Arrhenius-Kooij Fits to Experimentally Generated Thermal Rate Coefficients for $C + H_3^+$ forming CH^+ and CH_2^+

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ABSTRACT

The reaction of $C + H_3^+$ forming CH^+ and CH_2^+ is an important early link in the chain of astrochemical reactions leading to the formation of organic molecules in molecular clouds. In O'Connor et al. (2015), using a merged fast-beams apparatus, we measured the cross section for each reaction channel and generated thermal rate coefficients with an estimated accuracy of 15%. Here, we present fits to those thermal rate coefficients using the Arrhenius-Kooij equation, which can be readily incorporated into astrochemical models. The fits reproduce the thermal rate coefficient to better than 0.6% for temperatures from 10 to 10,000 K.

1. INTRODUCTION

One of the first steps in the astrochemical formation of organic molecules began when neutral atomic C was fixed into hydrocarbons in interstellar clouds (van Dishoeck et al. 1999; Herbst & van Dishoeck 2009). The initial chemical network involved is rather simple, primarily consisting of C reacting with H_3^+. The cosmic pathway from there to more complex hydrocarbons and other organic molecules passes through the molecular cations CH_n^+ ($n = 1 - 3$). In our studies, we have investigated the reactions

$$C + H_3^+ \rightarrow \begin{cases} CH^+ + H_2, & \text{(1a)} \\ CH_2^+ + H. & \text{(1b)} \end{cases}$$

The resulting CH^+ and CH_2^+ will then rapidly undergo sequential hydrogen abstraction with the abundant H_2 to form CH_3^+. In O'Connor et al. (2015), using a merged fast-beams apparatus, we measured the integral cross sections for reactions (1a) and (1b). Using these data, we generated thermal rate coefficients for each reaction channel for the temperature range of $10 - 10,000$ K, with an estimated accuracy of $\sim 15\%$ at an estimated 1σ confidence level. In Vissapragada et al. (2016), we fit the thermal rate coefficients of O'Connor et al. (2015) using the equation proposed by Novotný et al. (2013). One advantage of that fitting formula is that it is continuously differential and can accurately fit for complicated temperature dependencies. However, this equation is not currently supported by astrochemical databases such as KIDA (Wakelam et al. 2012) and UMIST (Millar et al. 2024), which use the mathematically simpler Arrhenius-Kooij (AK) formula. The disadvantage of the AK formula is that reactions with complicated temperature dependencies must be handled by dividing the temperature range into smaller intervals and fitting each interval separately. Here, we present fits to the thermal rate coefficient data of O'Connor et al. (2015) using the AK formula. In addition, since that work, we have developed a more reliable quantitative determination of the internal excitation of the reactant H_3^+ ions (Hillenbrand et al. 2019, Ivanov et al, in preparations). In Sec. 2, we show that this internal excitation has an insignificant effect on our measurements. Section 3 then presents our AK fits.

2. EXPERIMENTAL CONSIDERATIONS

The measurements of O'Connor et al. (2015) were performed with statistically populated $C(^2P_J)$ in the ground term and internally excited H_3^+. Thermal rate coefficients were generated using theoretical considerations to account for the temperature dependence of the fine-structure J levels. As for the internal excitation of the H_3^+, very good agreement

was found between the O'Connor et al. (2015) results and the mass-scaled results of Savic et al. (2005) for statistically populated C reacting with D_3^+ at an internal temperature of 77 K. Based on this agreement, the internal excitation of the H_3^+ was inferred to be unimportant, to within the level of the mutual experimental uncertainties. Here, we further explore any potential effects due to the internal excitation of the H_3^+.

The H_3^+ beam of O'Connor et al. (2015) was generated using a duoplasmatron ion source adjusted to maximize the H_3^+ current. There, we estimated the internal excitation of the H_3^+ from the measured relative collision energy at which the first competing endoergic reaction channel opened up, namely

$$C + H_3^+ \rightarrow C^+ + H + H_2. \tag{2}$$

This occurred at $\langle E_{\mathrm{int}} \rangle \approx 0.61$ eV below the theoretical threshold energy of $E_{\mathrm{th}} = 1.98$ eV. This was attributed to the H_3^+ internal excitation. Here, we have refit the merged-beams rate coefficient results of O'Connor et al. (2015) to more accurately determine $\langle E_{\mathrm{int}} \rangle$. We find that $\langle E_{\mathrm{int}} \rangle = 0.61^{+0.21}_{-0.28}$ eV, where the uncertainty is quoted at a 2σ confidence level. Using the partition function of Kylänpää & Rantala (2011), this corresponds to an internal temperature of $T_{\mathrm{int}} = 2415^{+500}_{-765}$ K.

Subsequent work by Hillenbrand et al. (2019) and Ivanov et al. (in preparation), on the same apparatus as that of O'Connor et al. (2015), has more accurately determined the internal excitation of the H_3^+ using the endoergic reaction

$$D + H_3^+ \rightarrow H_2D^+ + H. \tag{3}$$

This reaction has a barrier of $E_{\mathrm{b}} \approx 68$ meV. Any signal measured for collision energies below E_{b} is due solely to internal excitation of the H_3^+, enabling a more reliable determination of T_{int}. For ion source conditions adjusted to optimize the H_3^+ current, Those recent works find that $T_{\mathrm{int}} < 1600$ K, which corresponds to ($\langle E_{\mathrm{int}} \rangle < 0.28$ eV).

Based on our more reliable determination of T_{int}, we can re-investiage if the internal excitation of the H_3^+ has any effect on the experimentally generated thermal rate coefficient of O'Connor et al. (2015). The fraction of H_3^+ with sufficient internal energy to access competing endoergic reactions such as reaction (2) and those at higher energies is given by Hillenbrand et al. (2022) as

$$f_{E_{\mathrm{int}} > E_{\mathrm{th}}} = \exp\left(-\frac{E_{\mathrm{th}}}{\langle E_{\mathrm{int}} \rangle}\right). \tag{4}$$

Using this equation, we find that only 0.085% of the H_3^+ ions have an internal energy greater than E_{th}. As a worst-case scenario, we can assume that all reactions of H_3^+ ions with $E_{\mathrm{int}} > E_{\mathrm{th}}$ do not contribute to reactions (1a) or (1b). This would mean that the cross sections and rate coefficients reported by O'Connor et al. (2015) need to be scaled up by a factor of 1.085. This scaling lies well within the total experimental uncertainty limits. Moreover, it affects both channels in the same direction and therefore does not affect the branching ratios.

3. RECOMMENDED ARRHENIUS-KOOIJ FIT PARAMETERS

We used the AK formula to model the rate coefficients of both reaction channels. However, with one such function, we cannot model all the experimentally observed features in the rate coefficient correctly. Following the procedure described in Paul et al. (2022), we provide a representation of the thermal rate coefficient α using m piecewise-joined AK equations ($T \in [T_i, T_{i+1}], i \in 0, ...m$) with

$$\alpha(T)[\mathrm{cm}^3 \ \mathrm{s}^{-1}] = A_i \left(\frac{T[K]}{300}\right)^{\beta_i} \exp\left(-\frac{\gamma_i}{T[K]}\right), \tag{5}$$

where T is the gas temperature and A_i, β_i, and γ_i are fitting parameters. Following KIDA conventions, the uncertainty is described by a log-normal factor $F = \exp(\Delta\alpha/\alpha)$ for each interval with

$$F(T) = F_i \exp\left(g_i\left(\frac{1}{T[K]} - \frac{1}{300}\right)\right), \tag{6}$$

where F_i and g_i are the fit parameters. We construct the data for $F(T)$ as average of $F_{\mathrm{high}}(T) = \exp(\Delta_{\mathrm{high}}\alpha/\alpha)$ and $F_{\mathrm{low}}(T) = \exp(\Delta_{\mathrm{low}}\alpha/\alpha)$, where $\Delta_{\mathrm{high}}\alpha$ and $\Delta_{\mathrm{low}}\alpha$ correspond to the upper and lower one-sigma errors, calculated from the quadrature sum of the systematic uncertainty and the original thermal rate fitting accuracy. For astrochemical

Table 1. Fit Parameters for the Thermal Rate Coefficients for reaction (1a) and Equation (1b) And Its Relative Uncertainty, Using Equation (7) and (8).

	$C + H_3^+ \to CH^+ + H_2$			
Parameter	10 - 17.4 K	17.4 - 169 K	169 - 4440 K	4440 - 10000 K
i	1	2	3	4
A_i	5.54×10^{-10}	6.77×10^{-10}	6.44×10^{-10}	1.28×10^{-9}
β_i	-9.90×10^{-2}	9.73×10^{-3}	1.30×10^{-1}	-5.52×10^{-2}
γ_i	-7.85×10^{-2}	-1.97×10^{0}	-2.23×10^{1}	8.01×10^{2}
F_i	1.13×10^{0}	1.13×10^{0}	1.13×10^{0}	1.15×10^{0}
g_i	-1.09×10^{-4}	-7.93×10^{-4}	2.90×10^{-2}	4.77×10^{0}
	$C + H_3^+ \to CH_2^+ + H$			
Parameter	10 - 283 K	283 - 1330 K	1330 - 3760 K	3760 - 10000 K
i	1	2	3	4
A_i	3.28×10^{-10}	3.36×10^{-10}	4.71×10^{-10}	1.56×10^{-9}
β_i	-1.66×10^{-1}	-1.94×10^{-1}	-3.30×10^{-1}	-6.70×10^{-1}
γ_i	1.58×10^{-3}	7.39×10^{0}	1.89×10^{2}	1.47×10^{3}
F_i	1.18×10^{0}	1.18×10^{0}	1.18×10^{0}	1.17×10^{0}
g_i	-7.90×10^{-4}	-2.40×10^{-1}	-1.39×10^{0}	-3.75×10^{0}

calculations, a continuous behavior of the functions at the interval borders is typically desired, so we introduce a dependency of the A_i and F_i parameters in accordance with Paul et al. (2022) to obtain the continuous fit functions

$$\alpha(T)[\text{cm}^3 \text{ s}^{-1}] = A_0 \left(\frac{T[K]}{300} \right)^{\beta_i} \exp \left(-\frac{\gamma_i}{T[K]} \right) \times \prod_{j=1}^{i} \left(\frac{T_j}{300} \right)^{\beta_{j-1} - \beta_j} \exp \left(\frac{\gamma_j - \gamma_j - 1}{T_j} \right) \tag{7}$$

and

$$F(T) = F_0 \exp \left(\frac{g_i - g_0}{300} \right) \exp \left(g_i \left(\frac{1}{T[\text{K}]} - \frac{1}{300} \right) \right) \times \prod_{j=1}^{i} \exp \left(\frac{g_{j-1} - g_j}{T_j} \right), \tag{8}$$

for the rate coefficient and uncertainty fits, respectively. We note that for the first temperature interval ($i = 0$) the product terms evaluate to unity and that the functions show the same dependence on T_k as given by Equations (5) and (6), respectively. For the fit with Equation (7), we let the interval borders T_i vary as free parameters and subsequently fixed them for the fit with Equation (8). The Levenberg-Marquardt algorithm was implemented for a more robust and accurate fit as per Moré (1978).

The resulting parameters for Equations 5, using $m = 4$ temperature intervals, are listed in Table 1 for (1a) and (1b) For each reaction, the relative deviations of the fit functions to the rate coefficients are below 0.6% at all temperatures.

REFERENCES

Herbst, E., & van Dishoeck, E. F. 2009, ARA&A, 47, 427, doi: 10.1146/annurev-astro-082708-101654

Hillenbrand, P. M., Bowen, K. P., Liévin, J., Urbain, X., & Savin, D. W. 2019, ApJ, 877, 38, doi: 10.3847/1538-4357/ab16dc

Hillenbrand, P.-M., de Ruette, N., Urbain, X., & Savin, D. W. 2022, ApJ, 927, 47, doi: 10.3847/1538-4357/ac41ce

Kylänpää, I., & Rantala, T. T. 2011, JChPh, 135, 104310, doi: 10.1063/1.3633516

Millar, T. J., Walsh, C., Van de Sande, M., & Markwick, A. J. 2024, A&A, 682, A109, doi: 10.1051/0004-6361/202346908

Moré, J. J. 1978, Numerical Analysis, 105, doi: https://doi.org/10.1007/bfb0067700

Novotný, O., Becker, A., Buhr, H., et al. 2013, ApJ, 777, 54, doi: 10.1088/0004-637X/777/1/54

O'Connor, A. P., Urbain, X., Stützel, J., et al. 2015, ApJS, 219, 6, doi: 10.1088/0067-0049/219/1/6

Paul, D., Grieser, M., Grussie, F., et al. 2022, ApJ, 939, 122, doi: 10.3847/1538-4357/ac8e02

Savic, I., Cermák, I., & Gerlich, D. 2005, International Journal of Mass Spectrometry, 240, 139, doi: 10.1016/j.ijms.2004.10.015

van Dishoeck, E. F., Wright, C. M., Thi, W. F., & Boonman, A. M. S. 1999, in Astronomical Society of the Pacific Conference Series, Vol. 177, Astrophysics with Infrared Surveys: A Prelude to SIRTF, ed. M. D. Bicay, R. M. Cutri, & B. F. Madore, 288

Vissapragada, S., Buzard, C. F., Miller, K. A., et al. 2016, ApJ, 832, 31, doi: 10.3847/0004-637X/832/1/31

Wakelam, V., Herbst, E., Loison, J. C., et al. 2012, ApJS, 199, 21, doi: 10.1088/0067-0049/199/1/21