

Experimental electron-ion dissociative recombination rate constant and temperature dependence data for protonated methanol, ethanol, dimethyl ether and diethyl ether



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ABSTRACT

A flowing afterglow with an electrostatic Langmuir probe has been used to determine the electron-ion dissociative recombination (e-IDR) rate constants (α_e) and temperature dependencies (300–500 K) for a series of small alcohols and ethers. The species covered are protonated methanol (CH_3OH_2^+), protonated ethanol ($\text{C}_2\text{H}_5\text{OH}_2^+$), protonated dimethyl ether ($(\text{CH}_3)_2\text{OH}^+$) and protonated diethyl ether ($(\text{C}_2\text{H}_5)_2\text{OH}^+$). The e-IDR rate constants are $\alpha_e = 5.95 \times 10^{-7} (T/300)^{-0.57}$ for protonated methanol, $\alpha_e = 6.20 \times 10^{-7} (T/300)^{-0.87}$ for protonated ethanol, $\alpha_e = 5.52 \times 10^{-7} (T/300)^{-0.75}$ for protonated dimethyl ether, and $\alpha_e = 6.48 \times 10^{-7} (T/300)^{-1.05}$ for protonated diethyl ether. The experimental data are discussed in terms of the relevance to the chemical modeling of the interstellar medium.

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1. Introduction

To date approximately 160 molecules have been detected in the interstellar medium (ISM). Of these, a series of oxygen containing molecules have been observed, H_2O , [1] CH_3OH , [2] $\text{C}_2\text{H}_5\text{OH}$, [3] and $\text{O}(\text{CH}_3)_2$ [4–6]. In the modeling of the chemistry occurring within the ISM the production of these species is related to the electron-ion dissociative recombination (e-IDR) rate constants of the protonated forms. With this importance of the e-IDR rate constants to the modeling of interstellar chemistry, it is surprising that e-IDR rate constant data has only been obtained for H_3O^+ and CH_3OH_2^+ [7]. No e-IDR rate constant data are available for $\text{C}_2\text{H}_5\text{OH}_2^+$, $(\text{CH}_3)_2\text{OH}^+$ or $(\text{C}_2\text{H}_5)_2\text{OH}^+$. It is important to note that the e-IDR rate constant of $(\text{CD}_3)_2\text{OD}^+$ has been investigated [8]. The purpose of the present study has been to determine the e-IDR rate constants for the recombination reactions of these unmeasured species as a function of temperature for inclusion in ISM models. The rate constant of protonated methanol, CH_3OH_2^+ , has been re-measured in this study because of its critical importance to interstellar chemistry.

2. Experimental

Protonated methanol, CH_3OH_2^+ , protonated ethanol, $\text{C}_2\text{H}_5\text{OH}_2^+$, protonated dimethyl ether, $(\text{CH}_3)_2\text{OH}^+$, and protonated diethyl ether, $(\text{C}_2\text{H}_5)_2\text{OH}^+$, e-IDR rate constants were measured by a flowing afterglow equipped with an electrostatic Langmuir probe (FALP). This technique has been described in detail previously and thus only a brief description will be given here [9,10]. The FALP utilizes a Langmuir probe operating in the orbital motion limited configuration to measure the decrease in electron density as a function of distance along the flow tube. When operating in this mode with only one species undergoing recombination, it is possible to utilize Eq. (1) to determine α_e [11].

$$\frac{1}{[e]_z} - \frac{1}{[e]_0} = \frac{z\alpha_e}{V_p} \quad (1)$$

In Eq. (1) V_p is the plasma velocity, $[e]_0$ is the upstream electron density, and $[e]_z$ is measured electron density as a function of axial position, z . The FALP ionizes a helium (Airgas HP helium) flow in a upstream microwave cavity to create a quasi-neutral plasma. The ionized helium is carried downstream under the action of a Roots blower pump. Sequentially argon and hydrogen are added next. Argon (National Welders UHP Ar) is added to destroy He_2^+ , helium metastable's and increases the electron density. Following the addition of argon the plasma becomes a Ar^+ plasma. Hydrogen (Airgas UPC hydrogen) is added to the flow tube following the addition of argon to create an H_3^+ plasma. Once this has been

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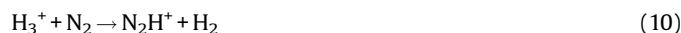
created the compound under study (X) is added and H_3^+ proton transfers to X creating the desired protonated species, XH^+ . Following creation, the XH^+ undergoes recombination with electrons in the plasma to form neutral products. This process is illustrated in Reactions (2)–(8). The positive ions are identified downstream by a quadrupole mass spectrometer equipped with an discreet dynode electron multiplier. This method allows the e-IDR rate constant to be measured with an accuracy of $\pm 15\%$ for 300 K and $\pm 20\%$ for all other temperatures.



Temperature dependencies are obtained by varying the temperature of the flow tube using a series of resistive heaters placed along the length of the flow tube. Protonated methanol could not be produced by direct introduction of methanol into the flow tube since fragmentation occurred because the proton transfer is too energetic, Eq. (9).

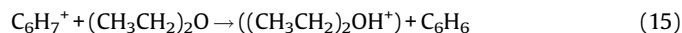


This problem has been experienced before [cite] and can be reduced by adding N_2 , CO, or benzene before the species to be protonated. Such addition creates a three step proton transfer reaction allowing a less energetic proton transfer, Eqs. (10) and (11).



This same three step protonation process was needed for all the species studied to reduce fragmentation. To form protonated dimethyl ether ($(CH_3)_2OH^+$) methane had to be used for an intermediate in the protonation process, Eqs. (12) and (13). Protonated ethanol, $CH_3CH_2OH_2^+$, and protonated diethyl ether

($(CH_3CH_2)_2OH^+$) were produced using benzene as an intermediate in the proton transfer process, Eqs. (14) and (15).



Through this three step protonation reaction it was possible to protonate methanol ($\geq 99\%$ anhydrous Sigma), ethanol ($\geq 99.5\%$ absolute Sigma), dimethyl ether ($\geq 99\%$ Sigma), and diethyl ether ($\geq 99.9\%$ Sigma) with no fragmentation observed in the mass spectra at the end of the flow tube. The compounds under study were introduced into the flow tube as mixtures of reactant vapor and helium (Airgas ultra-pure carrier grade Helium). These mixtures ranged from 0.5 to 5% in concentration. Low concentration mixtures allowed for the control of the formation of proton bound dimers and cluster ions in the flow tube, allowing for the measurement of only the protonated monomer species. It should be noted that temperatures below 300 K were not possible because of reactant vapor condensation and proton bound dimer formation at lower temperatures.

3. Results

The present data are included in Table 1. Plots of the e-IDR rate constant versus temperature for $CH_3OH_2^+$, $C_2H_5OH_2^+$, $(CH_3)_2OH^+$, and $(C_2H_5)_2OH^+$ are shown in Figs. 1–4 through 4 which also show the e-IDR rate constant and the temperature dependence. It is important to note that when taking into account the error associated with the measurement of each compound, the room temperature e-IDR rate constants have a similar value. Further work will need to focus on this and see if some correlation can be discovered which would increase our understanding of the e-IDR process in oxygen containing molecules.

When comparing the data in Table 1 for protonated methanol with previous measurements completed by the storage ring, $8.9 \pm 0.9 \times 10^{-7} (T/300)^{-0.59} \text{ cm}^3 \text{ s}^{-1}$, [12] we do not see good agreement with our present data, $5.95 \pm 0.89 \times 10^{-7} (T/300)^{-0.57} \text{ cm}^3 \text{ s}^{-1}$. It should be noted that storage ring e-IDR rate constants are obtained by experimentally measuring collisional cross section data as a function of energy. With the collisional cross section and the energy it is possible for the e-IDR rate constant to be obtained by integrating and solving the equation for the energy dependent cross section for all energies from 0 to ∞ [13]. While this method is used extensively for determining the e-IDR rate constant from storage ring datum, it is limited in that the equation neglects any vibrational or rotational excitations which might occur at temperatures above 300 K, $\sim 0.04 \text{ eV}$ [13]. The possible existence of vibrational and

Table 1

Electron-ion dissociative recombination rate constants and temperature dependencies (300–550 K) of protonated methanol and ethanol ($CH_3OH_2^+$ and $C_2H_5OH_2^+$ respectively) and protonated dimethyl and diethyl ethers ($(CH_3)_2OH^+$ and $(C_2H_5)_2OH^+$, respectively).

Compound	Formula	Electron-ion dissociative rate constant ($\text{cm}^3 \text{ s}^{-1}$)	Temperature dependence
Protonated methanol	$CH_3OH_2^+$	5.95×10^{-7}	$(T/300)^{-0.57}$
Protonated ethanol	$C_2H_5OH_2^+$	6.20×10^{-7}	$(T/300)^{-0.87}$
Protonated dimethyl ether	$(CH_3)_2OH^+$	5.52×10^{-7}	$(T/300)^{-0.75}$
Protonated diethyl ether	$(C_2H_5)_2OH^+$	6.48×10^{-7}	$(T/300)^{-1.05}$

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