# Variable Temperature Rate Studies for the Reaction $H_3O^+ + (C_2H_2)_2$ Measured with a Coaxial Molecular Beam Radio Frequency Ring Electrode Ion Trap

Mark A. Smith,<sup>\*,†,‡,§</sup> Bing Yuan,<sup>†</sup> and Andrei Sanov<sup>†</sup>

<sup>†</sup>Department of Chemistry and Biochemistry, University of Arizona, 1306 East University Boulevard, Tucson, Arizona 85721, United States

<sup>‡</sup>Department of Planetary Science, Lunar and Planetary Laboratory, University of Arizona, 1629 East University Boulevard, Tucson, Arizona 85721, United States

<sup>§</sup>Department of Chemistry, University of Houston, Houston, Texas 77204, United States

**ABSTRACT:** The independent molecule and ion temperature dependence of the rate coefficient for the  $H_3O^+$  and  $(C_2H_2)_2$  reaction producing  $C_2H_5O^+$  are determined using a coaxial molecular beam radio frequency ring electrode ion trap (CoMB-RET). The  $H_3O^+$  temperature is varied from 25 to 170 K, while the equilibrated  $C_2H_2/(C_2H_2)_2$  beam temperatures sampled are 160, 180, 200, and 220 K. The rate coefficient of the  $H_3O^+ + (C_2H_2)_2$  reaction is determined to be  $4.0 \times 10^{-10} \times (T_{react}/300)^{-2.5}$  in the reaction temperature



Article

pubs.acs.org/JPCA

4.0 ×  $10^{-10}$  ×  $(T_{\text{react}}/300)^{-2.5}$  in the reaction temperature range of  $T_{\text{react}} = 114-187$  K. The H<sub>3</sub>O<sup>+</sup> and C<sub>2</sub>H<sub>2</sub> radiative association reaction is found to have a rate coefficient below 1 ×  $10^{-13}$  cm<sup>3</sup>·s<sup>-1</sup> at 187 K. This result is consistent with Herbst's experimental determination.

## INTRODUCTION

Production of oxygenated organics in the interstellar medium (ISM) represents the first step toward the abiotic generation of molecules critical to life. The production mechanisms are important for understanding the plethora of complex organics now known to exist in the ISM<sup>1,2</sup> as well as on other planetary bodies beyond Earth. Acetaldehyde, CH<sub>3</sub>CHO, is ubiquitous in the ISM and has been detected in a variety of environments since it was first observed in 1973. These environments include hot cores, dark clouds, and regions of star formation.<sup>3,4</sup>

Radiative association plays a significant role in the gas-phase synthesis of molecular ions in dense interstellar clouds and planetary atmospheres.<sup>5–9</sup> The radiative association reaction between  $H_3O^+$  and the  $C_2H_2$  monomer is considered as one of the most important steps for acetaldehyde production in the interstellar medium

$$H_3O^+ + C_2H_2 \to C_2H_5O^+ + h\nu$$
 (1)

followed by electron recombination to produce CH<sub>3</sub>CHO.<sup>4</sup> Protonated water is one of the most stable forms of oxygencontaining molecular ions, and understanding its reactive potential with small hydrocarbons present in natural environments is critical.

Herbst and co-workers investigated both radiative and threebody  $H_3O^+ + C_2H_2$  association reactions in 1989.<sup>9,10</sup> The rate coefficient of eq 1 deduced from their three-body experimental value was  $4.75 \times 10^{-13}$  cm<sup>3</sup>·s<sup>-1</sup> at 50 K, 2 orders of magnitude lower than the theoretical prediction. Fairley and co-workers studied the three-body  $H_3O^+ + C_2H_2$  association reaction at 300 K using the Canterbury selected ion flow tube (SIFT) system in 1996,<sup>4</sup> and the rate coefficient that they measured was consistent with Herbst's result. To date, there has not been a direct rate coefficient measurement of radiative association for  $H_3O^+ + C_2H_2$ . Such direct determination is critical for the refinement of current models and insight into the generation of oxygenated organics in the ISM.

Molecular complexation of organic molecules is the basis for the generation of organic haze on Titan, as well as the possible first steps in the generation of organic condensation clouds in its stratosphere. It has been proposed that molecular dimers, specifically of diacetylene, exist in the dense atmosphere of Titan and may act as red-shifted chromophores.<sup>11</sup> Such chromophores may extend the photochemically important spectral range into the normal ultraviolet and thereby extend active photochemistry to lower, denser altitudes in the Titan atmosphere. In the low-temperature environment of Titan's atmosphere, molecular dimers and clusters can exist in appreciable concentrations to quite high altitudes. Their potential presence in the ionosphere would allow for new ion–molecule reaction mechanisms for the buildup of polyatomic organics in low-density binary chemical regimes.

Many weakly bound dimers and higher polymers have been observed in the ISM.<sup>12,13</sup> Owing to its polarizability, acetylene is one of the simplest organic molecules that readily form

```
Received:June 16, 2012Revised:August 31, 2012Published:September 4, 2012
```



Figure 1. Schematic of a coaxial molecular beam radio frequency ring electrode ion trap (CoMB-RET). (1) U-shaped radio frequency trap/electron bombardment ion source. (2) Quadrupole bender. (3) Quadrupole ion guide. (4) Mass selection quadrupole. (5) Gas inlet and pulsed value. (6) Ring electrode trap. (7) Multichannel plate detector. (8) Cryostat. (9) Effusive nozzle. (10) Skimmer. (11) Shutter. (12) RGA detector. (13) Cryopump. (14) Turbopump.

clusters. These clusters are important in low-temperature environments because of their inherent reactivity and ability to create larger hydrocarbons in reactions with ions and radicals.<sup>14</sup>

Oxygen in Titan's atmosphere is known to be present in the form of CO (50 ppm), while the reducing nature of the methane-rich atmosphere makes small concentrations of water vapor almost assured. With the high fractional ionization in these media, protonated water is expected to be a significant component of any of these dynamic plasmas. As such, the role of H<sub>3</sub>O<sup>+</sup> in the incorporation of oxygen into organic molecules is potentially an important channel in the production of complex prebiotic organics. Although the majority of reactions of protonated water with organic molecules involve simple proton transfer, removing oxygen from the ion chemistry, the potential for more complex chemistry with molecular clusters is intriguing. In the simplest form, ligand exchange provides a mechanism for the production of oxygen-containing organic ions. More profound reactions involving oxygen-carbon bonds can be thermodynamically favorable and may provide a key pathway for covalent oxygen incorporation into organics in rarefied environments. In the case of oxygen-containing ion complexes, subsequent ion-electron recombination will also provide possible mechanisms for carbon-oxygen bond formation.

In this paper, we report a temperature-dependent rate coefficient study for  $H_3O^+$  reactions with  $C_2H_2$  (reaction 1) and  $(C_2H_2)_2$ .

$$H_3O^+ + (C_2H_2)_2 \rightarrow C_2H_5O^+ + C_2H_2$$
 (2)

Both reactions produce  $C_2H_5O^+$ . The measurements are carried out in a ring electrode trap (RET) using collisions between  $H_3O^{\scriptscriptstyle +}$  at a variety of trap temperatures and a coaxial  $C_2H_2/$   $(C_2H_2)_2$  molecular beam with independent variation of the beam temperature.

## EXPERIMENTAL SECTION

A coaxial molecular beam ring electrode trap employed in this study has been specifically developed to minimize trap interactions with ion source gas or background contaminations. The trap in the current configuration is a ring electrode trap, which has been previously described in the literature.<sup>15</sup> The instrument is shown schematically in Figure 1.

The  $H_3O^+$  reactant ions are produced from  $H_2O$  vapor (5 ×  $10^{-5}$  Torr) by electron impact ionization in a U-shaped radio frequency source trap. The exit lens potential on the source trap is pulsed to ground to produce an ion packet (1 ms duration), which then passes through a 90° dc quadrupole bender, which separates the ion packet from the effusive gas exiting the source. After the bender, ions are focused into a double-quadrupole mass guide/selector. The first quadrupole is operated in RF-only mode, working as an ion guide, and the second quadrupole operates in mass selection mode, tuned to 19 amu, rejecting  $H_2O^+$  and other mass ions. After passing another electrostatic lens set, the mass-selected ion beam is turned 90° in a second dc quadrupole bender, bringing it coaxial with both the RET axis and the axis of the molecular beam.

Ions from this pulse are injected into the RET at low energy (<0.1 eV) by dropping the entrance guard ring potential. After a 1 ms ion loading period, the potential on the trap entrance is increased. The RET is mounted on the end of a thermally regulated liquid He cryostat (Janis Model ST-400), which is used in this study to vary the trap temperature between 25 and

400 K. Buffer gas admitted to the RET equilibrates to the defined wall temperature, as do the ions through buffer gas collisions.

The buffer gas inlet line employs a pulsed valve, which opens 100 ms prior to ion loading for a 3 ms period and is used to admit He buffer. A typical time profile of the trap pressure after one He buffer pulse is shown in Figure 2. The time scales of ion



**Figure 2.** Number density of helium in the RET after a single helium pulse. The highest He number density in the trap after a single pulse is  $1.8 \times 10^{14}$  molecule·cm<sup>-3</sup>, and the width of the He peak is about 150 ms. After 800 ms, all of the He buffer is pumped out. Ion loading, beam pulsing, and ion sampling time are all labeled in the figure. The beam pulsing time can be varied, depending on the different reaction times.

loading, beam pulsing, and ion sampling are also indicated in this figure. The highest number density of He in the trap is  $2 \times 10^{14}$  molecule·cm<sup>-3</sup>, the width of the density profile is approximately 150 ms, and it takes 800 ms to exhaust the majority of the He buffer. These conditions correspond to a maximum collision frequency between trapped ions and He buffer of  $3 \times 10^5$  s<sup>-1</sup> and an average number of collisions per ion experienced of approximately  $2 \times 10^4$  s<sup>-1</sup>, integrated across the buffer pulse. In previous studies, a buffer gas collision level of this magnitude was found to be effective in relaxing all degrees of freedom, and the internal temperature of ions was ultimately determined by the buffer collision temperature, which is close to the temperature of the trap walls.<sup>16,17</sup>

The cooled ions stored in the trap are then exposed to a chopped effusive beam of acetylene, containing C<sub>2</sub>H<sub>2</sub> monomers and molecular clusters, and the reaction takes place. The ion-molecule reaction period is typically regulated from several hundred milliseconds to several seconds. Following a determined reaction period, the electrostatic potential on the trap exit gate lens is dropped, and the remaining reactant and newly created product ions are allowed to enter the third quadrupole operated in mass selection mode, where they are accelerated, mass-selectively filtered, and detected using a fast microchannel plate (MCP) ion counting system. As demonstrated in these and earlier studies, the quadrupole analyzer has been tuned to demonstrate no measurable mass discrimination in the mass window from 15 to 75 amu. This is demonstrated by observing appreciable reaction extent across a temporal period much less than the ion trap loss period (around 40 s) with no significant change in the number of total ions detected.

The acetylene molecular beam source nozzle consists of a 40 mm long, 3.2 mm internal diameter (ID) tube terminating at a 1 mm thick wall with a 0.3 mm diameter aperture. This nozzle is mounted onto the end of a second thermally regulated

cryostat. The stagnation pressure of  $C_2H_2$  is 51 Torr. Under these conditions, the pressure drop across the 1 mm exit plate is very nearly the full 51 Torr stagnation condition, while the mean free path for neutral collisions in the aperture is 13  $\mu$ m. The thermally regulated beam expands into a chamber evacuated by a 10 000 L·s<sup>-1</sup> cryopump. The beam passes through a 0.5 mm orifice conical skimmer (Beam Dynamics, Inc.) mounted 20 mm downstream and enters a differentially pumped region (1000 L·s<sup>-1</sup> cryopump). The beam is then skimmed a second time, 300 mm downstream from the nozzle, using a 2 mm diameter flat aperture, and becomes coaxial with the trap.

In order to chop the effusive beam prior to the trap entrance, a regulated shutter (Schneider optics, Prontor magnetic shutter #0) is placed in the beam path at the second differential wall, which blocks better than 99.9% of all gas flow. The shutter is opened after the ions stored in the trap have been cooled and the He buffer gas is pumped out, allowing the ions to collide with the neutral beam molecules. The shutter is kept open for a time defining the reaction period in the trap. The center of the trap lies 450 mm away from the beam nozzle. The beam traverses the RET and exits without wall interactions through the 4 mm aperture exit gate lens. This is followed by a 6 mm aperture differential wall, a differentially pumped (250  $L\cdot s^{-1}$ ) quadrupole filter/ion detector, and a final 10 mm ID, 100 mm long tube directing the molecular beam into a beam dump pumped by a 70  $L\cdot s^{-1}$  turbopump. Here, the molecular beam terminates in the source chamber of a residual gas analyzer (RGA; Stanford Research Systems 200). The RGA is used to determine the beam flux, which is then calibrated to the RET neutral beam density using the calibration reaction  $N_2^+ + C_2H_2$ rate at 300 K. The acetylene beam density in the RET trap in this study is between  $1.41 \times 10^9$  and  $1.93 \times 10^9$  molecule cm<sup>-3</sup>, depending on the nozzle temperatures.

#### RESULT AND DISCUSSION

(1). Calibration Reaction:  $N_2^+ + C_2H_2$ . The highly exothermic charge-transfer reaction<sup>18</sup>

$$N_2^+ + C_2 H_2 \rightarrow N_2 + C_2 H_2^+$$
 (3)

is used to determine the number density of the acetylene beam in the RET. At 300 K, the rate coefficient of this reaction is 5.50  $\times 10^{-10}$  cm<sup>3</sup>·s<sup>-1</sup>,<sup>19</sup> and it is expected to be temperatureindependent. In addition to the primary reaction 3, its products may undergo the following secondary reactions:

$$C_2H_2^+ + C_2H_2 \rightarrow C_4H_2^+ + H_2$$
 (4)

$$C_2H_2^+ + C_2H_2 \to C_4H_3^+ + H$$
 (5)

The combined rate coefficient for reactions 4 and 5 is  $1.4 \times 10^{-9} \text{ cm}^3 \cdot \text{s}^{-1.19-21}$  As both of these reactions consume the product ions in reaction 3,  $C_2H_2^+$ , the sum of the observed  $C_4H_2^+$  and  $C_4H_3^+$  ion signals, combined with  $C_2H_2^+$ , is used for determination of the net rate of reaction 3.

Rate coefficients of radiative association reactions

$$C_4H_2^+ + C_2H_2 \to C_6H_4^+ + h\nu$$
 (6)

$$C_4 H_3^{+} + C_2 H_2 \rightarrow C_6 H_5^{+} + h\nu$$
 (7)

are  $2.8 \times 10^{-10}$  and  $2.0 \times 10^{-10}$  cm<sup>3</sup>·s<sup>-1</sup>, respectively.<sup>20–22</sup> In our reaction system, the observed changes in C<sub>6</sub>H<sub>4</sub><sup>+</sup> and C<sub>6</sub>H<sub>5</sub><sup>+</sup>

## The Journal of Physical Chemistry A

signals are small within the noise, and these products are neglected.

The calibration reaction 3 was studied at different beam temperatures, as well as by independently varying the ion temperature. One series of measurement was carried out with beam temperatures of 300, 250, 200, 180, and 160 K, while the ion temperature was set at 300 K. In the other series, the beam temperature was fixed at 160 K, while the ion temperature was varied between 80 and 300 K. In all of these measurements, the beam stagnation pressure was kept constant at  $(51 \pm 1)$  Torr. Under these conditions, the acetylene partial pressure reading at the RGA remained constant  $(1.20 \pm 0.10) \times 10^{-8}$  Torr, indicating that the flux of the molecular beam was constant, while its number density varied inversely with the square root of the beam temperature.

For ion–molecular beam reaction, the reaction rates are examined in regard to the reaction temperature  $T_{\text{react}}$  defined in our other studies<sup>23</sup> as

$$T_{\text{react}} = \left(\frac{3}{15}\right) T_{\text{coll}} + \left(\frac{3}{15}\right) T_{\text{ion}} + \left(\frac{9}{15}\right) T_{\text{b}}$$
(8)

$$T_{\rm coll} = \frac{T_{\rm ion}m_{\rm b} + T_{\rm b}m_{\rm ion}}{m_{\rm ion} + m_{\rm b}}$$
(9)

where  $T_{\rm b}$  and  $T_{\rm ion}$  are the molecular beam and ion temperatures, respectively, while  $m_{\rm b}$  and  $m_{\rm ion}$  are the corresponding molecular masses.  $T_{\rm coll}$  in eq 9 defines the translational temperature coresponding to the ion-molecule center-of-mass collision energy.<sup>17</sup> The second and third terms in eq 8 represent the mean (moment) of energy brought to the collision by internal degrees of freedom of the ion and neutral molecule, respectively. With 3 internal degrees of freedom in  $N_2^+$  and 9 for  $C_2H_2$ , we add the 3 relative collisional degrees of freedom, for a total of 15 degrees of freedom in the reaction system potentially available to participate in the chemical transformation. A given collision on average delivers a weighted energy, described here in terms of the temperatures corresponding to the three energy baths, collisional translation, ion (internal), and beam neutral (internal). The measured rate coefficient of the calibration reaction 3 as a function of reaction temperature is plotted in Figure 3. The result indicates that the rate coefficient of the calibration reaction is indeed temperature-independent, supporting this analysis.

From reaction 3, the beam density of acetylene in the RET in this study is determined to be  $1.41 \times 10^9$  molecules cm<sup>-3</sup> at a beam temperature of 300 K. In addition, as discussed below, it is found that at a beam temperature of 300 K, there is 0.05% of acetylene dimer in the molecular beam, while at 160 K, the dimer fraction increases to 0.6%. The dimer present in the beam is likely to react with N<sub>2</sub><sup>+</sup> to produce C<sub>4</sub>H<sub>3</sub><sup>+</sup> and C<sub>4</sub>H<sub>2</sub><sup>+</sup> at a rate coefficient nearing the capture rate, which is of the same magnitude as the rate coefficient of the C<sub>2</sub>H<sub>2</sub><sup>+</sup> + C<sub>2</sub>H<sub>2</sub> ion–molecule reaction. However, as the dimer fraction in the beam is less than 1.0%, the effect of acetylene dimer in the calibration analysis of beam density is insignificant.

(2).  $H_3O^+ + C_2H_2$  and  $H_3O^+ + (C_2H_2)_2$  Reactions. The  $H_3O^+ + C_2H_2$  reaction was studied in our system by independently varying the molecular beam and ion temperatures. Representative results are presented in Figures 4 and 5. Figure 4 shows the growth of  $C_2H_5O^+$  product ions observed in the trap upon exposure of  $H_3O^+$  ions to a  $C_2H_2$  beam. Figure 5 shows the measured second-order rate coefficient  $k'(T_{react})$  for



**Figure 3.** Rate coefficient of the observed calibration reaction  $N_2^+ + C_2H_2$  as a function of reaction temperature from 134 to 299 K. In these measurements, the acetylene beam flux is held constant as measured by the RGA. The number density of the acetylene beam at 160 K is  $1.93 \times 10^9$  molecule·cm<sup>-3</sup> and is inversely proportional to the square root of the beam temperature. The reaction temperature is defined in eq 8. (blue  $\blacklozenge$ ) The trap temperature is 298 K, while the beam temperature is varied from 160 to 300 K. (pink  $\blacksquare$ ) The trap temperature is 160 K.



**Figure 4.** The number of reactants  $H_3O^+$  and products  $C_2H_5O^+$  as a function of trapping time at a trap temperature of 80 K and a beam temperature of 200 K. The number density of the molecular beam is  $1.72 \times 10^9$  molecule·cm<sup>-3</sup>. (blue  $\blacklozenge$ )  $H_3O^+$  ions; (pink  $\blacksquare$ )  $C_2H_5O^+$  ions.



**Figure 5.** Second-order rate coefficient measurements based on the acetylene monomer density  $k'(T_{\text{react}})$  for C<sub>2</sub>H<sub>5</sub>O<sup>+</sup> product formation in reaction of H<sub>3</sub>O<sup>+</sup> with the components of the acetylene beam. The rate coefficients are determined using the acetylene beam density. The lines in the figure are simple nonlinear fits to the data to guide the eye. (blue ♦) The trap temperature is 80 K, while the beam temperature is varied from 160 to 220 K. (pink ■) The trap temperature is 125 K, while the beam temperature is varied from 160 to 220 K. (brown ▲) The trap temperature is varied from 25 to 170 K, while beam temperature is 160 K.

product formation based on the acetylene monomer density in the trap at different reactions temperatures. The reaction temperature is defined similar to eq 8, which for the  $H_3O^+ + C_2H_2$  reaction, must be written as

$$T_{\text{react}} = \left(\frac{3}{21}\right) T_{\text{coll}} + \left(\frac{9}{21}\right) T_{\text{ion}} + \left(\frac{9}{21}\right) T_{\text{b}}$$
(10)

As seen in Figure 5, with a constant molecular beam temperature, the reaction rate shows a slight increase as the ion temperature decreases. However, when the ion temperature is held constant, the reaction rate increases dramatically with decreasing temperature of the molecular beam. Therefore, the reaction rate exhibits a strong dependence on  $C_2H_2$  beam temperature while being only weakly dependent on the temperature of the ions. Under the present conditions, production of  $C_2H_5O^+$  from acetylene could only be accounted for by radiative association.

According to Herbst and Bates, the temperature dependence of rate coefficient for radiative association is given by

$$k_{\rm ra} \propto T^{-(l/2+\delta)} \tag{11}$$

where *l* is the number of rotational degrees of freedom of all of the reactants and  $\delta$  is a typically small correction factor ( $\delta \ll 1$ ) accounting for the product stabilization step.<sup>8,24–26</sup> Equation 11 describes the behavior of many known association rate coefficients well.

Typically, the limiting values of the exponent *b* in eq 11 ( $b = l/2 - \delta$ ) are b < 3. For the H<sub>3</sub>O<sup>+</sup> + C<sub>2</sub>H<sub>2</sub> reaction system, the theoretical limit of *b* is 2.5 (including three rotational degrees of freedom for H<sub>3</sub>O<sup>+</sup> and two for the linear C<sub>2</sub>H<sub>2</sub> molecule, neglecting  $\delta$ ). If assuming that all of the C<sub>2</sub>H<sub>5</sub>O<sup>+</sup> products observed in the experimental system are from radiative association reaction 1, it is determined that the experimental value of the exponent in eq 11 is around 1 with respect to ion temperature, which is a reasonable value if some of the rotational degrees of freedom are not coupled in the reaction. In regard to the molecular beam temperature, the observed exponent is near 8.5. This high exponent value cannot be explained through Herbst and Bates' model and appears physically unreasonable by any statistical reaction model.

Attempting to explain the high exponents (b > 5) observed in some association reactions, Viggiano found that the assumption of a unit vibrational partition function in Herbst's model in eq 11 is not valid in certain temperature ranges, and the contribution of reactant vibrational degrees of freedom sometimes cannot be neglected. The temperature-dependent rate coefficient of the radiative association reaction in Viggiano's model takes the form

$$k_{\rm ra} \propto T^{-(l/2+\delta)} \prod_i \left[1 - \exp(-h\nu_i/kT)\right]$$
(12)

Viggiano's model could explain some of the known association reactions with high exponent values<sup>27,28</sup> at the high-temperature range. The vibrational contribution of reactants in radiative association reactions was also discussed by Dunbar.<sup>29,30</sup> The total internal partition function of the acetylene molecule in the reaction temperature range can be calculated from Herman<sup>31</sup> and applied to the Viggiano model. The temperature dependence of the acetylene internal state distribution cannot account for anything near the rate coefficient exponent observed.

Therefore, it appears that the  $C_2H_5O^+$  products do not derive from the radiative association reaction only. A possible additional channel is the reaction of  $H_3O^+$  with the acetylene dimer present in the gas flow. What's more, at a trap temperature of 80 K and beam temperature of 160 K, product ions,  $C_4H_7O^+$ , are observed in the reaction system (near 10% compared to  $C_2H_5O^+$  products). The existence of  $C_4H_7O^+$ would appear to be due to displacement of  $C_2H_2$  from ( $C_2H_2$ )<sub>3</sub>, supporting the effect of clusters. We hypothesize that  $C_2H_5O^+$  products observed at low molecular beam temperatures are due to dimer reaction and that higher-order cluster derivatives cannot account for this product. It is also verified in part 3 of this section that less than 1% of  $C_2H_5O^+$  products are created by the radiative association reaction.

A quantitative model for the acetylene dimer and monomer equilibrium was proposed by Colussi and co-workers<sup>12</sup> in 1994 based on spectroscopic observation. In the equilibrium system

$$2\text{HCCH} \Leftrightarrow (\text{HCCH})_2 \tag{13}$$

the dimer to monomer ratio  $P_{\rm d}/P_{\rm m}$  is given by the expression

$$\frac{P_{\rm d}}{P_{\rm m}} = K_{\rm p}(T)P_{\rm m}\frac{f_{\rm m}^{\ 2}}{f_{\rm d}}$$
(14)

where  $K_{\rm p}(T)$  is the equilibrium constant of eq 13 in pressure units,  $P_{\rm d}$  is the partial pressure of the dimer,  $P_{\rm m}$  is the partial pressure of the monomer, and  $f_{\rm m}$  and  $f_{\rm d}$  are the fugacity coefficients of the monomer and dimer, respectively. For acetylene,  $f_{\rm m}^2/f_{\rm d} \approx 0.99.^{12}$  In Colussi's model,  $K_{\rm p}(T)$  can be simplified as

$$K_{\rm p}(T) = 6.7T^{-4}Q(z) \cdot \exp\left(\frac{D_0}{kT}\right)$$
(15)

where  $K_p(T)$  is in units of atm<sup>-1</sup>,  $D_0$  is the dimer binding energy, and Q(z) is the partition function.

Before calculating the acetylene dimer fraction  $P_d/P_m$  in eq 14 from our beam conditions, it is important to verify that the partial pressure of the acetylene monomer  $P_m$  in the molecular beam is determined by the stagnation conditions and does not change significantly during passage through the source nozzle. The pressure drop in the nozzle is completely across the 1 mm thick aperture, which takes  $2 \times 10^{-7}$  s for a molecule to transit.

This transit time should be compared to the time scale of dimer dissociation. To estimate the latter, we express the equilibrium constant  $K_p(T)$  of eq 15 as the association rate coefficient for the monomers producing dimers,  $k_a$ , divided by the dimer dissociation rate coefficient,  $k_d$ . Using  $K_p(T) = k_a/k_d$ , the dimer dissociation rate coefficient,  $k_d$ , can be calculated from  $K_p(T)$  and  $k_a$ .

The value of  $k_a$  can be estimated using

$$k_{\rm a} = 145.5\sigma^5 q \sqrt{D_{\rm e}^2/kTm}$$
(16)

where  $\sigma$  is zero potential radius,  $D_e$  is the potential well depth, and q is the collision effectiveness, <sup>32,33</sup> which is

$$q = 0.4 \cdot \exp\left(\frac{-0.6D_{\rm e}}{kT}\right) \tag{17}$$

For acetylene dimer,  $\sigma = 0.43 \text{ nm}$ ,<sup>34</sup> while  $D_e$  is between 478 and 610 cm<sup>-1</sup>.<sup>35–38</sup> Assuming the midrange value  $D_e = 544$  cm<sup>-1</sup>,  $k_a$  is calculated using eq 16 to be  $4.59 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$  at 160 K and  $6.39 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$  at 220 K. Then,  $K_p(T)$  calculated according to eq 15 at different binding energies, is between  $3.1 \times 10^{-22}$  and  $9.3 \times 10^{-21} \text{ cm}^3$  in the experimental temperature range from 220 to 160 K.

Thus, it can be estimated that in the experimental temperature range from 160 to 220 K,  $k_d$  varies from 5 ×  $10^{-12}$  to 2 ×  $10^{-10}$  cm<sup>3</sup>·s<sup>-1</sup>, while the stagnation number density of the acetylene dimer is between 2.0 ×  $10^{16}$  and 2.5 ×  $10^{16}$  molecule·cm<sup>-3</sup>. As a result, the acetylene dimer dissociates with a time constant near 0.5 ms, which is 3 orders of magnitude

Table 1. Calculated Dimer/Monomer Equilibrium Constant  $K_p(T)$  and Dimer Fraction  $P_d/P_m$  Values at Binding Energy  $D_0 = 404 \text{ cm}^{-1}$  from Colusi et al.<sup>12</sup>

		temperature (K)					
$D_0  ({\rm cm}^{-1})  /Z$	$K_{\rm p}$ and $P_{\rm d}/P_{\rm m}$	160	170	180	190	200	220
404/0.32	$K_{\rm p}~({\rm atm}^{-1})$	$9.1 \times 10^{-2}$	$7.2 \times 10^{-2}$	$5.8 \times 10^{-2}$	$4.7 \times 10^{-2}$	$3.9 \times 10^{-2}$	$2.8 \times 10^{-2}$
	$P_{\rm d}/P_{\rm m}$	0.60%	0.48%	0.38%	0.31%	0.26%	0.19%

greater than the nozzle transit time. Therefore, the stagnation dimer fraction is completely transferred to the RET.

As  $P_{\rm m}$  is verified to be the acetylene stagnation pressure, the rate coefficient of the H<sub>3</sub>O<sup>+</sup> + (C<sub>2</sub>H<sub>2</sub>)<sub>2</sub> reaction can be derived from Colussi's dimer model and the experimental data. In the calculation of the equilibrium constant  $K_{\rm p}(T)$  in eq 15, the ab initio value of  $D_0 = 404 \text{ cm}^{-1}$  is used, while the parameter *z* for the partition function is set to be 0.32, consistent with Colussi's observations. Under this condition, the equilibrium constant  $K_{\rm p}(T)$  of eq 15 and the dimer fraction  $P_{\rm d}/P_{\rm m}$  can be obtained, and the result is in shown in Table 1. The rate coefficient  $k_2$  of the bimolecular reaction  $H_3O^+ + (C_2H_2)_2$  is deduced from the expression

$$k_{2} = \frac{k_{1}(T_{\text{react}})}{n_{\rm d}(T_{\rm b})} = \frac{k_{1}(T_{\text{react}})}{n_{\rm m}(T_{\rm b}) \times (P_{\rm d}/P_{\rm m})}$$
(18)

where  $k_1(T_{\text{react}})$  is the experimental first-order rate coefficient of  $C_2H_5O^+$  formation and  $n_m(T_b)$  and  $n_d(T_b)$  are the number density of acetylene monomer and dimer at different beam temperatures, respectively. The  $H_3O^+ + (C_2H_2)_2$  reaction temperature  $T_{\text{react}}$  is written as

$$T_{\text{react}} = \left(\frac{3}{33}\right) T_{\text{coll}} + \left(\frac{9}{33}\right) T_{\text{ion}} + \left(\frac{21}{33}\right) T_{\text{b}}$$
(19)

using 9 internal degrees of freedom for  $H_3O^+$  and 21 for  $(C_2H_2)_2$ . Adding the 3 relative collisional degrees of freedom, the total degrees of freedom for the reaction system is 33. The rate coefficient of the  $H_3O^+ + (C_2H_2)_2$  reaction calculated from eq 18 at different reaction temperatures is shown in Figure 6. The calculated rate coefficient curve is fit as  $4.0 \times 10^{-10} (T_{react}/300)^{-2.5}$ .

The result demonstrates that Colussi's dimer model explains the experimental rate observation well, and the product  $C_2H_5O^+$  is created through the dimer reaction. The acetylene



**Figure 6.** The rate coefficient defined in eq 18 of the H<sub>3</sub>O<sup>+</sup> + (C<sub>2</sub>H<sub>2</sub>)<sub>2</sub> reaction versus the reaction temperature with the expression of eq 19 in the three experimental temperature series. The calculated rate coefficient is fitted to the line at 4.0 × 10<sup>-10</sup> ( $T_{\text{react}}/300$ )<sup>-2.5</sup>. (blue ◆) The trap temperature is 80 K, while the beam temperature is varied from 160 to 220 K. (orange ■) The trap temperature is 125 K, while the beam temperature is varied from 160 to 220 K. (pink ▲) The trap temperature is varied from 25 to 170 K, while the beam temperature is 160 K.

dimer rate coefficient is temperature-dependent as the acetylene dimer,  $(C_2H_2)_{2^{j}}$  is known from microwave and infrared spectroscopic studies to have a T-shaped ( $C_{2\nu}$  symmetry) structure<sup>35,39,40</sup> with a permanent dipole moment of 0.27 D.<sup>41</sup>

(3). Radiative Association of  $H_3O^+$  and  $C_2H_2$ . The  $H_3O^+$ +  $C_2H_2$  radiative association reaction was studied by Herbst in 1985, through both theory and experiment. Assuming the structure of product  $C_2H_5O^+$  is  $CH_3CHOH^+$ , which is the most stable isomer, the rate coefficient of the radiative association reaction is theoretically calculated as  $4.5 \times 10^{-12} \times (T/300)^{-1.6}$ in the temperature range from 10 to 50 K.<sup>9</sup> However, the rate coefficient deduced from three-body association data is 2 orders of magnitude lower in the same temperature range with  $k_{obs} =$  $2.7 \times 10^{-14} \times (T/300)^{-1.6.9}$ . To explain the difference between theory and experiment, Herbst concluded that product  $C_2H_5O^+$ being formed during the reaction does not lead to the lowestenergy isomer,  $CH_3CHOH^+$ .

In our study, at a trap temperature of 80 K and beam temperature of 300 K (reaction temperature of 187 K), no  $C_2H_5O^+$  products were observed. Under these conditions, the beam contains a dimer fraction of only 0.04%, effectively negating contributions of the dimer in any observed product formation. Considering the instrument detection limit for product detection at these beam densities, the rate coefficient of the  $H_3O^+ + C_2H_2$  radiative association reaction must be below  $1 \times 10^{-13}$  cm<sup>3</sup>·s<sup>-1</sup> at this temperature. When the reaction temperature is 121 K (beam, 160 K; trap, 80 K), the rate coefficient calculated from Herbst is  $1.2 \times 10^{-13}$  cm<sup>3</sup>·s<sup>-1</sup>. From the discussion above, the plot of the observed second-order rate of  $C_2H_5O^+$  formation divided by the acetylene monomer number density is approximately  $10^{-11}$  cm<sup>3</sup>·s<sup>-1</sup>. Therefore, only 1% of observed  $C_2H_5O^+$  product is produced from  $H_3O^+$ - $C_2H_2$  radiative association.

In Vigren's study of dark cloud TMC-1 in 2010,<sup>3</sup> there is a discussion of the rate for the  $H_3O^+ + C_2H_2$  radiative association reaction. As mentioned in the paper, if the rate coefficient follows Herbst's deduced experimental value, their model shows a large decrease in the calculated acetaldehyde abundance at TMC-1 for the estimated chemical age and gas-phase chemistry cannot reproduce the observed amount of acetaldehyde might be from grain–surface chemistry. Our conclusion that the rate coefficient of the  $H_3O^+-C_2H_2$  radiative association reaction is mostly likely Herbst's experimental value would seem to support a conclusion of a purely gas-phase product can lead to acetaldehyde through electron–ion recombination.

## 

The reaction between  $H_3O^+$  and the acetylene/acetylene dimer was studied using a molecular beam radio frequency ring electrode trap method. The temperatures of both the beam and trap were controlled independently, and the collision temperature was used to analyze the temperature dependence of the rate coefficient. It is found that the rate coefficient of the  $H_3O^+$  +  $C_2H_2$  radiative association reaction is below 1 × 10<sup>-13</sup> cm<sup>3</sup>·s<sup>-1</sup>, which supports the experimental rate coefficient value of Herbst. The sharp temperature dependence of the rate coefficient by varying the beam temperature can be explained by the increase of acetylene dimer at lower temperatures, and Colussi's dimer model is used in the acetylene dimer calculation. On the basis of the model, the rate coefficient of the  $H_3O^+ + (C_2H_2)_2$  reaction is determined to behave as  $4.0 \times 10^{-10} \times (T_{tran}/300)^{-b}$ , with b = 2.5, in the reaction temperature range of 114–187 K.

#### AUTHOR INFORMATION

## **Corresponding Author**

\*Address: College of Natural Sciences and Mathematics, University of Houston, 214 Science & Research Bldg. 1, Houston, TX 77204-5008. Phone: 713/743-3755. Fax: 713/ 743-8630. E-mail: markasmith@nsm.uh.edu.

#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

We would like to acknowledge the National Science Foundation for partial support of this work through Awards CHE-0618735 and CHE-0513364 and the Office of the Vice President for Research, University of Arizona for their contributing support. In addition, we must thank Dr. Dieter Gerlich, Dr. George Tikhonov, and Zachary Scott for their assistance in instrument design and construction. We would like to thank Dr. Darin Latimer and Sciex for their assistance with the development of the quadrupole filters. We would also like to thank Prof. Bonner Denton and Paul Wendtholt for assistance with this development effort.

#### REFERENCES

(1) Ziurys, L. M. Proc. Natl. Acad. Sci. U.S.A. 2006, 103, 12274– 12279.

(2) Klemperer, W. Annu. Rev. Phys. Chem. 2011, 62, 173-184.

- (3) Vigren, E.; Hamberg, M.; Zhaunerchyk, V.; Kaminska, M.; Thomas, R. D.; Trippel, S.; Zhang, M.; Kashperka, I.; Ugglas, M.; Walsh, C. W. D.; et al. *Phys. Chem. Chem. Phys.* **2010**, *12*, 11670– 11673.
- (4) Fairly, D. A.; Scott, G. B.; Freeman, C. G.; Maclagan, R. G. A. R.; McEwan, M. J. Chem. Soc., Faraday Trans. **1996**, 92, 1305–1309.
- (5) Gerlich, D.; Horning, S. Chem. Rev. 1992, 92, 1509-1539.
- (6) Ryzhov, V.; Dunbar, R. C. Int. J. Mass Spectrom. Ion Processes 1997, 167/168, 627-635.
- (7) Dunbar, R. C. Int. J. Mass Spectrom. Ion Processes 1997, 160, 1–16.
- (8) Herbst, E. Astrophys. J. 1976, 205, 94-102.
- (9) Herbst, E. J. Chem. Soc., Faraday Trans. 1989, 85, 1655-1664.
- (10) Herbst, E. Astrophys. J. 1987, 313, 867-876.
- (11) Zwier, T. S.; Allen, M. Icarus 1996, 123, 578-583.
- (12) Colussi, A. J.; Sander, S. P.; Friedl, R. R. Chem. Phys. Lett. 1991, 178, 497-503.

(13) Storey, J. W. V.; Cheung, A. C. Astrophy. Lett. 1978, 19, 89–91.
(14) Momoh, P. O.; Hamid, A. M.; Abrash, S. A.; El-Shall, M. S. J. Chem. Phys. 2011, 134, 204315.

(15) Gerlich, D. Inhomogeneous RF Fields: A Versatile Tool for the Study of Processes with Slow Ions. In *State-Selected and State-to-State Ion-Molecular Reaction Dynamics. Part 1. Experimental*; Advances in Chemical Physics Series; Baer, M., Ng, C. Y., Eds.; John Wiley & Sons: New York, 1992; Vol. LXXXII.

(16) Gerlich, D.; Borodi, G. Faraday Discuss. 2009, 142, 57-72.

(17) Gerlich, D. the Production and Study of Ultra-Cold Molecular Ions. In *Low Temperatures and Cold Molecules*; Smith, L., Ed.; Imperial College Press: London, 2008; pp 13–14.

(18) Hunter, E. P.; Lisa, S. G. Gas Phase Ion Energetics Data. In *NIST Chemistry WebBook*; Mallard, W. G., Linstrom, P. J., Eds.; NIST Standard Reference Database Number 69; National Institute of Standards and Technology: Gaithersburg, MD, 1998; http://webbook. nist.gov.

- (19) Anicich, V. G. J. Am. Soc. Mass. Spectrom. 2004, 15, 1148–1155.
  (20) Anicich, V. G.; Sen, A. D.; Huntress, W. T., Jr. J. Chem. Phys. 1990, 93, 7163–7172.
- (21) Anicich, V. G.; Huntress, W. T., Jr.; McEwan, M. J. J. Phys. Chem. **1986**, 90, 2446–2450.
- (22) Knight, J. S.; Freeman, C. G.; McEwan, M. J. J. Phys. Chem. 1987, 91, 3898-3902.
- (23) Yuan, B.; Sanov, A. M.; Smith, M. A. J. Phys. Chem. A 2012, Submitted for publication.
- (24) Bate, D. R. J. Chem. Phys. 1989, 90, 87-90.
- (25) Adams, N. G.; Smith, D. Chem. Phys. Lett. 1981, 79, 563-567.
- (26) Herbst, E. J. Chem. Phys. 1979, 70, 2201-2204.
- (27) Viggiano, A. A. J. Chem. Phys. 1986, 84, 244-249.
- (28) Viggiano, A. A.; Dale, F.; Paulson, J. F. J. Geophys. Res. 1985, 90, 7977–7984.
- (29) Klippenstein, S. J.; Yang, Y. C.; Ryzhov, V.; Dunbar, R. C. J. Chem. Phys. **1996**, 104, 4502-4516.
- (30) Ryzhov, V.; Yang, Y. C.; Klippenstein, S. J.; Dunbar, R. C. J. Phys. Chem. A 1998, 102, 8865–8870.
- (31) Herman, M.; Campargue, A.; Idrissi, M. I. E.; Auwera, J. V. J. Phys. Chem. Ref. Data 2003, 32, 921–1361.
- (32) Winkler, C. Chem. Phys. Lett. 1995, 242, 39-42.
- (33) Kunth, E. L. J. Chem. Phys. 1977, 66, 3515-3525.
- (34) Bone, R. G. A.; Handy, N. C. Theor. Chem. Acta 1990, 78, 133– 163.
- (35) Karthikeyan, S.; Lee, H. M.; Kim, K. S. J. Chem. Theory Comput. 2010, 6, 3190-3197.
- (36) Shuler, K.; Dykstra, C. E. J. Phys. Chem. A 2000, 104, 4562–4570.
- (37) Alberts, I. L.; Rowlands, T. W.; Handy, N. C. J. Chem. Phys. 1988, 88, 3811-3816.
- (38) Dykstra, C. E. J. Phys. Chem. 1995, 99, 11680-11686.
- (39) Resende, S.; Almeida, W. B. D. Chem. Phys. 1996, 206, 1-8.
- (40) Takeuchi, H. J. Comput. Chem. 2010, 31, 1699-1706.
- (41) Prichard, D. G.; Nandi, R. N.; Muenter, J. S. *J. Chem. Phys.* **1988**, 89, 115–123.