

GAS PHASE STUDY OF C^+ REACTIONS OF INTERSTELLAR RELEVANCE

OSCAR MARTINEZ, JR.,¹ NICHOLAS B. BETTS,¹ STEPHANIE M. VILLANO,¹ NICOLE EYET,¹
THEODORE P. SNOW,^{2,3} AND VERONICA M. BIERBAUM^{1,2}

Received 2008 May 19; accepted 2008 June 29

ABSTRACT

The current uncertainty in many reaction rate constants causes difficulties in providing satisfactory models of interstellar chemistry. Here we present new measurements of the rate constants and product branching ratios for the gas phase reactions of C^+ with NH_3 , CH_4 , O_2 , H_2O , and C_2H_2 , using the flowing afterglow-selected ion flow tube (FASIFT) technique. Results were obtained using two instruments that were separately calibrated and optimized; in addition, low ionization energies were used to ensure formation of ground-state C^+ , the purities of the neutral reactants were verified, and mass discrimination was minimized.

Subject headings: astrochemistry — ISM: clouds — ISM: molecules — methods: laboratory — molecular processes

1. INTRODUCTION

Gas phase ion-neutral reactions are critical processes in a variety of astrophysical environments. Chemical models attempt to predict the effects of these reactions on the development and evolution of the interstellar medium (ISM). Accurate experimental values of rate constants and product branching ratios for interstellar reactions are essential for accurate theoretical predictions. Markwick-Kemper has modeled a small dark cloud using 2955 reactions and 281 total species to determine how errors in reaction rate constants affect the concentrations of various species in the ISM. His results prioritize which reactions, due to their large uncertainty, most affect the calculated abundance of these species (Markwick-Kemper 2005). Several reactions of C^+ are included in this list due to the importance of this ion in the ISM. Markwick-Kemper used reaction rate coefficients tabulated in the University of Manchester Institute of Science and Technology (UMIST)⁴ database (Woodall et al. 2007), many of which have uncertainties in their rate constants of more than a factor of 2. In addition, values in a second compilation, the Ohio State database⁵, sometimes differ from those in the UMIST database.

In areas of the ISM with extremely low temperatures, chemistry not involving surfaces is dominated by ion-atom/molecule reactions, which require no activation energy. Due to its low ionization energy (11.26 eV), the carbon atom is readily ionized by the ambient radiation (<13.60 eV) in diffuse regions of the ISM. Therefore, the carbon cation exists in most diffuse atomic, diffuse molecular, and translucent cloud regions, and it is the dominant form of carbon in diffuse atomic and molecular regions. In these regions, carbon cation chemistry primarily involves atomic neutrals. At the boundary between the diffuse molecular and translucent regions the local density of carbon changes from cationic

to neutral, since there is significant attenuation of ionizing radiation (Snow & McCall 2006). As one crosses to the dense molecular region, there is a shift to high densities of CO, which is the major form of carbon and the second most abundant molecule in dense clouds. While the inner molecular regions are shielded from interstellar radiation, C^+ is formed by cosmic-ray particles that penetrate into these dense regions. Cosmic-ray ionization of helium initiates the dissociative ionization of CO (i.e., $He^+ + CO \rightarrow C^+ + O + He$); this process is a primary source of ground-state C^+ in dense clouds (Herbst & Klemperer 1973; Watson 1974).

The reactions of C^+ studied here are most relevant in the denser translucent and molecular cloud regions. Although the concentration of carbon cations is several orders of magnitude smaller in these regions than in diffuse atomic clouds, their existence has a significant impact on the chemistry. Because of its low reactivity with major components of the ISM, including H_2 , CO, and free electrons, C^+ is available for reaction with a variety of polyatomic neutrals that are important in dense cloud chemistry (Herbst & Klemperer 1973). These reactions form other ions and molecules which are often more complex, including multicarbon species. Errors in the rate constants and branching ratios of these reactions can have a serious impact on chemical models of these regions.

We have studied the gas phase reactions of carbon cation with NH_3 , CH_4 , O_2 , H_2O , and C_2H_2 . Of the reactions reported in this paper, all but the CHN^+ and H_3N^+ product channels produced by the reaction with ammonia (discussed below) are ranked among the top 100 reactions of Markwick-Kemper's study. The goal of this research is to increase the accuracy of the data provided to the astronomical community, and to reconcile the discrepancies between the databases and the current literature.

2. EXPERIMENTAL METHODS

Two similar flowing afterglow-selected ion flow tube (FASIFT) instruments at the University of Colorado at Boulder were used for these studies. The experimental parameters for both instruments were separately optimized and calibrated, including reaction flow tube pressure, reaction distance, helium flow rate, and neutral reactant flow rate; mass discrimination was minimized.

These instruments have been described in detail elsewhere (Bierbaum 2003; Van Doren et al. 1987). In brief, C^+ is formed

¹ Department of Chemistry and Biochemistry, 215 UCB, University of Colorado, Boulder, CO 80309-0215; Oscar.Martinez@colorado.edu, Bettsn@colorado.edu, Stephanie.Villano@colorado.edu, Eyet@colorado.edu, Veronica.Bierbaum@colorado.edu.

² Center for Astrophysics and Space Astronomy, 389 UCB, University of Colorado, Boulder, CO 80309-0389; Theodore.Snow@colorado.edu.

³ Department of Astronomy and Planetary Sciences, 391 UCB, University of Colorado, Boulder, CO 80309-0391.

⁴ See <http://www.udfa.net>.

⁵ See E. Herbst 2007, Ohio State Chemical Database, available at <http://www.physics.ohio-state.edu/~eric>, listed under "gas phase model."

by electron impact ionization on a trace amount of carbon monoxide gas, CO (Airgas Inc., 99.5% pure), entrained in a flow of helium buffer gas. A SIFT quadrupole is used to mass select C^+ , which is then injected into a reaction flow tube at 300 ± 2 K; ions are thermalized by $\sim 10^4$ collisions with the helium carrier gas (pressure = 0.5 torr; flow = $220 \text{ std cm}^3 \text{ s}^{-1}$). A measured flow of neutral reactant is added into the reaction flow tube through a manifold of fixed inlets. The decrease of reactant ion signal and the formation of product ions are monitored as a function of reaction distance, and hence time, by a quadrupole mass filter coupled to an electron multiplier. Rate constants and product ion branching ratios are measured under pseudo-first-order conditions using a standard kinetic analysis, as described below. The neutral reactants include ammonia, NH_3 (Air Products & Chemicals Inc., 99.99+%); methane, CH_4 (Airgas Inc., 99.0%); oxygen, O_2 (Airgas Inc., 99.994%); water, H_2O (in house deionized water); and acetylene, C_2H_2 (Airgas Inc., 99+%). Helium (Airgas Inc., 99.998%) is purified by flow through a molecular sieve trap immersed in liquid N_2 .

A concern in these studies is the possible generation of electronically excited carbon cations, which would skew the rate constant determinations and product ion branching ratio measurements. Ionization energies of ~ 70 eV have been found to produce small amounts of excited state species (Tichy et al. 1979; Xu et al. 1990). Lower energy electron ionization (~ 30 eV) has been shown (Twiddy et al. 1986) to create strong signals of ground-state $C^+(^2P)$ while minimizing formation of electronically excited metastable $C^+(^4P)$. We have therefore used 30 eV electron ionization in these studies. We have confirmed the absence of electronically excited C^+ by the lack of reaction of injected C^+ with CO. Twiddy et al. (1986) have found that $C^+(^4P)$ reacts with CO with a rate constant of $k \sim 3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. In separate experiments, we have increased the electron ionization energy to 70 eV and confirmed that the branching ratio for the $C^+ + O_2$ changes so that CO^+ becomes the dominant product ion.

In our tabulation of results, we have noted prior literature values where higher ionization energies were used and where, therefore, excited C^+ may exist. The tables include all published values for experiments near 300 K.

Collision rate constants were calculated using parameterized trajectory theory for reactants with a dipole moment (NH_3 and H_2O) or Langevin theory for reactants without a dipole moment (CH_4 , O_2 , and C_2H_2) (Gioumoussis & Stevenson 1958; Su & Chesnavich 1982). Reaction efficiencies are the ratio of the experimental rate constant to the collision rate constant.

3. RESULTS AND DISCUSSION

Figure 1 shows a typical kinetics plot for the reaction of C^+ with CH_4 . The reactant ion shows a linear semilogarithmic decay as a function of reaction distance; the reaction rate constant is determined from the slope of this line and other measured experimental parameters. The buildup of the two product ions, $C_2H_2^+$ and $C_2H_3^+$, is also shown; the determination of quantitative branching ratios is described below.

We have found good agreement between the results from our series of experiments on two FASIFT instruments (measured rate constants agree within 10%), thus confirming that calibration of instrumental parameters and systematic error have been correctly addressed. In addition, our measured values are in agreement with some of those previously reported in the literature. However, caution must be used when comparing FASIFT measurements to those obtained by other means. For example, measurements using ion cyclotron resonance (ICR) can include electronically

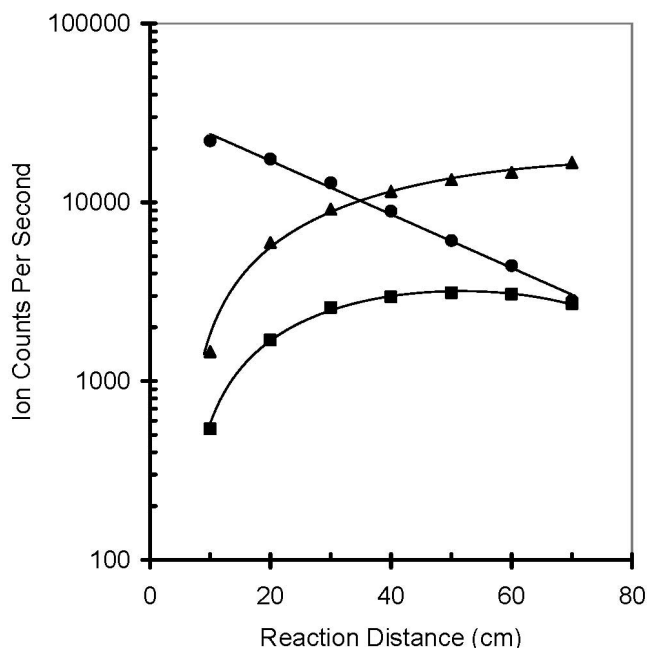


FIG. 1.—Primary reactant ion depletion and product ion growth for $C^+ + CH_4$. Filled circles: C^+ ; filled squares: $C_2H_2^+$; filled triangles: $C_2H_3^+$.

excited or nonthermal reactant ions, and therefore often have larger rate constants than measurements where only the ground-state species is present. In traditional flowing afterglow (FA) instruments, ions are formed directly in the reaction flow tube, and therefore these measurements can include contamination from the presence of other species. In addition, many of these reactions have been previously studied at a range of temperatures and kinetic energies. However, past research and theoretical predictions have shown either a slightly negative or no temperature dependence of rate constants for many ion-molecule reactions. The reactions studied here all proceed at relatively high efficiencies ($>63\%$), and therefore only minor temperature effects are expected.

An experimental complication in the SIFT method is that different-mass ions are transmitted with different efficiencies through the detection region. While mass discrimination does not affect the reaction rate constant measurements, it can lead to erroneous product ion branching ratio determinations. However, a comparison of ion counts before reaction (C^+ ions only) and after reaction (C^+ and product ions) showed constant signals indicating that mass discrimination effects are not substantial for these studies. An additional difficulty in making accurate branching ratio measurements is the occurrence of secondary reactions. We therefore use a method similar to that of Adams & Smith (1976), in which the percentage of each product ion is plotted as a function of the extent of reaction; Adams & Smith use the neutral reactant flow rate for this latter parameter, whereas we have used the ion-neutral reaction distance, as shown in Figure 2. Extrapolation to zero distance yields the primary product ion distribution, where secondary reactions and differential ion diffusion have been eliminated. We note that this latter effect is small since the $C_2H_2^+$ and $C_2H_3^+$ product ions are expected to have similar diffusion coefficients in helium buffer gas. These branching ratio plots are reasonably fit by linear extrapolation; a full modeling of the kinetics and ion diffusion generally yields similar results. In addition, we evaluated and corrected for minor drift in mass position (m/z). These

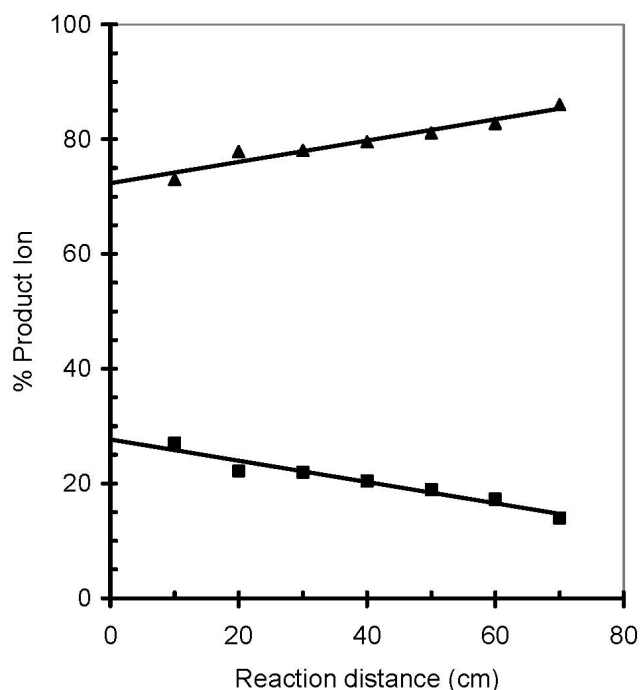


FIG. 2.— Sample branching ratio determination for $C^+ + CH_4$. Filled squares: $C_2H_2^+$; filled triangles: $C_2H_3^+$.

branching ratio values were compared to those obtained by taking the percentage of product ion (both primary and secondary reactions) and finding the distance where secondary products extrapolate to zero abundance; the percent of product ions at this distance then determines the primary product branching ratios. The two methods produced results that are in good agreement. Nevertheless, the relatively large error bars on the branching ratios for the reactions of $C^+ + NH_3$ and $C^+ + O_2$ reflect the inherent difficulties in accurately determining quantitative product distributions due to secondary reaction and residual mass discrimination.

With careful calibration of instrumental parameters, a total systematic error of $\pm 13.4\%$ is attainable (Van Doren 1987). In this work, we report a slightly more conservative systematic error of $\pm 15\%$. In Tables 1–6, the reported error bars for the reaction rate constants and branching ratios represent one standard deviation of the mean, and therefore indicate the precision of these values. The reported experimental rate constants represent an average of 8–15 measurements, and the branching ratios represent an average of 6–14 measurements.

3.1. $C^+ + NH_3$

The reaction of carbon cations with ammonia is significant in the ISM as a pathway leading to the formation of HNC and HCN in dense interstellar clouds through primary and secondary reaction pathways. These reactions create ions and molecules that may serve as reagents for the production of more complicated interstellar species. The reaction of carbon cations with ammonia,

TABLE 1
REACTION RATE CONSTANTS AND PRODUCT BRANCHING RATIOS FOR $C^+ + NH_3$

k ($10^{-9} \text{ cm}^3 \text{ s}^{-1}$)	Products	Branching Ratio (%)	Instrument/Reference
2.3 ± 0.2	$H_3N^+ + C$	50	ICR ^a /Anicich et al. (1976)
	$CH_2N^+ + H$	47	ICR ^a /Anicich et al. (1976)
	$CHN^+ + H_2$	3	ICR ^a /Anicich et al. (1976)
$2.0 \pm 30\%$	$H_3N^+ + C$	70	FA/Liddy et al. (1977)
	$CH_2N^+ + H$	<30	FA/Liddy et al. (1977)
	$CHN^+ + H_2$	>0	FA/Liddy et al. (1977)
2.3 ± 0.2	$H_3N^+ + C$	95	FA ^b /Schiff et al. (1974)
	$CH_2N^+ + H$	5	FA ^b /Schiff et al. (1974)
2.3	$H_3N^+ + C$	Not Reported	FA ^c /Schiff & Bohme (1979)
	$CH_2N^+ + H$	~50	FA ^c /Schiff & Bohme (1979)
	$CHN^+ + H_2$	Not Reported	FA ^c /Schiff & Bohme (1979)
2.3	$H_3N^+ + C$	23	FASIFT/Tichy et al. (1979)
	$CH_2N^+ + H$	68	FASIFT/Tichy et al. (1979)
	$CHN^+ + H_2$	9	FASIFT/Tichy et al. (1979)
$2.3 \pm 20\%$	$H_3N^+ + C$	22	FASIFT ^d /Smith & Adams (1977c)
	$CH_2N^+ + H$	75	FASIFT ^d /Smith & Adams (1977c)
	$CHN^+ + H_2$	3	FASIFT ^d /Smith & Adams (1977c)
2.1	$H_3N^+ + C$	32	Ohio State Database/E. Herbst (2007)
	$CH_2N^+ + H$	63	Ohio State Database/E. Herbst (2007)
	$CHN^+ + H_2$	5	Ohio State Database/E. Herbst (2007)
$2.3 \pm 20\%$	$H_3N^+ + C$	22	UMIST Database/Smith & Adams (1977c), Woodall et al. (2007)
	$CH_2N^+ + H$	75	UMIST Database/Smith & Adams (1977c), Woodall et al. (2007)
	$CHN^+ + H_2$	3	UMIST Database/Smith & Adams (1977c), Woodall et al. (2007)
2.36 ± 0.15	$H_3N^+ + C$	28 ± 12	FASIFT/This work
	$CH_2N^+ + H$	67 ± 11	FASIFT/This work
	$CHN^+ + H_2$	5 ± 2	FASIFT/This work

^a Injection energy <0.1 eV. Product distributions accurate to ~3% of total distribution.

^b Reactants in thermal equilibrium at 297 K.

^c Product distribution given only for CH_2N^+ ; reported as 0.5 ± 0.2 .

^d ~70 eV electron impact ionization (EI).

TABLE 2
REACTION RATE CONSTANTS AND PRODUCT BRANCHING RATIOS FOR $C^+ + CH_4$

k ($10^{-9} \text{ cm}^3 \text{ s}^{-1}$)	Products	Branching Ratio (%)	Instrument/Reference
1.45 ± 0.12	$C_2H_2^+ + H_2$	29	ICR ^a /Anicich et al. (1976)
	$C_2H_3^+ + H$	71	ICR ^a /Anicich et al. (1976)
1.43.....	Not Reported	Not Reported	MS ^b /Mackenzie Peers & Milhaud (1974)
1.5.....	Not Reported	Not Reported	TI ^c /Herod & Harrison (1970)
0.76 ± 0.30	$C_2H_3^+ + H$	Not Reported	HP ^d /Chong & Franklin (1971)
$1.00 \pm 20\%$	Not Reported	Not Reported	FA/Hemsworth et al. (1970)
1.6.....	$C_2H_2^+ + H_2$	Not Reported	FA/Schiff & Bohme (1979)
	$C_2H_3^+ + H$	Not Reported	FA/Schiff & Bohme (1979)
$1.2 \pm 20\%$	$C_2H_2^+ + H_2$	33	FASIFT/Adams & Smith (1977)
	$C_2H_3^+ + H$	67	FASIFT/Adams & Smith (1977)
1.3 ± 0.4	$C_2H_2^+ + H_2$	25	FASIFT ^e /Bohme et al. (1982)
	$C_2H_3^+ + H$	75	FASIFT ^e /Bohme et al. (1982)
1.2.....	$C_2H_2^+ + H_2$	50	FASIFT/Tichy et al. 1979)
	$C_2H_3^+ + H$	50	FASIFT/Tichy et al. 1979)
1.5.....	$C_2H_2^+ + H_2$	33	Ohio State Database/E. Herbst (2007)
	$C_2H_3^+ + H$	67	Ohio State Database/E. Herbst (2007)
1.5.....	$C_2H_2^+ + H_2$	25	UMIST Database ^f /Schiff & Bohme (1979), Woodall et al. (2007)
	$C_2H_3^+ + H$	75	UMIST Database ^f /Schiff & Bohme (1979), Woodall et al. (2007)
1.39 ± 0.054	$C_2H_2^+ + H_2$	28 ± 2	FASIFT/This work
	$C_2H_3^+ + H$	72 ± 2	FASIFT/This work

^a Injection energy < 0.1 eV. Product distributions accurate to $\sim 3\%$ of total distribution.

^b Rate constant obtained from a disappearance cross section of primary ions in methane with terminal kinetic energy ranging from near thermal to 5 eV; ~ 100 eV EI; gas temperature of 100°C .

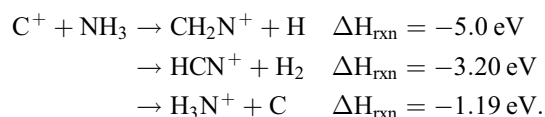
^c ~ 30 eV EI. Reactant ion kinetic energies from 0.3 to 0.5 eV. Rate constants determined relative to $CH_4^+ + CH_4$ and therefore reported in a corrected form relative to the methane reaction. Rate constants originally reported as cross sections.

^d ~ 150 eV EI. Uncertainty in the rate constant based on uncertainty in the mobility of C^+ in carbon monoxide. Authors report three rate values (0.46, 0.81, or $1.06 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$), based on referenced values and a Langevin equation value for C^+ mobility in carbon monoxide. Value reported here, as in other sources, as $(0.76 \pm 0.30) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

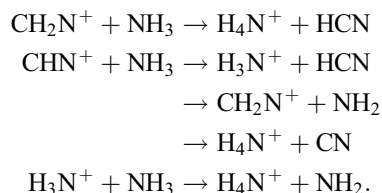
^e Mass discrimination effects cited as negligible for ionic products within a mass range ~ 5 amu. Branching ratio error up to 30% estimated outside this range.

^f Database cites reference as: Schiff, H. I., Mackay, G. I., Vlachos, G. D., & Bohme, D. K. 1980, in IAU Symp. 87, Interstellar Molecules, ed. B. H. Andrews (Dordrecht: Reidel), 307; Schiff, H. I., & Bohme, D. K. 1979, ApJ, 232, 740. However, the first citation gives no data for the $C^+ + CH_4$ reaction, and the second reference gives its rate as $1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, not $1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

NH_3 , occurs through the following ion-atom exchange and charge transfer channels⁶:



As shown in Table 1, our reported value for the overall rate constant [$(2.36 \pm 0.15) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$] is in good agreement with previous literature values. The first measurement of the reaction $C^+ + NH_3$ (Schiff et al. 1974) did not show evidence of the CHN^+ formation channel. This is likely due to the secondary reactions of the primary product ions with ammonia as shown below:



While all reported values of branching ratios indicate that formation of CHN^+ is a minor product, the abundance of the other primary products is not clearly established. Past measurements

⁶ ΔH_{rxn} for CH_2N^+ channel reported by Tichy et al. (1979); ΔH_{rxn} for HCN^+ channel is for hydrogen cyanide isomer (HCN) in particular.

are in disagreement, with some identifying H_3N^+ as the major product and others determining CH_2N^+ as the major product. While the two major astronomical databases are in agreement with the identity of the primary product, CH_2N^+ , their choice of branching ratios differs slightly, as does their choice of rate constants (see Table 1). Our results, 28% NH_3^+ , 67% CH_2N^+ , and 5% CHN^+ , are consistent with those reported by Smith & Adams (1977c) and by Tichy et al. (1979). It should be noted that isomeric structures of the latter two ions are possible but not readily distinguishable by mass spectrometric techniques.

3.2. $C^+ + CH_4$

The reaction of carbon cations with methane is likely important for the formation of hydrocarbons in interstellar clouds, as first hypothesized by Adams & Smith (1977). Similarly, Schiff & Bohme (1979) reported a viable scheme for hydrocarbon synthesis occurring through condensation of C^+ with neutrals of the type CH_x , as demonstrated by reactions of this type ($C^+ + CH_x$). The reaction of C^+ with methane occurs through two addition-fragmentation reactions:

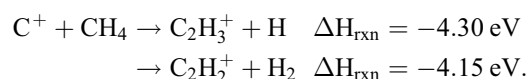


Table 2 shows that the value for the rate constant of this reaction provided by this study [$(1.39 \pm 0.05) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$] compares reasonably well with earlier literature values.

TABLE 3
REACTION RATE CONSTANTS AND PRODUCT BRANCHING RATIOS FOR $C^+ + O_2$

k ($10^{-9} \text{ cm}^3 \text{ s}^{-1}$)	Products	Branching Ratio (%)	Instrument/Reference
0.90.....	$O^+ + CO$	Not Reported	MS/Franklin & Munson (1964)
	$CO^+ + O$	Not Reported	MS/Franklin & Munson (1964)
1.22 ± 0.10	$O^+ + CO$	36	ICR ^a /Anicich et al. (1976)
	$CO^+ + O$	64	ICR ^a /Anicich et al. (1976)
0.6.....	$O^+ + CO$	60	ICR ^b /Rincon et al. (1987)
	$CO^+ + O$	40	ICR ^b /Rincon et al. (1987)
0.76 ± 0.23	$O^+ + CO$	60	GIB/Burley & Armentrout (1988)
	$CO^+ + O$	40	GIB/Burley & Armentrout (1988)
$1.1 \pm 30\%$	$CO^+ + O$	Not Reported	FA/Fehsenfeld et al. (1966)
0.90 ± 0.18	Not Reported	Not Reported	FA ^c /Rakshit et al. (1978)
$0.99 \pm 20\%$	$O^+ + CO$	62	FASIFT/Adams & Smith (1976)
	$CO^+ + O$	38	FASIFT/Adams & Smith (1976)
$0.93 \pm 25\%$	$O^+ + CO$	62	FASIFT ^d /Miller et al. (1984)
	$CO^+ + O$	<38	FASIFT ^d /Miller et al. (1984)
	$O_2^+ + C$	<38	FASIFT ^d /Miller et al. (1984)
0.74.....	$O^+ + CO$	53	FASIFT/Tichy et al. (1979)
	$CO^+ + O$	47	FASIFT/Tichy et al. (1979)
1.2.....	$O^+ + CO$	35	Ohio State Database/E. Herbst (2007)
	$CO^+ + O$	65	Ohio State Database/E. Herbst (2007)
$1.0 \pm 20\%$	$O^+ + CO$	62	UMIST Database ^e /Smith & Adams (1977b), Woodall et al. (2007)
	$CO^+ + O$	38	UMIST Database ^e /Smith & Adams (1977b), Woodall et al. (2007)
0.796 ± 0.024	$O^+ + CO$	57 ± 12	FASIFT/This work
	$CO^+ + O$	43 ± 12	FASIFT/This work

^a Injection energy <0.1 eV. Product distributions accurate to ~3% of total distribution.

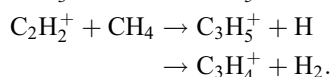
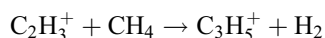
^b Ground electronic state carbon cation reactant formed by reaction of He^+ with CO.

^c Rate constant unchanged at 100 and 300 K.

^d Reaction found independent of temperature over the range 90–450 K. Following additional rate constants measured at indicated temperatures (all in units of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$): 0.83 (96 K), 0.85 (150 K), 0.88 (200 K), 0.90 (250 K), 0.89 (395 K), and 0.85 (450 K).

^e Authors' reference contains a previously cited value (Adams & Smith 1976).

The products of the primary reactions can further react with neutral methane:



Of the primary product channels reported in the literature, all but one paper report the observation of $C_2H_3^+$ and $C_2H_2^+$ pathways; however, there is some disagreement in the percentages of these two products. The two available databases have chosen the same value of the rate constant, but slightly different branching ratios.

Our reported values, 28% $C_2H_2^+$ and 72% $C_2H_3^+$, are more consistent with data chosen by the UMIST database. Tichy et al. (1979) infer that the reaction of electronically excited C^+ exclusively forms the $C_2H_2^+$ product; therefore, generation of only ground-state C^+ is essential for measurement of accurate branching ratios.

3.3. $C^+ + O_2$

The reaction of carbon cations with oxygen is important in the ISM due to the relatively high abundance of both reactants in many environments. This reaction occurs via two pathways:



TABLE 4
REACTION RATE CONSTANTS AND PRODUCT BRANCHING RATIOS FOR $C^+ + H_2O$

k ($10^{-9} \text{ cm}^3 \text{ s}^{-1}$)	Products	Branching Ratio (%)	Instrument/Reference
2.7 ± 0.5	$HOC^+ + H$	Not Reported	ICR ^a /Anicich et al. (1976)
$2.03 \pm 30\%$	$HOC^+ + H$	Not Reported	FA/Bolden & Twiddy (1972)
$2.5 \pm 30\%$	$HOC^+ + H$	Not Reported	FASIFT ^b /Smith & Adams (1977b)
2.4.....	$HOC^+ + H$	Not Reported	FASIFT/Tichy et al. (1979)
2.7.....	$HCO^+ + H$	33	Ohio State Database/E. Herbst (2007)
	$HOC^+ + H$	67	Ohio State Database/E. Herbst (2007)
2.7 ± 0.5	$HCO^+ + H$	33	UMIST Database ^c /Anicich, et al. (1976), Woodall, et al. (2007)
	$HOC^+ + H$	67	UMIST Database ^c /Anicich, et al. (1976), Woodall, et al. (2007)
2.09 ± 0.17	$HOC^+ + H$	Not Reported	FASIFT/This work

^a Injection energy <0.1 eV. Product distributions accurate to ~3% of total distribution.

^b ~70 eV EI.

^c Source for the HCO^+/HOC^+ branching ratio is not cited.

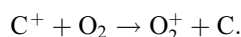
TABLE 5
REACTION RATE CONSTANTS AND PRODUCT BRANCHING RATIOS FOR $C^+ + C_2H_2$

k ($10^{-9} \text{ cm}^3 \text{ s}^{-1}$)	Products	Instrument/Reference
2.8.....	$C_3H^+ + H$	ICR ^a /Anicich et al. (1986)
2.7.....	$C_3H^+ + H$	FA/Schiff & Bohme (1979)
2.2 ± 0.7	$C_3H^+ + H$	FASIFT ^b /Bohme et al. (1982)
2.7.....	$C_3H^+ + H$	Ohio State Database/E. Herbst (2007)
2.2 ± 0.7	$C_3H^+ + H$	UMIST Database/Bohme et al. (1982), Woodall et al. (2007)
1.78 ± 0.15	$C_3H^+ + H$	FASIFT/This work

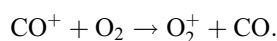
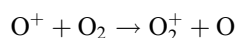
^a ≤ 30 eV EI. ICR experiments at 298 K.

^b Mass discrimination effects cited as negligible for ionic products within a mass range ~ 5 amu. Branching ratio error up to 30% estimated outside this range; 296 K.

Our measurements provide a slightly lower rate constant value [$(0.796 \pm 0.024) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$], as shown in Table 3, than those chosen for the two databases; however, it is in agreement with the rate constants reported by Tichy et al. (1979) and Burley & Armentrout (1988). A charge transfer pathway is not observed since this pathway is endothermic by 0.81 eV:



While Miller et al. (1984) report this pathway, it is likely that they instead observed secondary reactions of the primary product ions:

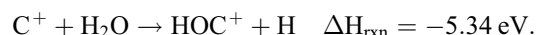


The two databases have chosen very different values for the branching ratios of the primary products. Our measurements, 57% O^+ and 43% CO^+ , are in closer agreement with the values in the UMIST database and with the results of most researchers. Several papers address the mechanism of the reaction. Rincon et al. (1987) and Burley & Armentrout (1988) discuss the possibility that strong spin-orbit coupling between states correlated to the CO^+ and O^+ channels provides for an efficient curve-crossing mechanism that produces O^+ . Adams & Smith (1976) suggest the formation of a short-lived intermediate complex with exit channels of comparable exothermicity. The slightly greater abundance of O^+ relative to CO^+ has also been attributed to the $CO^+ + O$ charge transfer reaction, which Fehsenfeld & Ferguson (1972) have shown to be quite rapid ($k = 1.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$); thus, charge transfer within the reaction complex is likely.

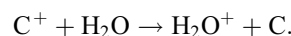
In their studies of metastable carbon cations, Tichy et al. (1979) find that the CO^+ channel becomes 100% for reaction of electronically excited C^+ . We have similarly observed that CO^+ becomes the dominant product channel when C^+ is produced using 70 eV rather than 30 eV electrons. In addition, Rincon et al. (1987) report a translational energy dependence of the branching ratio that favors the CO^+ channel with increased ion kinetic energy.

3.4. $C^+ + H_2O$

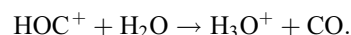
The reaction of carbon cations with water results in OH radical abstraction with H atom elimination:



The charge transfer pathway is endothermic by 1.36 eV, and is not observed:



However, Tichy et al. (1979) infer that this channel becomes the sole pathway for the reaction of electronically excited C^+ . A secondary reaction occurs with water:



While the Ohio State and UMIST databases account for and agree on branching ratios for the formation of the HCO^+ and HOC^+ isomers, our studies cannot readily distinguish these ions. However, since the formation of HCO^+ requires carbon insertion into the O-H bond, the formation of HOC^+ by direct attack at the oxygen is more likely (Ishikawa et al. 2001).

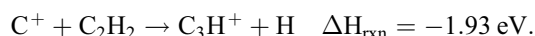
TABLE 6
RECOMMENDED REACTION RATE CONSTANTS AND BRANCHING RATIO VALUES FOR REACTIONS OF C^+ WITH NH_3 , CH_4 , O_2 , H_2O , AND C_2H_2

Reaction	k ($10^{-9} \text{ cm}^3 \text{ s}^{-1}$)	Reaction Efficiency	Products	Branching Ratios
$C^+ + NH_3$	2.4 ± 0.2	0.79	$H_3N^+ + C$ $CH_2N^+ + H$ $CHN^+ + H_2$	28 ± 12 67 ± 11 5 ± 2
$C^+ + CH_4$	1.4 ± 0.1	0.97	$C_2H_2^+ + H_2$ $C_2H_3^+ + H$	28 ± 2 72 ± 2
$C^+ + O_2$	0.8 ± 0.03	0.73	$O^+ + CO$ $CO^+ + O$	57 ± 12 43 ± 12
$C^+ + H_2O$	2.1 ± 0.2	0.63	$HOC^+ + H$	100
$C^+ + C_2H_2$	1.8 ± 0.2	1.1	$C_3H^+ + H$	100

Table 4 shows that our rate constant measurement $[(2.09 \pm 0.17) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}]$ results in a lower value than currently recommended by either of the databases. Our value includes measurements from both FASIFT instruments and represents an average of 10 determinations that are in good agreement with one another. The lower rate constant value obtained in this work may result from careful exclusion of electronically excited C^+ .

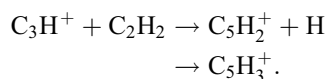
3.5. $\text{C}^+ + \text{C}_2\text{H}_2$

Acetylene formation in the ISM can arise through the neutralization of the primary ions from the carbon cation reaction with methane. Schiff & Bohme (1979) have suggested that reactions of this type ($\text{C}_n\text{H}_x^+ + \text{C}_2\text{H}_2$) are important in the buildup of hydrocarbon frames, resulting in the addition of two carbon atoms at a time. Reaction of acetylene with carbon cation occurs through a single observed pathway (Anicich et al. 1986):



Bohme et al. (1982) suggest that the product ion has carbene character, and that both linear and nonlinear resonance-stabilized structures are thermodynamically possible.

The following secondary reactions of the primary product ion have been observed:



However, since only one primary product is formed, the secondary reactions do not influence the branching ratio measurement.

Values for the rate constant of this reaction are summarized in Table 5. Our rate constant value $[(1.78 \pm 0.15) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}]$ falls within the error bars of the Bohme et al. (1982) measurement, but appears significantly lower than prior literature values. Commercially available cylinders of acetylene generally contain a trace amount of acetone to prevent polymerization of the acetylene. Acetone is extremely reactive with C^+ [SIFT measurement by Bohme et al. 1982; $k = (2.2 \pm 0.7) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$; 47% efficient] and its presence will therefore lead to an artificially faster

reaction rate measurement. We employed two different, relatively new cylinders of acetylene, where the vapor pressure of acetone should be a minor contributor to the total pressure and flow of acetylene. As a precautionary measure, acetylene was passed through a coiled trap immersed in an ice-salt slush bath (-6°C) to remove any possible acetone impurities. In addition, we did not observe the formation of $\text{C}_3\text{H}_6\text{O}^+$ and $\text{C}_2\text{H}_3\text{O}^+$, products of the reaction of C^+ with acetone. Thus, our lower rate constant value may be due to the absence of trace acetone impurities, as well as the absence of electronically excited C^+ reactant ions. Our measured rate constant slightly exceeds the Langevin value, which suggests that even larger rate constants are not likely correct.

4. CONCLUSIONS

The chemistry of the ISM involves a rich network of ions and neutral species. Errors in reaction rate constants and branching ratios in interstellar models can propagate uncertainties in concentrations of interstellar species. This paper addresses five reactions for which improvements in kinetic data have been identified as critical for increased accuracy of model calculations. Table 6 summarizes our recommended rate constants and branching ratios for the reactions of C^+ with NH_3 , CH_4 , O_2 , H_2O , and C_2H_2 , for inclusion in astrochemical models; the calculated reaction efficiencies are also indicated. These experiments utilized two calibrated and optimized FASIFT instruments, in which ground state C^+ was cleanly generated; in addition, we systematically addressed reactant purity, mass discrimination, and secondary reactions. We report these final numbers with two significant figures to properly reflect the combined reproducibility and systematic error. Further studies of these reactions as a function of temperature would be valuable for more accurate astrochemical modeling.

We express our sincere gratitude for financial support from NASA and from the NASA Graduate Student Researchers Program (GSRP). We thank Joshua Destree for assistance with figures.

REFERENCES

- Adams, N. G., & Smith, D. 1976, *J. Phys. B*, 9, 1439
 ———. 1977, *Chem. Phys. Lett.*, 47, 383
 Anicich, V. G., Huntress, W. T., & Futrell, J. H. 1976, *Chem. Phys. Lett.*, 40, 233
 Anicich, V. G., Huntress, W. T., & McEwan, M. J. 1986, *J. Phys. Chem.*, 90, 2446
 Bierbaum, V. M. 2003, in *Encyclopedia of Mass Spectrometry*, ed. P. B. Armentrout (Amsterdam: Elsevier), 940
 Bohme, D. K., Rakshit, A. B., & Schiff, H. I. 1982, *Chem. Phys. Lett.*, 93, 592
 Bolden, R. C., & Twiddy, N. D. 1972, *Faraday Discussions of the Chemical Society*, 53, 192
 Burley, J. D., & Armentrout, P. B. 1988, *Int. J. Mass Spectrom. Ion Processes*, 84, 157
 Chong, S.-L., & Franklin, J. L. 1971, *J. Chem. Phys.*, 54, 1487
 Fehsenfeld, F. C., & Ferguson, E. E. 1972, *J. Chem. Phys.*, 56, 3066
 Fehsenfeld, F. C., Schmeltekopf, A. L., & Ferguson, E. E. 1966, *J. Chem. Phys.*, 45, 23
 Franklin, J. L., & Munson, M. S. B. 1964, in *Proc. Tenth Symp. (International) on Combustion*, ed. W. G. Berl (Pittsburgh: Combustion Inst.), 1488
 Gioumoussis, G., & Stevenson, D. P. 1958, *J. Chem. Phys.*, 29, 294
 Hemsworth, R. S., Bolden, R. C., Shaw, M. J., & Twiddy, N. D. 1970, *Chem. Phys. Lett.*, 5, 237
 Herbst, E., & Klemperer, W. 1973, *ApJ*, 185, 505
 Herod, A. A., & Harrison, A. G. 1970, *Int. J. Mass Spectrom. Ion Processes*, 4, 415
 Ishikawa, Y., Binning, R. C., & Ikegami, T. 2001, *Chem. Phys. Lett.*, 343, 413
 Liddy, J. P., Freeman, C. G., & McEwan, M. J. 1977, *MNRAS*, 180, 683
 Mackenzie Peers, A., & Milhau, J. 1974, *Int. J. Mass Spectrom. Ion Processes*, 15, 145
 Markwick-Kemper, A. J. 2005, in *Proc. IAU Symp. 231, Astrochemistry: Recent Successes and Current Challenges*, ed. D. C. Lis, G. A. Blake, & E. Herbst (Cambridge: Cambridge Univ. Press), 204
 Miller, T. M., Wetterskog, R. E., & Paulson, J. F. 1984, *J. Chem. Phys.*, 80, 4922
 Rakshit, A. B., Stock, H. M. P., Wareing, D. P., & Twiddy, N. D. 1978, *J. Phys. B*, 11, 4237
 Rincon, M., Pearson, J., & Bowers, M. T. 1987, *Int. J. Mass Spectrom. Ion Processes*, 80, 133
 Schiff, H. I., & Bohme, D. K. 1979, *ApJ*, 232, 740
 Schiff, H. I., Hemsworth, R. S., Payzant, J. D., & Bohme, D. K. 1974, *ApJ*, 191, L49
 Smith, D., & Adams, N. G. 1977b, *Int. J. Mass Spectrom. Ion Processes*, 23, 123
 ———. 1977c, *Chem. Phys. Lett.*, 47, 145
 Snow, T. P., & McCall, B. J. 2006, *ARA&A*, 44, 367
 Su, T., & Chesnavich, W. J. 1982, *J. Chem. Phys.*, 76, 5183
 Tichy, M., Rakshit, A. B., Lister, D. G., Twiddy, N. D., Adams, N. G., & Smith, D. 1979, *Int. J. Mass Spectrom. Ion Processes*, 29, 231
 Twiddy, N. D., Mohebati, A., & Tichy, M. 1986, *Int. J. Mass Spectrom. Ion Processes*, 74, 251
 Van Doren, J. M. 1987, in *Chem. Phys. (Boulder: Univ. Colorado)*, 341
 Van Doren, J. M., Barlow, S. E., Depuy, C. H., & Bierbaum, V. M. 1987, *Int. J. Mass Spectrom. Ion Processes*, 81, 85
 Watson, W. D. 1974, *ApJ*, 188, 35
 Woodall, J., Agúndez, M., Markwick-Kemper, A. J., & Millar, T. J. 2007, *A&A*, 466, 1197
 Xu, Y., Moran, T. F., & Thomas, E. W. 1990, *Phys. Rev. A*, 41, 1408