching, which would be facilitated if the CH_3^+/CH_3OH was excited $(CH_3)_2OH^+$ that had access to the $CH_3^+{\cdot}CH_3OH$ form. This product is not generated in the reaction of CH_3^+ with C_3H_6 as deduced from our other studies of this reaction.

CH_2CCH_2:Allene. The same products are produced for the two ions but with different distributions, more $C_3H_7^+$ being observed for CH_3^+/CH_3OH. This reaction channel could be exo- or endothermic for $(CH_3)_2OH^+$ depending on the structural form of the neutral products. For CH_3^+/CH_3OH, this channel could also be driven by excess energy in the reactant ion or access to a different structural form.

$CH_3C_6H_5$. The major product is proton transfer in both cases, which for ground vibrational state $(CH_3)_2OH^+$ is apparently

endothermic by 2.3 kcal mol^{-1}. This and other evidence indicates that the proton affinity of $CH_3C_6H_5$ is somewhat larger than the literature suggests, perhaps larger than that of CH_3CO_2H (see below). In this case an association product is observed for $(CH_3)_2OH^+$, in addition to proton transfer, but not for CH_3^+/CH_3OH. Again, this is consistent with additional energy being available in the latter ion, either as internal excitation or by virtue of a different structural form. Such energy would also cause the proton transfer reaction to be less endothermic or exothermic, making it more facile, and would inhibit association by reducing the lifetime of the proton bound intermediate. In contrast, note that as discussed below, the H_3O^+/C_2H_4 reactions with *c*-C_3H_6, C_3H_4, $(CH_3)_2CHOH$, and C_2H_5OCHO show an enhancement of the association channel over that obtained for the $C_2H_5OH_2^+$ isomer. That an enhancement does not occur in this case may be a result of steric hindrance by the benzene ring of $CH_3C_6H_5$.

CH_3CO_2H. As in the case of *c*-C_3H_6, in addition to association, a significant product which could be $CH_3^+{\cdot}CH_3CO_2H$ is observed in the CH_3^+/CH_3OH reaction, also indicating some access to an intermediate of the form $CH_3^+{\cdot}CH_3OH$. Alternatively, if the product ion is a more strongly bonded $C_3H_7O_2^+$ isomer, this reaction channel could be exothermic or somewhat endothermic for ground vibrational state $(CH_3)_2OH^+$, depending on the isomer involved. Note that this channel is not observed in the $(CH_3)_2OH^+$ reaction.

$(CH_3)_2CHOH$. Here again, a channel that could be considered as ligand switching is observed to occur for CH_3^+/CH_3OH, in addition to the association that is also observed for $(CH_3)_2OH^+$. Such a ligand switch would require a cluster ion form to be accessible. It should be noted that the reaction would be exothermic for ground vibrational state $(CH_3)_2OH^+$ if the product ion is one of the more strongly bound isomers. The fact that this product was not seen for $(CH_3)_2OH^+$ suggests that it is not the strongly bound isomeric form in the CH_3^+/CH_3OH reaction.

To summarize, there is a body of evidence to suggest that the $C_2H_7O^+$ produced in the association $CH_3^+ + CH_3OH$ is to a large degree in the form of protonated $(CH_3)_2O$; however, there is evidence within the products of the *c*-C_3H_6, C_3H_4, $CH_3C_6H_5$, CH_3CO_2H, and $(CH_3)_2CHOH$ reactions for either some residual excitation within the CH_3^+/CH_3OH that allows it access to $CH_3^+{\cdot}CH_3OH$ or that it is in this stable form with its small barrier to $(CH_3)_2OH^+$.

Also, the fact that association occurs with CH_3CO_2H, $(CH_3)_2CHOH$, and C_2H_5OCHO, which apparently have larger proton affinities than $CH_3C_6H_5$ for which proton transfer is endothermic by 2.3 kcal mol^{-1}, but is observed as the major product, suggests that the proton affinity of $CH_3C_6H_5$ is somewhat larger than given in the literature. This conclusion is based on the fact that proton transfer is usually rapid when it is exothermic, and association is enhanced when proton transfer is close to thermoneutral. The latter occurs since a proton bound dimer can be produced that has an enhanced lifetime and is more likely to be stabilized.

H_3O^+/C_2H_4 and $C_2H_5OH_2^+$. In the association $H_3O^+ + C_2H_4$, according to the potential surfaces of Radom[2] and of Fairley et al.,[6] a weakly bonded $H_3O^+{\cdot}C_2H_4$ is produced, which presumably couples via a small barrier through the weakly bonded proton bound dimer $H_2O{\cdots}H^+{\cdots}C_2H_4$ to $C_2H_5^+{\cdot}H_2O$. A similar barrier then connects to the $C_2H_5OH_2^+$ global minimum, the barriers being such that the global minimum can be accessed by the association of H_3O^+ with C_2H_4. The experimental data for H_3O^+/C_2H_4 and $C_2H_5OH_2^+$ in Table 1 show a strong correlation in both the magnitudes of the rate coefficients and the product ions indicating, as suggested by the CID experiments of Jarrold et al.[3] and the reactivity studies of Fairley et al.[6] with C_7H_7F and CH_2CHCN, that the H_3O^+/C_2H_4 is to a large degree in the form of protonated C_2H_5OH. However, as in the case of CH_3^+/CH_3OH, there are some differences in some of the products (for *c*-C_3H_6, C_3H_4, CH_3CO_2H, $(CH_3)_2CHOH$, and C_2H_5OCHO). In all cases, the decay of the associated ion was linear with reactant gas flow indicating, as for CH_3^+/CH_3OH case, that only one isomer was present.

c-C_3H_6. In the H_3O^+/C_2H_4 reaction with *c*-C_3H_6, only association is observed. $C_3H_7^+$ is not observed as a product whereas it is in the $C_2H_5OH_2^+$ reaction. Note that for $C_2H_5OH_2^+$ this proton transfer is endothermic by 8 kcal mol^{-1} if the product is protonated cyclopropane, but only 0.8 kcal mol^{-1} if it is protonated propylene. The latter endothermicity is consistent with the magnitude of the rate coefficient into this channel. If the associated ion is in the form of $H_3O^+{\cdot}C_2H_4$, or internally excited $C_2H_5OH_2^+$, on the basis of energy, proton transfer should be more facile and association diminished. That this does not occur suggests that H_3O^+/C_2H_4 is not purely a high-energy form of $C_2H_5OH_2^+$ but rather that the structural form is partly $H_3O^+{\cdot}C_2H_4$ or $C_2H_5^+{\cdot}H_2O$, i.e., a proton bound dimer, $H_2O{\cdots}H^+{\cdots}C_2H_4$. This seems reasonable since the proton is screened by the H_2O and C_2H_4 entities and also these would be widely separated so that, if the proton were to transfer, the C_2H_5OH would be highly vibrationally excited, perhaps to a degree that makes the overall reaction endothermic.

H_2CCCH_2. For H_3O^+/C_2H_4 there is a small association product in addition to a $C_3H_7O^+$ product that is also observed for $C_2H_5OH_2^+$. Note that as discussed recently,[7] for this latter reaction the $C_3H_7O^+$ has to be a more strongly bonded form such as $(CH_3)_2COH^+$, for which the reaction is exothermic rather than the $H_3O^+{\cdot}C_3H_4$ cluster. However, this cluster could be produced in ligand switching in reaction with $H_3O^+{\cdot}C_2H_4$. It is surprising that association occurs with H_3O^+/C_2H_4 but not with $C_2H_5OH_2^+$, which may have lower energy. That this is so may indicate that the proton initially bonds the H_2O, C_2H_4, and C_3H_4 (with proton affinities of 166.5, 162.6, and 186.3 kcal mol^{-1} respectively) together in an excited trimer which is then collisionally stabilized. The proton then presumably resides closest to the higher proton affinity species. Note, though, that a large concentration of C_2H_4 is present in the flow tube and the apparent association product could be $C_3H_7O^+{\cdot}C_2H_4$ in this case, produced by the association of the $C_3H_7O^+$ product with the C_2H_4. However, this is the only case where such an association could apparently be occurring.

CH_3CO_2H. In the reactions of CH_3CO_2H, both of the reactant ions give two of the same product ions in similar proportions, but for $C_2H_5OH_2^+$ there is an additional product that is intermediate between proton transfer and association, this being proton transfer but with C_2H_4 attached to the ion. Such a channel would only be exothermic if the strength of the C_2H_4 ligand bond is greater than 9 kcal mol^{-1} or if a more strongly bonded isomer of $C_4H_9O_2^+$ is produced. Several isomeric forms, including $(C_2H_5CO_2CH_3)H^+$ and $(CH_3CO_2C_2H_5)H^+$, are energetically accessible.

$(CH_3)_2CHOH$. In both cases the major product is proton transfer, but there the similarity ends. For H_3O^+/C_2H_4, there is an association product where none is seen for $C_2H_5OH_2^+$ (perhaps due to the production of an excited proton bound trimer as postulated for the C_3H_4 and CH_3CO_2H reactions above). In the latter case, an apparent proton transfer product is observed but with C_2H_4 attached and H_2O ejected. This is the same

mechanism as in the CH_3CO_2H reaction. If the ligand bond strength is greater than 7.8 kcal mol^{-1}, then this route is exothermic, although production of more strongly bonded $C_5H_{13}O^+$ isomers is also possible. Such a reaction product should be possible for H_3O^+/C_2H_4, although if a longer lived intermediate is produced perhaps association could be stabilized before ejection of H_2O. It may be significant that the product percentage is the similar in the two cases. Note that the $(CH_3)_2CHO^+$ product of the H_3O^+/C_2H_4 reaction has the same composition, but perhaps is a different isomeric form, as the major product in the H_3O^+/C_2H_4 and $C_2H_5OH_2^+$ reactions with C_3H_4 (allene). In the $(CH_3)_2CHOH$ reaction, the $(CH_3)_2CHO^+$ channel may be exo- or endothermic for ground vibrational state $C_2H_5OH_2^+$ depending on whether the $(CH_3)_2CHO^+$ product is a strongly bonded form and whether the neutral products are C_2H_6 and H_2O or C_2H_5OH and H_2. Thus, such an ion product is not unreasonable for H_3O^+/C_2H_4.

C_2H_5OCHO. The major product here is also proton transfer in both cases, but for H_3O^+/C_2H_4 there is a 10% association product, consistent with the studies discussed above.

Much of the data on rate coefficients and product ions indicate that H_3O^+/C_2H_4 and $C_2H_5OH_2^+$ are very similar species; however, there is evidence that there are some differences especially in terms of the product ions that are generated. The H_3O^+/C_2H_4 ion, in the state that exists in our flow tube (i.e., with the degree of relaxation that is achieved), appears to be a higher energy form which interconverts to the $C_2H_5OH_2^+$ structure. The fact that association occurs more readily for this higher energy form (an unusual occurrence), rather than reacting in other ways not energetically accessible for ground vibrational state $C_2H_5OH_2^+$, implies that it has the proton bound dimer structure with the proton shielded from binary reaction, but with it available to produce perhaps a proton bound trimer with the reactant neutral that is sufficiently long lived to be collisionally stabilized. A detailed additional research program, employing CID and/or reactivity to distinguish the many isomeric forms of the product ions, would be necessary to further clarify the situation.

Summary and Conclusions

A comparison between the reactivities and product ion distributions for the associated ions, CH_3^+/CH_3OH and H_3O^+/C_2H_4, and the strongly bonded protonated $(CH_3)_2O$ and C_2H_5OH indicates that the associated ions are a single higher energy form of $(CH_3)_2OH^+$ and $C_2H_5OH_2^+$ respectively with access to the weak ligand bonded forms $CH_3^+{\cdot}CH_3OH$ and $H_3O^+{\cdot}C_2H_4$. The comparison also suggests that the reaction rates are controlled by an early barrier and the product ions by the energy in the associated ion and by the predominant molecular conformation after the barrier has been surmounted. This implies that, although the collisions with He are efficient at stabilizing the ions after association, they are not efficient (within the ~2 ms lifetime before further reaction) in totally relaxing the ions. This is surprising since, in the vast literature on collisionally stabilized association reactions[25] and on equilibrium in such reactions,[26] it is assumed that the product ion is thermally relaxed. However, the present situations may be special cases. When an associated ion can readily isomerize between an excited strongly bonded form (e.g., $C_2H_5OH_2^+$) and a much less excited weakly bonded form (e.g., H_3O^+/C_2H_4) of higher heat of formation, the ion will spend different fractions of time in the two isomeric forms. Without complete potential surfaces, detailed calculations are not warranted; however, insight into this situation can be gained by considering the simpler situation of a double square potential well with the two well depths approximating to the two isomeric forms.[27] Analysis of this, by determining the wave functions and probability density distributions, shows that the fraction of time spent in the weakly bonded form varies with vibrational level. The magnitude of this variation is dependent on the well depths and the relative widths of the wells in a nonstraightforward way. For certain relative widths, the fraction of time spent in the weakly bonded form can be more than 0.9, exhibiting an irregular oscillation with vibrational quantum number. Initially, collisions with He will vibrationally relax both species, the rate of relaxation depending on the individual vibrational energy spacings. However, when the lowest level in the shallower potential is reached, it cannot be further relaxed when in this form, and the relaxation rate, which then depends on the proportions of time spent in the two forms, will be reduced. Eventually, of course, a He collision will occur when in the strongly bonded form, and further relaxation to the bottom of this well will occur as for a single-well situation. The rate of relaxation could be probed further by adding more efficient quenchers to the flow tube such as Ar, N_2, or CH_4.

In each of the present cases, however, theory suggests that there is a small potential barrier between the two forms and thus collisional stabilization to both forms might be expected. That the data do not show two separate isomeric forms indicates that understanding of the stabilization process is lacking. The difficulty could perhaps be resolved if the barrier is narrow as well as shallow. For this situation, tunneling through the barrier could enable the two forms to efficiently interconvert. Consideration of the structures calculated by Fairley et al.[6] shows that this requires H-atom and electron tunneling for the CH_3^+/CH_3OH system and only H-atom tunneling for H_3O^+/C_2H_4. Both types of tunneling will be efficient because of the small mass of the tunneling particle. The involvement of such a process could be investigated further by changing the tunneling particle to a D-atom using deuterated reagents. Tunneling has been invoked on several occasions to explain behavior in ion−molecule reactions[28,29] and in dissociative electron−ion recombination.[30] This may be a general mechanism in association reactions and needs to be investigated further, both theoretically and experimentally.

For the application to the chemistry of the interstellar medium (ISM), these data imply that the analogous radiative associations of $CH_3^+ + CH_3OH$ and $H_3O^+ + C_2H_4$ lead predominantly to higher energy forms of $(CH_3)_2OH^+$ and $C_2H_5OH_2^+$ respectively, which might be expected to slowly radiatively relax to the ground vibrational state of $(CH_3)_2OH^+$ and $C_2H_5OH_2^+$ before further reaction. This can occur since the collision times in the ISM are very long (of the order of a day even for collisions with the most abundant species H_2) compared with the millisecond reaction times in the laboratory experiments. Thus the reactivities of these ions in the ISM will be those of the ground vibrational state protonated molecules (as determined in our earlier study[7]). Dissociative recombination of these product ions with electrons is then most likely to give reaction channels to $(CH_3)_2O$ and C_2H_5OH respectively. Therefore, it is expected that, in the ISM, the presence of CH_4 (which is related to the CH_3^+ concentration) and CH_3OH will be related to $(CH_3)_2O$ and that the presence of H_2O or OH (the dissociative electron−ion recombination products of H_3O^+ [13]) and C_2H_4 will be related to C_2H_5OH. Consistent with this, observational data for the Orion molecular cloud (OMC-1) show that the fractional abundancies relative to hydrogen of CH_3OH and $(CH_3)_2O$ are large with that of C_2H_5OH being small, whereas in Sagittarius B2, where the fractional abundance of CH_3OH is smaller, that of $(CH_3)_2O$ is also smaller and more comparable to that of C_2H_5-

OH.[31] More detailed observations are required and modeling needs to be done before more definitive conclusions can be reached.

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