Low temperature reactions between stored ions and condensable gases: formation of protonated methanol via radiative association

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Abstract

A low temperature radio-frequency 22-pole ion trap has been combined with a molecular beam for studying ion-molecular association processes at low number densities and at temperatures where an effusive gas inlet cannot be used due to condensation. This paper reports the first experimental observation of CH$_3^+$ + H$_2$O association at an effective temperature of (50 ± 30) K and at He number densities ranging from 7 × 10$^{13}$ cm$^{-3}$ down to so low densities, 5 × 10$^{11}$ cm$^{-3}$, that radiative association is expected to be more probable than ternary collisions. The three body association rate coefficient has been determined as $k_3 = (5.8 \pm 0.4) \times 10^{-25}$ cm$^6$ s$^{-1}$. For radiative association, an upper limit for the rate coefficient has been estimated from the measurements, $k_r < 2 \times 10^{-12}$ cm$^3$ s$^{-1}$. This is at least one order of magnitude smaller than the value currently used in model calculations.

Introduction

The gas-phase chemistry in interstellar clouds is restricted by the low density and low temperature prevailing in these regions. Therefore, since the early times of model calculations [Herbst and Klemperer, 1973], only exothermic binary reactions without activation energy are accounted for. It also was generally assumed that the synthesis of many interstellar molecules is due to ion-molecular reactions since neutral reactions are often hindered by barriers. If, for certain products, no exothermic reaction path could be identified at all, the process of radiative association was included into the model calculations. The best known example is the start in the reaction chain of hydrocarbons with C or C$^+$. Here the only important way to produce a product in collisions with H or H$_2$ is the stabilization of the strongly bound CH$_2^+$ collision complex via spontaneous emission of a photon. There are several other reaction pathways where radiative association is assumed to be an important process [Herbst and Dunbar, 1991].

For atom-atom interactions, e.g., C$^+$ + H, the predicted radiative association rate coefficients are rather low, typically below 10$^{-18}$ cm$^3$ s$^{-1}$. For triatomic systems, such as H$^+$ + H$_2$ or C$^+$ + H$_2$, values of several 10$^{-15}$ cm$^3$ s$^{-1}$ can be obtained [Gerlich and Horning, 1992, Gerlich, 1993, 1994]. If a larger number of atoms is involved and if the collision complex corresponds to a chemically bound molecule, the complex life time, $\tau_c$, can become longer than the radiative life time of the complex, $\tau_r$. A typical example is C$_3$H$^+$ + H$_2$ [Sorgenfrei and Gerlich, 1994]. For even larger systems, it is often assumed that the collision partners just stick, i.e., every collision leads to an association product. In these cases radiative association can reach the saturation limit, i.e. a rate coefficient larger than 10$^{-9}$ cm$^3$ s$^{-1}$ [Herbst and Dunbar, 1991]. Such assumptions have been made to explain the formation of interstellar methyl alcohol that has been detected in large abundances in some interstellar clouds [Gottlieb et al., 1979]. Since the synthesis of this molecule on the surface of interstellar grains fails in producing a significant amount of methanol [Allen and Robinson, 1977] radiative association of CH$_3^+$ and H$_2$O followed by dissociative electron-ion recombination was proposed as most probable pathway to form CH$_3$OH [Smith and Adams, 1977]. The measured interstellar abundances imply that $k_r$ must be in the range $8 \times 10^{-12}$ cm$^3$ s$^{-1} < k_r R < 8 \times 10^{-8}$ cm$^3$ s$^{-1}$. In this equation $R$ denotes the fraction of CH$_3$OH molecules produced by the dielectronic recombination process, CH$_3$OH$^2+$ + e$^-$. Since there are no experimental data on this reaction, the models must rely on theoretical predictions [Herbst, 1980, 1985, Bates, 1983].

In order to study experimentally association one has to separate radiative and ternary processes by varying the neutral density of both reactant and buffer gas over a wide range of densities.
There are only a few techniques available which have sufficient sensitivity and flexibility to reach this goal. The most common techniques used in ion chemistry are the ion cyclotron resonance (ICR) apparatus and the Paul trap. In 1986, Dunn et al. used a low pressure Penning ion trap which could be operated at temperatures below 10 K. This leads to the first direct measurements of radiative association for small systems [Barlow et al., 1986]. The development of traps with large field free volume by Gerlich [Gerlich, 1992] allows additionally cooling of ions by collisions with buffer gas down to 10 K. For several systems of fundamental importance, radiative and ternary association rate coefficients have been measured [Gerlich and Horning, 1992, Schlemmer et al., 2002a]. In this trapping experiment the neutrals are present as ambient gas surrounded by cold walls. Unfortunately cryogenic temperatures restrict the choice to few species. Therefore at low temperatures for more complicated target molecules are only theoretical methods and extrapolation of experimental results at 300 K available [Smith and Adams, 1978a].

In recent years, several attempts have been made to extend the versatility of low temperature trapping machines by combining them with atomic and molecular beams [Haufler, 1996, Luca, 2001, Schlemmer, 2002b]. Especially important for astrochemical applications are the combinations of a trap with an H-atom beam [Luca, 2002] or with a beam of carbon atoms [Cermak et al., 2002]. In order to cool down the target molecules supersonic expansion in free jet sources is used. Rotational temperatures of few K are obtainable. Also the translational temperature can be very low; nonetheless the mean velocity of the neutrals in the laboratory frame can be quite high. Using the seeding technique, i.e. expanding light molecules in a heavy buffer gas, the velocity of these molecules is slowed down to that of the buffer gas. By variation of the expansion conditions, the collision energy can be varied in the meV range.

In the present paper we focus on the reaction CH$_3^+$ + H$_2$O $\rightarrow$ CH$_5$O$^+$ + hv. In this collision the strongly bound protonated methanol is formed in a highly exothermic reaction, $\Delta H^\theta = -2.9$ eV. This radiative association process can be regarded as a sequential process represented by the following steps:

$$\rightarrow \text{CH}_3\text{O}^+ + \text{hv} \quad (1)$$

$$\text{CH}_3^+ + \text{H}_2\text{O} \rightarrow \left(\text{CH}_3\text{O}^+\right)^* \rightarrow \text{CH}_3^+ + \text{H}_2\text{O} \quad (2)$$

First, the collision complex $(\text{CH}_3\text{O}^+)^*$ is formed in a highly excited state. The rate coefficient for forming this complex is usually approximated by the collision rate coefficient, $k_c$, which can be predicted by Langevin or ADO theories. In the second step $(\text{CH}_3\text{O}^+)^*$ can either be stabilized by emission of a photon (1) with a rate $1/\tau_r$, or dissociate back to its constituents (2) with a rate $1/\tau_d$. More details can be found in [Gerlich and Horning, 1992]. In most laboratory experiments these two pathways compete in addition with ternary association,

$$\left(\text{CH}_3\text{O}^+\right)^* + \text{M} \rightarrow \text{CH}_5\text{O}^+ + \text{M}. \quad (3)$$

In this process, energy is removed from the collision complex via a collision with the third body M. At low enough densities, the overall rate coefficient for forming stable CH$_5$O$^+$ products, $k^*$, can be approximated by $k^* = k_3 [\text{M}] + k_o$, where $k_3$ is the ternary rate coefficient. As discussed in detail in [Gerlich and Horning, 1992] the ternary association rate coefficient can be approximated by $k_3 = k_c \tau_d k_M f$ where $k_M$ is the binary rate coefficient for a collision of the complex with M and $f$ represents the fraction of such collisions that leads to stabilization of the collision complex. Since usually $1/\tau_d >> 1/\tau_r$, radiative association is given by $k_r = k_c \tau_d / \tau_r$.

**Experimental**

The measurements have been performed in a radio-frequency 22-pole ion trap which has been described elsewhere [Gerlich, 1992, 1995]. Therefore only the main features are briefly repeated here. The experimental setup is shown in Fig. 1. Ions are confined by an inhomogeneous rf field in a region surrounded by walls cooled by a closed cycle refrigeration system. The nominal temperature of the trap can be varied between 10 K and 300 K. The translational and internal degrees of freedom of the ions are coupled to the cold environment by inelastic collisions with a buffer gas, usually helium. This gas has typically number densities in
the range of $10^{11} \text{ cm}^{-3}$ to $10^{14} \text{ cm}^{-3}$. Ions are sequentially injected, stored and extracted from the trap via pulsed entrance and exit electrodes closing the linear multipole on the sides. The storage time can be varied from microseconds to minutes or more. In the absence of target gas the mean decay time is determined by reactions with background gas, the pressure of which is estimated to be below $10^{-11} \text{ mbar}$ at 10 K. For the study of reaction processes target gas is added to the buffer gas and by choosing a suitable combination of number densities and storage time rates of rather fast as well as very slow bimolecular reactions can be measured. This makes this device unique because ternary and radiative association can be distinguished. In the present case CH$_3^+$ ions were prepared externally in an electron-impact storage ion source [Gerlich, 1992], mass selected and formed to a very slow beam before entering the trap. A slow and rotationally cold molecular beam has been produced by supersonic expansion of H$_2$O seeded in Xe buffer gas. The gas beam passes through the trap along its axis. The jet was pulsed at a frequency of 1 kHz. The H$_2$O density was calibrated directly in the trap by measuring the rate for charge transfer from H$_2$O to N$^+$ and using a rate coefficient of $5 \times 10^{-9} \text{ cm}^3 \text{s}^{-1}$. This corresponds to the value determined with the help of a merged beam apparatus at a collision energy which is adequate for describing our experimental conditions [Wick, 1994]. An average density of $8 \times 10^7 \text{ cm}^{-3}$ was derived. The temporal width of the gas pulses is about 160 µs, what gives a momentary density of about $6.5 \times 10^8 \text{ cm}^{-3}$. The jet nozzle had a diameter of 0.1 mm and typically the stagnation pressure was 365 mbar for Xe with a 7% admixture of H$_2$O. Under similar conditions a rotational temperature of ~ 50 K has been achieved [Page et al., 1988]. In a full expansion, a kinetic energy of 13 meV should be achieved for H$_2$O. Time of flight test was carried out with different Xe/H$_2$O mixture to ensure the quality of the supersonic expansion. These tests showed a good agreement with theoretical estimates.

The effective temperature of the collision complex has been calculated using the assumption that all the energy contained in the different degrees of freedom of the reactants is distributed equally over all degrees of freedom of the collision complex. It is rather safe to assume that vibrational excitation of the reactants can be ignored at the low temperature of the ions and the neutrals. Therefore, the total energy of the collision complex is the sum of the rotational

![Figure 1: Cross sectional view of an 22-pole ion trap apparatus combined with a pulsed supersonic beam. The central element is the rf multipole trap [Gerlich, 1992], which can be cooled down to 10 K. Primary CH$_3^+$ ions are produced from methane by electron bombardment in an ion storage source, mass selected and injected to the trap filled with He buffer gas. The pulsed molecular beam of H$_2$O seeded in Xe is skimmed as indicated in order to avoid interaction with the cold surfaces. After a variable reaction time products are extracted, mass analyzed and counted.](image)
energies, $3/2 kT$, of each of the reactants, with $T_{\text{neutral}} = 50$ K, and $T_{\text{ion}} = 20$ K and the center of mass collision energy, $\sim 1.8$ meV. Assuming full mixing of the phase space, leads to the conclusion, that our non-equilibrium conditions are equivalent to a system which has been fully thermalized at 36 K. Since there are still some uncertainties in the real population of the rotational states in our pulsed supersonic beam, we conservatively report our measured rate coefficient to correspond to a thermal value which would be obtained at a temperature of $50 \pm 30$ K.

In the experiment, the ions have been stored each time for a period 2 s, i.e., the ion source has been operated at a frequency of 0.5 Hz. During the first 180 ms after injection, the primary CH$_3^+$ ions collided with the ambient He buffer gas and thermalized to the low temperature of the trap.

In Fig. 2, the temporal evolution of stored ions at [He] = 4.3 × 10$^{13}$ cm$^{-3}$ and [H$_2$O] = 8 × 10$^7$ cm$^{-3}$ (time averaged value). Solid lines are solutions of an adequate kinetic equation. The number of primary ions, CH$_3^+$, is almost unchanged since the reaction rate is very small. The number of association products, CH$_5^+$, increases linearly. In addition, some C$^+$, CH$^+$ and CH$_2^+$ are injected from the source. They are not shown but included in the sum, $\Sigma$. As discussed in the text they do not contribute directly to the product of interest.

Then, the pulsed H$_2$O jet was turned on for a duration of 1.8 s, i.e., several hundred pulses of the target gas vent across the stored ion cloud. After various storage times the exit electrode was lowered and the product ions were transferred via a quadrupole mass spectrometer to an MCP detector. A typical example of the temporal evolution of the stored ions is shown in Fig. 2. Due to the low number density of the target gas, the reaction rate is usually so low that the primary CH$_3^+$ ions do not drop significantly; nonetheless, the increase of association products CH$_5$O$^+$ can be observed. Some other ions, C$^+$, CH$^+$, CH$_2^+$, were present in the trap during the measurements but they either did not contribute to CH$_5$O$^+$ or were in so minute concentration that their contribution is insignificant (CH$_3^+$: max contribution < 10$^{-12}$ cm$^3$ s$^{-1}$). Each measurement point was averaged over a large number of cycles and the whole process was repeated for He densities in the range of 5 × 10$^{13}$ cm$^{-3}$ to 7 × 10$^{13}$ cm$^{-3}$. Dividing the production rate by the average H$_2$O density, the effective rate coefficient, $k^*$, for CH$_5$O$^+$ production is obtained and is plotted in Fig. 3 as function of He density.
Results and discussion

The linear dependence of $k^*$ clearly shows that the collision complexes are stabilized by collisions with He and ternary association predominates. From the slope the ternary rate coefficient was determined, $k_3 = (5.8 \pm 0.4) \times 10^{-25}\text{ cm}^6\text{s}^{-1}$. This result is consistent with data obtained with swarm technique, where due to high buffer gas densities and saturation only the lower limits of $k_3$ were obtained for different temperatures, see Tab. 1.

The linear dependence of $k^*$ slightly levels off at low densities, see Fig. 3. This is emphasized by the solid line which represents the function $k^* = k_3 [\text{He}] + k_r$ with $k_3$ from Tab. 1 and $k_r = 5 \times 10^{-13}\text{ cm}^3\text{s}^{-1}$. This value, however, has to be taken with some precaution because it may deviate in both directions from the real thermal value $k_r (50\text{ K})$. A careful inspection of the data in Fig. 3 can lead to the conclusion, that, at the lowest number densities reached experimentally, ternary association still prevails. This means that radiative association is even less efficient than deduced from the fit. On the other hand the real value of $k_r$ may be larger because, at low buffer gas densities, the ions may not undergo enough collisions for cooling them to the ambient temperature. These problems will be solved in a future experiment by adding a pulsed gas inlet or by increasing the initial relaxation time.

Despite these uncertainties, our result, which can be summarized by $k_r ((50 \pm 30)\text{ K}) < 2 \times 10^{-12}\text{ cm}^3\text{s}^{-1}$ is very important because it shows that radiative association of the two threeatomic molecules which certainly can form a strongly bound product, may not be as efficient as assumed in current model calculations describing interstellar chemistry. The derived value is significantly smaller than the theoretical estimates. For example, at 50 K, Herbst proposes a value of $1.2 \times 10^{-10}\text{ cm}^3\text{s}^{-1}$ [Herbst, 1985] while Bates reports a temperature

**Figure 3**: Dependence of the effective rate coefficient for $\text{CH}_3^+ + \text{H}_2\text{O}$ association as a function of the He number density. The ion trap was operated at 20 K. The average $\text{H}_2\text{O}$ density was $8 \times 10^7\text{ cm}^{-3}$. The measured values have been approximated by the function $k^* = k_3 [\text{He}] + k_r$ (thick solid line) leading to the values presented in Tab. 1 and $k_r = 5 \times 10^{-13}\text{ cm}^3\text{s}^{-1}$. The thin linear line simulates pure ternary regime.
dependence, leading to $1 \times 10^{-11}$ cm$^3$ s$^{-1}$ [Bates, 1983]. Smith extrapolates experimental value obtained at 300 K with estimated temperature dependence of $\tau_d$ and reports $k_r > 2 \times 10^{-9}$ cm$^3$ s$^{-1}$ [Smith and Adams, 1978a].

Table 1: Ternary rate coefficients measured with various methods and at different temperatures

<table>
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<th>$k_3 / \text{cm}^6\text{s}^{-1}$</th>
<th>T / K</th>
<th>$[\text{He}] / \text{cm}^{-3}$</th>
<th>method</th>
<th>reference</th>
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<td>$&gt; 3 \times 10^{-26}$</td>
<td>300</td>
<td>$6.4 \times 10^{15}$ - $2.6 \times 10^{16}$</td>
<td>SIFT</td>
<td>[Smith and Adams, 1978b]</td>
</tr>
<tr>
<td>$&gt; 7 \times 10^{-26}$</td>
<td>23</td>
<td>$4.7 \times 10^{16}$</td>
<td>CRESU</td>
<td>[Voulot et al., 2002]</td>
</tr>
<tr>
<td>$&gt; 6.8 \times 10^{-26}$</td>
<td>36</td>
<td>$5.3 \times 10^{16}$</td>
<td>CRESU</td>
<td>[Voulot et al., 2002]</td>
</tr>
<tr>
<td>$&gt; 4 \times 10^{-26}$</td>
<td>72</td>
<td>$6.0 \times 10^{16}$</td>
<td>CRESU</td>
<td>[Voulot et al., 2002]</td>
</tr>
<tr>
<td>$5.8 \times 10^{-25}$</td>
<td>50</td>
<td>$5 \times 10^{11}$ - $7 \times 10^{13}$</td>
<td>MB-22PT</td>
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</tr>
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This huge discrepancy raises a number of questions concerning the validity of the assumptions made in the theoretical models, but it also calls for a careful analysis of the experiment in order to exclude possible errors. In our case checks were made to ensure that the ion cloud could be completely attenuated by reaction with the water jet indicating the absence of background. The possibility of further reaction of the products with the water molecules is precluded by the low density of the jet. The main concern is in fact the actual energy the collision complexes have in our experiment. The largest uncertainty concerns the internal energy of the water molecules. But even in the worst case the effective temperature is within the limit given by 50 ± 30 K.

Using in the above discussed model $k_r = 5 \times 10^{-9}$ cm$^3$ s$^{-1}$ and $k_{He} = 5.5 \times 10^{-10}$ cm$^3$ s$^{-1}$ and taking $f = 1$ we get from $k_r = 5.2 \times 10^{-25}$ cm$^6$ s$^{-1}$ the dissociation lifetime $\tau_d = 0.2 \mu$s. Similarly the radiative lifetime can be calculated from the measured $k_r$, resulting in $\tau_r = 2$ ms. This result is in good agreement with the radiative lifetime of some ms used in calculations; but in order to get Herbst value of $1.2 \times 10^{-10}$ cm$^3$ s$^{-1}$ at 50 K the complex lifetime must be of the order of 0.1 ms which is much longer than our measured value. With such a long complex lifetime, radiative association would be clearly observed in our apparatus. It finally should be added that stabilization of the collision complex via collisions with the Xe seeding gas also can be excluded since the temporal Xe density of $1 \times 10^{10}$ cm$^{-3}$ was so low that for a rate coefficient of $10^{-9}$ cm$^3$ s$^{-1}$ the time constant of 100 ms is much longer than the complex lifetime.

Conclusion

Combining a low temperature ion trap with a supersonic beam allows one to study radiative association processes between cold stored molecules and cold neutrals at collision energies of a few meV. In the case of CH$_3^+$ and H$_2$O, the experimental conditions were such that during even for complex lifetimes longer than 1 ms no perturbation could interfere with the collision complex. Therefore we conclude that the radiative association rate coefficient is much smaller than the value used in current models and that one has to look for other reaction paths for forming protonated methanol or for neutral channels leading directly to methanol. From the present results it also can be concluded that more measurements are needed. Future plans include to vary the expansion conditions in order to achieve lower and better defined internal temperatures of the molecular reactants. It is also planned to study radiative association in CH$_3^+$ + CO collisions. In this case CO can be leaked into the trap both from an effusive gas inlet and from the supersonic beam. This will allow to compare real thermal conditions with results from the attractive new experimental method.

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