Reactions of $CH_3OH_2^+$, $CH_3OH_2^+{\cdot}CH_3OH$, and $(CH_3)_2OH^+$ with Methanol: Effect of Solvation

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Abstract: Rate constants for the reactions of the ions $CH_3OH_2^+$ and $CH_3OH_2^+{\cdot}CH_3OH$ with methanol have been measured by using a variable-temperature selected ion flow tube (SIFT) instrument at 300 and 450 K. The measurements were conducted as a function of helium buffer gas pressure in the range 0.26–0.59 Torr. For the reaction of $CH_3OH_2^+$ with methanol, two channels were observed: association and displacement. The rate constants for the association channel at 0.4 Torr were measured to be 2.8×10^{-26} and 5.3×10^{-27} cm^6 s^{-1} at 300 and 450 K, respectively, and exhibited falloff behavior at 300 K. The rate constants for displacement were found to equal 7.6×10^{-11} and 4.6×10^{-11} cm^3 s^{-1} at 300 and 450 K, respectively. The ionic product of displacement was observed to be $(CH_3)_2OH^+$. The second-order rate constants for the association channel increased with increasing total pressure, but the rate constants for displacement were independent of pressure. The reaction of $CH_3OH_2^+{\cdot}CH_3OH$ with methanol was also studied and found to produce only the association product, with a rate constant of 1.3×10^{-26} cm^6 s^{-1} at 300 K and 0.4 Torr. When $CH_3OH_2^+$ was solvated with CH_3OH, the displacement reaction was quenched. Displacement would require CH_3OH transfer from reactant to product ion, and the quenching is consistent with a barrier to this transfer. The reaction of $(CH_3)_2OH^+$ with methanol was studied at 300 K and found to proceed solely by association. The rate constant was measured to be 3.0×10^{-26} cm^6 s^{-1} at 0.4 Torr.

Introduction

The effect of reagent solvation on chemical reactivity in the gas phase is a topic of interest to many chemists. Comparing the intrinsic reactivity of unsolvated reactants in the gas phase with their corresponding reactivity in solution probes how solvation affects reaction in solution. Measuring the reactivity of partially solvated reactants in the gas phase explores how these two extremes are connected. Effects due to gas-phase ion solvation have been reviewed by Bohme.[1] Several experimental studies have found that ion solvation often has a pronounced effect on reactivity. We have been interested in the effects of solvation on ion–molecule reactions, including nucleophilic displacement reactions. There has been no discussion in the literature, to our knowledge, comparing solvation effects in nucleophilic displacement reactions for negative and positive ions. The reaction of $CH_3OH_2^+$ with methanol is known to proceed by nucleophilic displacement.[2,3] Solvation is known to quench this reaction.[4] In light of these previous studies, we have reinvestigated the gas-phase reactions of $CH_3OH_2^+$, $CH_3OH_2^+{\cdot}CH_3OH$, and $(CH_3)_2OH^+$ with methanol using a variable-temperature selected ion flow tube (SIFT) apparatus.

Previous investigations of the kinetics of the reaction of $CH_3OH_2^+$ with methanol[4-8] include a study using a variable-temperature ion cyclotron resonance (ICR) apparatus,[4] which operates in a significantly lower regime of pressure (10^{-3}–10^{-4} Torr) compared with that of the SIFT (on the order of 0.5 Torr). The present study allows some interesting comparisons to be made with the ICR results. The pressure regime of the SIFT corresponds to the falloff region[9] for the association reaction of $CH_3OH_2^+$ with CH_3OH at 300 K in this study, whereas the pressures in the ICR experiment[4] correspond to the low-pressure limit[9] for association. Association reactions, in general, contribute more to the overall reactivity in SIFT experiments than in ICR experiments and can compete with other reaction channels. This leads to questions as to how the association channel might affect the nucleophilic displacement channel.

In addition to interest in the effects of the different pressure regimes, there is interest in the comparison of the capabilities for temperature variation in the two techniques. Specifically, there have been questions raised in the ion–molecule literature concerning the accuracy of quoted temperatures in ICR experiments.[10] The present study allows a comparison of temperature dependences of second- and third-order rate constants measured by the two techniques.

Experimental Section

The experiments were performed in a variable-temperature selected ion flow tube instrument. The apparatus has been described elsewhere,[11] and a detailed description of a similar apparatus has been published recently by Smith and Adams.[12] Only those details pertinent to the present study are given here. The ions $CH_3OH_2^+$, $CH_3OH_2^+{\cdot}CH_3OH$, and $(CH_3)_2OH^+$ were generated by electron impact on CH_3OH in a moderate-pressure (0.1-1 Torr) ion source. The ions were then mass-selected in a quadrupole mass spectrometer and injected into the flow tube through a Venturi inlet. The neutral reactant, CH_3OH, was introduced downstream through one of two ring inlets and allowed to react with the ions for a known reaction time in a fast flow ($\sim 10^4$ cm s^{-1}) of He buffer gas. Experiments were conducted at a number of different flow tube pressures in the range from 0.26 to 0.59 Torr. The reactant and product ions were mass-analyzed in a second quadrupole mass spectrometer and detected by a channel particle multiplier. Rate constants were extracted from least-squares fits of the logarithm of the reactant ion signal plotted versus the concentration of added CH_3OH neutral reactant vapor. The reaction time was determined from ion time-of-flight measurements. For the experiments conducted at 450 K, the temperature of the flow tube was raised by using electrical resistance heaters. The accuracy of the measured overall rate constants is ±25%, the accuracy for the rate constants for individual channels is ±40%, and the relative accuracy is ±15%.[11]

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Table I. Measured Rate Constants for Reactions 1–3: Ion–Molecule Reactions of CH_3OH

displacement reacn	rate const, 10^{-11} cm^3 s^{-1} 300 K	450 K		ref
1a	7.6	4.6		present
	9			*a*
	10.5			*b*
	8			*c*
2a	<0.3[d]	<0.15[d]		present
association reacn	**rate const, 10^{-26} cm^6 s^{-1} 300 K**	**450 K**	**M**	**ref**
1b	2.8[e]	0.53	He	present
	62[f]		CH_3OH	*a*
2c	1.3	*g*	He	present
	46[f]		CH_3OH	*a*
3	3.0		He	present
	62[f]		CH_3OH	*a*

[a] Reference 4. [b] Reference 6. [c] Reference 5. [d] Rate constant upper limits were derived from the minimum detectable signal intensity, the signal intensity for the observed product of reaction 2c, and the rate constant for 2c. [e] Present values for association given for pressure of 0.4 Torr. [f] Third-order rate constants from ref 4 are given for 294 K at 5 × 10^{-4} Torr. [g] Not measured due to contribution by reverse reaction at 450 K (see text).

The branching ratio between the displacement and association channels was determined by recording the product ion count rates as a function of the flow rate of the CH_3OH added. Due to complications introduced by secondary association reactions of the product ions with CH_3OH, the true branching ratios were found by extrapolation of the product ion count rates to zero flow rate of CH_3OH. In some of the experiments, the downstream mass spectrometer was set to high resolution, which led to significant mass discrimination between product ions. This was accounted for by measuring the ion current flowing to the sampling nose cone when each of the product ions of interest was injected into the flow tube (with no other ions present). For the different ions, the ratios of the ion currents to the ion count rates at the detector were compared. This procedure yielded mass discrimination factors with which the product ion count rates were corrected. No attempt was made to account for the possible effect of reactant and product ions diffusing to the wall of the flow tube at different rates. We attempted to study reactions of the ion $CH_3OH_2^+{\cdot}2CH_3OH$ but found that, upon injection into the flow tube, this ion fragmented to form the ion $CH_3OH_2^+{\cdot}CH_3OH$.

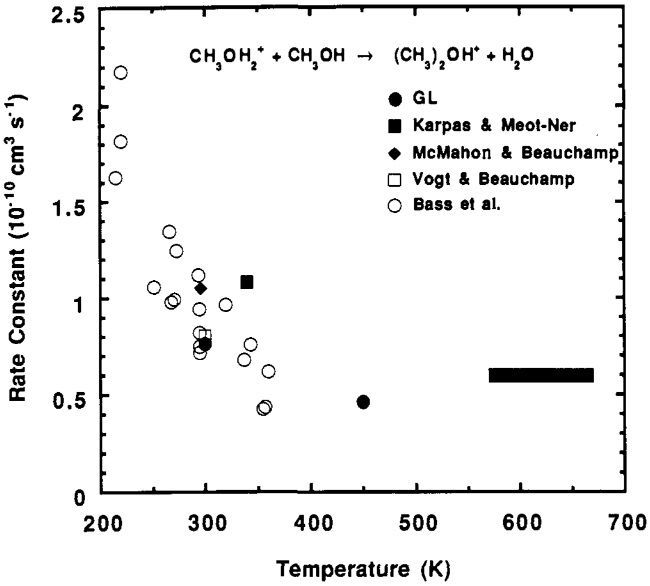

Figure 1. Rate constants for the displacement reaction of $CH_3OH_2^+$ with CH_3OH as a function of temperature. The labels in the legend refer to the following references: GL, present data; Karpas & Meot-Ner, ref 8 (includes the solid bar); McMahon & Beauchamp, ref 6; Vogt & Beauchamp, ref 5; Bass et al., ref 4.

The CH_3OH used was spectrophotometric grade (99.9%) and was purified in a series of freeze–pump–thaw cycles to remove dissolved atmospheric gases and other impurities of high vapor pressure. The He was high-purity grade (99.997%) and was passed through a zeolite trap, cooled by liquid nitrogen, before use.

Results

The experimental results are presented in Tables I and II. In Table I, rate constants for the displacement and association reactions are reported for a nominal total pressure of 0.4 Torr. Also given are previously reported rate constants measured at or near 300 K by using ICR, FTMS, and HPMS. The results of Bass

Table II. Measured Rate Constants for the Displacement and Association Channels of Reactions 1–3 as a Function of Total Pressure

			rate constant		
			association		
reactants	temp, K	press., Torr	second-order 10^{-11} cm^3 s^{-1}	third-order 10^{-26} cm^6 s^{-1}	displacement 10^{-11} cm^3 s^{-1}
$CH_3OH_2^+ + CH_3OH$ (+He)[a]	300	0.26	28	3.3	7.0
		0.33	31	2.9	7.2
		0.41	37	2.9	8.0
		0.48	41	2.6	8.3
		0.55	42	2.4	7.6
	450	0.31	3.6	0.54	4.2
		0.35	4.3	0.58	5.1
		0.40	4.5	0.52	4.3
		0.41	4.8	0.54	5.0
		0.48	4.5	0.44	4.1
		0.51	5.7	0.52	4.4
		0.54	5.7	0.50	5.4
		0.59	5.7	0.46	4.2
$CH_3OH_2^+{\cdot}CH_3OH + CH_3OH + He$	300	0.26	11	1.3	
		0.30	14	1.4	
		0.38	17	1.4	
		0.43	14	1.0	
		0.45	19	1.3	
		0.50	19	1.2	
		0.50	21	1.3	
		0.53	20	1.1	
		0.53	20	1.2	
		0.57	24	1.3	
$(CH_3)_2OH^+ + CH_3OH + He$	300	0.27	29	3.3	
		0.48	43	2.8	

[a] In the case of the association channel.

et al.[4] are given for the conditions 294 K and 5×10^{-4} Torr total pressure. Table II lists the effective second-order and third-order rate constants for the association reactions and the rate constants for displacement as a function of temperature and pressure.

For the reaction of $CH_3OH_2^+$ with methanol, we observed two reaction channels: displacement, producing $(CH_3)_2OH^+$ and H_2O, and association, forming $CH_3OH_2^+{\cdot}CH_3OH$.

$$CH_3OH_2^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + H_2O \quad (1a)$$

$$\Delta H^\circ = -65 \text{ kJ mol}^{-1}\ {}^{13}$$

$$CH_3OH_2^+ + CH_3OH \rightarrow CH_3OH_2^+{\cdot}CH_3OH \quad (1b)$$

$$\Delta H^\circ = -134 \text{ kJ mol}^{-1}\ {}^{14}$$

These reactions were observed by Munson,[15] and the identity of the product ion from reaction 1a, $(CH_3)_2OH^+$, was later confirmed by Henis.[16] In the present study, the rate constants for displacement were found to equal 7.6×10^{-11} and 4.6×10^{-11} cm^3 s^{-1} at 300 and 450 K, respectively. The rate constant for displacement was independent of pressure within experimental uncertainty.

For the association reaction of $CH_3OH_2^+$ with CH_3OH (reaction 1b), it can be seen in Table II that neither the second-order nor the third-order rate constants measured at 300 K are independent of pressure in the experimental pressure range of 0.26–0.55 Torr. This implies that the present pressure range corresponds to the falloff regime for this association reaction. The present third-order rate constants measured at 450 K exhibit a systematic decrease with increasing pressure, but this effect is within the experimental precision of ±15%, and conclusions regarding falloff behavior at 450 K are therefore less meaningful. At a pressure of 0.4 Torr, the rate constants for reaction 1b are 2.8×10^{-26} and 5.3×10^{-27} cm^6 s^{-1} at 300 and 450 K, respectively.

The reaction of $CH_3OH_2^+{\cdot}CH_3OH$ with methanol was found to proceed by association (reaction 2c), producing $CH_3OH_2^+{\cdot}2CH_3OH$, with no evidence for displacement, despite the fact that displacement, producing $CH_3OH{\cdot}H^+{\cdot}O(CH_3)_2$ and H_2O, is exothermic by 41 kJ mol^{-1}.[13,14,17]

$$CH_3OH_2^+{\cdot}CH_3OH + CH_3OH \rightarrow CH_3OH{\cdot}H^+{\cdot}O(CH_3)_2 + H_2O \quad (2a)$$

$$\Delta H^\circ = -41 \text{ kJ mol}^{-1}$$

$$CH_3OH_2^+{\cdot}CH_3OH + CH_3OH \rightarrow (CH_3)_2OH^+ + CH_3OH + H_2O \quad (2b)$$

$$\Delta H^\circ = +69 \text{ kJ mol}^{-1}$$

$$CH_3OH_2^+{\cdot}CH_3OH + CH_3OH \rightarrow CH_3OH_2^+{\cdot}2CH_3OH \quad (2c)$$

$$\Delta H^\circ = -87 \text{ kJ mol}^{-1}$$

Upper limits to the rate constant for a possible minor displacement channel are given in Table I together with the rate constant for the association reaction, which is equal to 1.3×10^{-26} cm^6 s^{-1} at 0.4 Torr and 300 K.

The rate of the reverse reaction (thermal dissociation of $CH_3OH_2^+{\cdot}2CH_3OH$), calculated from the observed forward rate constant and the equilibrium constant for the reaction from published enthalpy and entropy data,[14] was significant at 450 K. Since the reverse reaction affected the observed forward reaction rate, no reliable rate constant was obtained at 450 K for the forward reaction (2c).

The ionic product of the bimolecular displacement reaction between $CH_3OH_2^+$ and methanol is protonated dimethyl ether, $(CH_3)_2OH^+$, which undergoes a secondary association reaction with the methanol in the flow tube to produce $CH_3OH{\cdot}H^+{\cdot}O(CH_3)_2$.

$$(CH_3)_2OH^+ + CH_3OH \rightarrow CH_3OH{\cdot}H^+{\cdot}O(CH_3)_2 \quad (3)$$

$$\Delta H^\circ = -110 \text{ kJ mol}^{-1}$$

The rate constant for this process was measured at 300 K and has a value of 3.0×10^{-26} cm^6 s^{-1} at 0.4 Torr.

Discussion

(A) Comparison with Previous Work. (i) Displacement. Figure 1 shows the present and previously published rate constants for reaction 1a as a function of temperature. There is good agreement between the present data and the previously published results. It is interesting that the temperature dependences measured by the SIFT and ICR techniques are in agreement, given the very different operating pressures and despite the large contribution to the overall reaction by the association reaction channel in the SIFT experiments. The combined data indicate a weakening of the negative temperature dependence with increasing temperature below 500 K and a flat dependence in the range 570–670 K. Negative temperature dependences that weaken with increasing temperature are not uncommon in ion–molecule reactions and have been discussed in the literature by Magnera and Kebarle[18] and Troe,[19,20] among others. Weakening of the negative temperature dependence of the rate constant for a nucleophilic displacement reaction with increasing temperature has been observed previously, e.g., in the reaction of $OD^- + CH_3Cl$.[21] Various theoretical treatments of negative temperature dependences of rate constants for ion–molecule reactions have been published.[4,18–20,22,23] In view of the fact that several different models with different conceptual bases are able to simulate negative temperature dependences of rate constants, it is not possible to use the data available to choose between these models at the present time.

The involvement of two different complexes in reaction 1 has been suggested by Sheldon et al.[24] and by Graul and Squires.[3] This idea is supported by the agreement between the SIFT and ICR results on the displacement reaction 1a and by the observation that the rate constant for association increases with increasing pressure while the rate constant for displacement is invariant with pressure. This result can be explained in two ways. The first possibility is that only one complex leads to both association and displacement. The fact that association and displacement do not compete might then be explained by the association channel resulting from the low-energy portion of the energy distribution of the complex and displacement resulting from the high-energy portion. This model would predict a positive temperature dependence of the rate constant for displacement, contrary to the experimental results. We feel that a more likely explanation is as follows. Two complexes are formed. The complex that leads to displacement is relatively short-lived due to the weaker bond and dissociates on a time scale short compared with that for collisions with the buffer gas. Because of its stronger bond, the association complex lives long enough to be stabilized by collisions with the buffer. This mechanism is supported by previous work. Graul and Squires[3] have shown evidence that the displacement channel proceeds through a complex different from that for the fast proton-transfer channel. The proton-transfer channel is unobservable in our experiment but was observed by Graul and Squires by means of isotopically labeled reagents. Their results indicate a proton-bound intermediate for proton transfer and a

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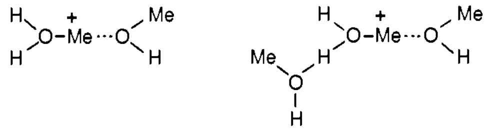
methyl-bound intermediate (backside attack) for displacement. The cluster bond in the proton-bound intermediate is 87 kJ mol^{-1} stronger than that in the methyl-bound intermediate,[14,25] suggesting that the proton-bound complex would be the likely structure of the complex leading to association. The results of Graul and Squires[3] also suggest that interconversion between the two complexes is inefficient. Sheldon et al.[24] have presented ab initio calculations that indicate two complexes can be formed in this reaction. The idea of distinct complexes for the two reaction channels is consistent with our finding that association does not attenuate displacement.

The data appear to eliminate the possibility that the association channel proceeds as a displacement reaction in which the products remain associated. For this possibility to hold, one would expect the intermediate to be the same as that for the displacement reaction (1a); and association would then compete with reaction 1a, in contradiction with the data.

(ii) Association. The absolute value of the present third-order rate constant for the association reaction of $CH_3OH_2^+$ with methanol (reaction 1b) is significantly less (by a factor of 22 at 300 K) than that obtained in the low-pressure limit by Bass et al.[4] The third-order rate constants for the association reactions of $CH_3OH_2^+{\cdot}CH_3OH$ (reaction 2c) and $(CH_3)_2OH^+$ (reaction 3) reported here are also substantially smaller than those measured by Bass et al. Differences in third-order rate constants measured in SIFT and ICR experiments have been reported previously.[26,27] We attribute the present differences in third-order rate constants from the two experiments to two factors. The first factor is the difference in adduct stabilization efficiencies of the respective bath gases. The ICR experiment[4] uses the parent gas methanol as the bath gas, whereas the SIFT experiment utilizes He buffer gas. The efficiency of collisional stabilization by a monatomic gas such as He is generally much lower than that by a polyatomic gas such as methanol. In addition, methanol is the solvent in this system, allowing the possibility of solvent exchange as a route for efficient stabilization of the adduct.[6] Some of the difference in efficiency is due to the fact that the collision rate constant of the complex with He is significantly less than the collision rate constant of the complex with CH_3OH. The collision rate constant at 300 K for the CH_3OH third body is 3.7 times as large as that for He. The second factor reducing the third-order rate constant is the difference between the falloff and low pressure regimes. A third-order rate constant measured in the falloff regime, as obtains in the SIFT, will have a lower value than that measured in the low-pressure limit.

The association rate constant for $CH_3OH_2^+{\cdot}CH_3OH$ is smaller than that for $CH_3OH_2^+$, despite the additional degrees of freedom available in the solvated ion. However, the bond strength for clustering of $CH_3OH_2^+$ to methanol is about 50% greater than that for clustering of $CH_3OH_2^+{\cdot}CH_3OH$ with methanol.[14] The additional degrees of freedom in the solvated ion would be expected to increase the association rate constant, while the weaker cluster bond strength should tend to lower the rate constant. Whether the association rate constant will increase or decrease with increasing solvation is determined by the tradeoff between these two factors. The effects of this type of tradeoff on association rate constants with increasing cluster size have been observed previously.[28-30]

The present rate constants for association of $CH_3OH_2^+$ to CH_3OH (reaction 1b) measured at 300 and 450 K may be expressed in the form $k = CT^{-m}$ and yield a value of 4.2 ± 1 for m. The ICR measurements of Bass et al.[4] yield a value of 4.6 ± 1.2 for m for reaction 1b over the temperature range 220–360 K. The present temperature dependence is then equal to that found in the ICR experiment within rather large experimental uncertainty.



I II

Figure 2. Proposed structures of displacement reaction intermediates. Structures I and II correspond to the reactions of $CH_3OH_2^+$ and $CH_3OH_2^+{\cdot}CH_3OH$ with CH_3OH, respectively.

These temperature dependences can be compared with two theoretical treatments. The theories apply strictly to the low-pressure limit. Even though the present results correspond to the falloff regime, this is a useful comparison since the pressures in the SIFT may be close to the low-pressure limit and since no simple theory is available for the falloff pressure regime. (Phase space theory can be used at higher pressures, but the published results on this reaction[4] apply only to the low-pressure limit.) Bass et al.[4] have used phase space theory to predict a temperature dependence of $T^{-4.45}$ over the temperature range 220–360 K. A theory that can be used very conveniently[31] predicts a value of m that varies with temperature. This variation arises from the fact that more vibrational modes become active at higher temperatures. Using this theory, we find an m value of 4.1 in the range from 250 to 350 K and an m value of 4.8 from 300 to 450 K. Thus both theories predict the temperature dependence shown by the data. The agreement between the two theoretical treatments demonstrates that the present approach provides useful, simple predictions.

Bass et al. found strong negative temperature dependences for the association reactions of $CH_3OH_2^+$, $(CH_3)_2OH^+$, and $CH_3OH_2^+{\cdot}CH_3OH$ with methanol. The steepness of the dependences was found to increase in the series $CH_3OH_2^+$, $(CH_3)_2OH^+$, $CH_3OH_2^+{\cdot}CH_3OH$, respectively. The steepness of these negative temperature dependences, increasing with increasing complexity of the system, can be correlated with the increasing number of active vibrational degrees of freedom.[31] The increasingly negative temperature dependences with increasing cluster size are consistent with results from our laboratory on association reactions of the cluster ions $NO_3^-{\cdot}nHNO_3$ and $HSO_4^-{\cdot}nH_2SO_4$ with HCl.[28,29]

(B) Effect of Solvation. One of the motivations for this study was to compare the effects of solvation on nucleophilic displacement reactions of positive and negative ions. In contrast with the situation for negative ions, relatively little is known on this subject for positive ions.[32] Despite the existence of the ICR data of Bass et al.,[4] the issue of the solvation effect in the present reactions has not been discussed to our knowledge.

The displacement channel for $CH_3OH_2^+{\cdot}CH_3OH$, while unobserved in both the present study and that of Bass et al.,[4] has been observed as an inefficient process under approximately single-collision conditions in a triple-quadrupole apparatus at energies on the order of 0.5 eV.[3,33] In the same study, the analogous displacement process for $CH_3OH_2^+{\cdot}2CH_3OH$ + CH_3OH producing $2CH_3OH{\cdot}H^+{\cdot}O(CH_3)_2$ and H_2O was also observed but found to be very inefficient (rate constants were not measured). Isotopic-labeling experiments[2,3] have indicated a backside-attack nucleophilic-displacement (S_N2) mechanism for the $CH_3OH_2^+$ reaction, involving a methyl-bound intermediate shown as I in Figure 2. For the same mechanism to hold for $CH_3OH_2^+{\cdot}CH_3OH$ (reaction 2a), intermediate II would be formed and the methanol solvent molecule would be transferred to the $(CH_3)_2OH^+$ product ion. Such a transfer would require a six-

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center cyclic transition state held together by hydrogen bonds. It is possible that unsolvated reactants may undergo displacement (reaction 1a), whereas solvated reactants may not (i.e., reaction 2a is not observed) simply because the solvent transfer is not efficient, and without solvent transfer the reaction is endothermic. This is consistent with a growing body of information on the effect of solvent molecules on ion–molecule reactions in the gas phase. Where the structure of the intermediate is such that solvent molecules may be readily transferred from reactant to product ion, solvated product ions are observed and solvation does not quench reaction (proton transfer,[34] nucleophilic addition[35]). In contrast, where the intermediate does not allow efficient solvent transfer, as in the present case, solvated products are not observed and the reaction may be quenched by solvation (nucleophilic displacement[21,36]).

There has been extensive discussion of the intermediate for reaction 1a, some workers invoking a proton-bound dimer intermediate, some invoking intermediate I, and others suggesting that the former may rearrange to produce the latter. Current opinion seems to favor the methyl-bound structure I.[2,3,8,37] The results of the present study may be interpreted to support this conclusion. Unlike intermediate II (the solvated analogue of I), the proton-bound dimer intermediate would be expected to allow facile solvent transfer, enabling displacement for $CH_3OH_2^+\cdot CH_3OH$.

The above interpretation assumes that there is no complication due to possible competition between displacement and association. Association in a SIFT experiment can, in some cases, compete with and dominate over reaction channels that are the major channels at the low pressures of an ICR experiment.[38] In the present system, this appears not to be the case. The efficiency of the association reaction (at 300 K) for $CH_3OH_2^+$ is 16%, and displacement is also observed in the overall reaction. The efficiency of association is only 8% for $CH_3OH_2^+\cdot CH_3OH$, yet the latter, less efficient association reaction represents the only observed channel. Still more convincing evidence is provided by the ICR results.[4] No displacement was observed for $CH_3OH_2^+\cdot CH_3OH$ in the ICR experiment in spite of the very small second-order association rate constant (a factor of 25 lower than the present value at 300 K). Therefore, it is extremely unlikely that the association reaction is responsible for the lack of observable displacement for $CH_3OH_2^+\cdot CH_3OH$. The absence of displacement in the SIFT and ICR experiments almost certainly results from a solvation effect.

Conclusions

In agreement with previous investigations, the reaction of $CH_3OH_2^+$ with methanol was found to proceed by two channels: displacement, forming $(CH_3)_2OH^+$, and association. The temperature dependence of the rate constants for the displacement channel, measured here at 300 and 450 K, is in agreement with results from other studies. The negative temperature dependence weakens with increasing temperature below 500 K and then levels off. There appears to be no competition between displacement and association in this reaction. This suggests that displacement and association proceed through different intermediates and that the association channel is not a displacement reaction in which the products remain associated.

The corresponding solvated-ion reaction $CH_3OH_2^+\cdot CH_3OH$ with methanol proceeds only by association with no displacement. Upper limits for the rate constants for displacement are $<3 \times 10^{-12}$ and $<1.5 \times 10^{-12}$ $cm^3\ s^{-1}$ at 300 and 450 K, respectively. The suppression of the displacement channel by solvation of the reactant ion may be attributed to the difficulty of transferring the solvent from the reactant to the product ion within the intermediate—a generalization that appears to be successful in correlating the effect of solvation on gas-phase ion–molecule reactions. The quenching of the displacement reaction by solvation would seem to be consistent with an S_N2 type of mechanism for the displacement.

The association reactions of $CH_3OH_2^+$, $CH_3OH_2^+\cdot CH_3OH$, and $(CH_3)_2OH^+$ with methanol in He buffer gas were studied as a function of pressure in the range from 0.26 to 0.59 Torr. The pressure dependence of the reaction of $CH_3OH_2^+$ at 300 K suggests that the pressure range employed corresponds to the falloff regime for this reaction. The third-order rate constants for the association reactions are significantly lower than those measured in the low-pressure limit in an ICR experiment,[4] but the differences are not surprising in light of the different buffer gases and pressure regimes of the two experiments.

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Registry No. $CH_3OH_2^+$, 17836-08-7; $(CH_3)_4OH^+$, 17009-82-4; CH_3OH, 67-56-1.

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