HOC$^+$ + H$_2$ ISOMERIZATION RATE AT 25 K: IMPLICATIONS FOR THE OBSERVED [HCO$^+$]/[HOC$^+$] RATIOS IN THE INTERSTELLAR MEDIUM

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ABSTRACT

The recent detection of the metastable HOC$^+$ isomer toward a wide range of interstellar environments has demonstrated abundances that cannot be explained within current chemical models. The abundance of HOC$^+$ in these models relies heavily on the rate of the isomerization of HOC$^+$ by H$_2$ to the lowest energy isomer, HCO$^+$. A variable temperature 22-pole ion-trap apparatus is employed to study the isomerization of HOC$^+$ by H$_2$ at 25 K. The observed rate coefficient for isomerization is $(3.8 \pm 0.5) \times 10^{-10}$ cm^3 s^{-1}. This indicates that there is probably no temperature dependence in this reaction below 300 K, suggesting the absence of any significant energetic barrier on the lowest adiabatic H$_3$CO$^+$ potential surface. This result argues that in regions where abundant HOC$^+$ is observed, the production of this isomer must be strongly favored or that there is a concomitant rapid physicochemical loss for the isomer HCO$^+$. Some results for forming DCO$^+$ are briefly mentioned.

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

1. INTRODUCTION

Recent observations have clearly identified the metastable ion HOC$^+$ in the presence of its stable isomer HCO$^+$ in a wide variety of interstellar molecular environments (Ziurys & Apponi 1995; Apponi & Ziurys 1997). The HOC$^+$ isomer occurs significantly in both photon-dominated regions (Sgr B2, NGC 7538, and NGC 2024) and dense molecular clouds [DR 21(OR), W51M, W3(OR), Orion(3N, IE), Orion KL, and G34.3]. Isomer ratios, [HCO$^+$]/[HOC$^+$], between 300 and 6000 are observed in these varied objects. The formation, conversion, and destruction of HOC$^+$ and HCO$^+$ through ion-molecule reaction channels allows for a stringent comparison between observed values for the isomer ratio [HCO$^+$]/[HOC$^+$] and the validity of the chemical models of these environments. The isomer ratio is a sensitive function of the hydrogen-catalyzed isomerization rate coefficient for the reaction

$$HOC^+ + H_2 \rightarrow HCO^+ + H_2 \qquad (1)$$
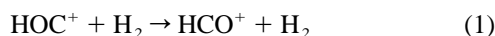
and its temperature dependence (Jarrold et al. 1986; Herbst & Woon 1996). Uncertainty in the low-temperature rate coefficient for reaction (1) has contributed to a general disagreement between the simple models and recent observations.
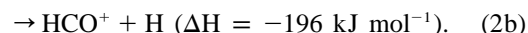
Early calculations on this reaction showed that the reaction potential surface possesses a substantial energy barrier preventing reaction (1) from playing a significant role in the destruction of HOC$^+$ in the interstellar medium (ISM; DeFrees, McLean, & Herbst 1984). Subsequent calculations suggested that this barrier was much smaller (2 ± 3 kcal mol^{-1} or 1000 ± 1500 K), including the effects of zero-point energy (Jarrold et al. 1986). The most recent potential surface calculations (Herbst & Woon 1996) suggest a negative barrier height of -1.5 kcal mol^{-1}; however, when corrected for zero-point energy, the effective barrier rises to $+1.4$ kcal mol^{-1}. Phase-space calculations on this potential surface yield rate coefficients below 2×10^{-11} cm^3 s^{-1} between 10 and 80 K (Herbst & Woon 1996). Use of the reasonably low predicted rate co-

efficients is necessary if the Herbst & Woon model is to explain the small [HCO$^+$]/[HOC$^+$] ratios observed in the ISM.

The rate coefficient for reaction (1) has been previously measured at 300 K to be 4.7×10^{-10} cm^3 s^{-1} (Freeman et al. 1987). In order to fit this rate coefficient to a reaction potential surface, it is essentially necessary to remove any effective positive barrier (including zero-point energy). Calculations employing a negative barrier of -0.7 kcal mol^{-1} (Herbst & Woon 1996) predict a rate coefficient at 300 K consistent with that observed. However, this result also predicts the rate coefficient for reaction (1) to have an inverse temperature dependence and to exceed values of 1×10^{-9} cm^3 s^{-1} below 80 K. Within the current reaction model, use of these rate coefficients overestimates the observed values of the [HCO$^+$]/[HOC$^+$] ratio, owing to the rapid chemical quenching of HOC$^+$. Possible discrepancies in source reactions for both HOC$^+$ and HCO$^+$ are not expected to be a cause in this disagreement. At low temperatures, the tremendous rate sensitivity to small errors in a nearly attractive potential surface, as well as to the errors associated with the only measured rate coefficient at 300 K, leads to a bottleneck in the ability to bring together observation and modeling to learn more regarding the chemical and physical properties in the observed objects.

2. EXPERIMENTAL

The temperature-variable 22-pole ion-trap apparatus used in these experiments has been well documented (Gerlich & Horning 1992; Schlemmer et al. 1999). Mass-selected CO$^+$ ions are injected from a storage ion source containing CO into the cooled 22-pole ion trap where they are stored in the presence of molecular hydrogen (with number densities between 10^{10} and 10^{12} cm^{-3}) for times varying between milliseconds and minutes. During this time, the CO$^+$ is rapidly converted to HOC$^+$ and HCO$^+$ by the reactions

$$CO^+ + H_2 \rightarrow HOC^+ + H \ (\Delta H = -30 \text{ kJ mol}^{-1}), \qquad (2a)$$

$$\rightarrow HCO^+ + H \ (\Delta H = -196 \text{ kJ mol}^{-1}). \qquad (2b)$$

In competition with the accumulation of both reaction products according to the two channels (reactions [2a] and [2b]), HOC$^+$ isomerization takes place according to reaction (1). For

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determining experimentally the abundance of the two isomers as a function of time, the method of chemical probing has been applied. At some time delay following CO$^+$ injection, a pulse of NO is admitted to the trap in sufficient density to rapidly convert or quench all remaining metastable HOC$^+$ ions through the two additional reactions

$$HOC^+ + NO \rightarrow NOH^+ + CO, \qquad (3a)$$

$$\rightarrow HCO^+ + NO. \qquad (3b)$$
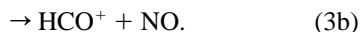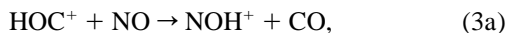
alternatively, methane has also been used, leading to

$$HOC^+ + CH_4 \rightarrow CH_5^+ + CO, \qquad (4a)$$

$$\rightarrow HCO^+ + CH_4. \qquad (4b)$$
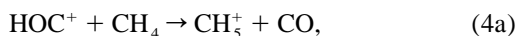
Both probing species have proton affinities in excess of that for CO on the O end (427 kJ mol^{-1}) but less than that for CO on the C end (594 kJ mol^{-1}) (Freeman et al. 1987). Thus, only the proton transfer from the more energetic HOC$^+$ is exoergic. Those HCO$^+$ ions that have been produced by reaction (2a) are unchanged by the presence of the probing gas; however, the total number of HCO$^+$ grows because of the quenching reactions (3b) and (4b). Unfortunately, simple mass analysis does not allow the determination of the branching fraction of reactions (3a) and (3b) and reactions (4a) and (4b). However, the number of NOH$^+$ and CH$_5^+$ products only depends on the number of HOC$^+$ products at the time of the quenching pulse. Therefore, the unknown branching does not affect the determination of k_1 from the data.

As usual in this type of trapping experiment (Schlemmer et al. 1999), the total number of ions of a given mass is determined by emptying the trap contents into a quadrupole mass spectrometer after a given delay time. In the present experiment, in addition, the intense probing pulse is injected before extraction. Within a few milliseconds, this converts most metastable isomers via reactions (3a) and (3b) or reactions (4a) and (4b). A low number of observed NOH$^+$ or CH$_5^+$ at late times demonstrates the temporal loss of HOC$^+$ due to reaction (1). From a fit to the full ion temporal profiles, a reliable measure of k_1 is determined.

3. RESULTS AND DISCUSSION

In the top panel of Figure 1, the number of late trapping time product ions, CH$_5^+$ and $m = 29$ u products (HOC$^+$ and HCO$^+$), are displayed as a function of the time with and without adding the CH$_4$ probing gas pulse. The top curve, without the CH$_4$ monitor pulse, shows the gain of the products HOC$^+$ and HCO$^+$, both having $m = 29$ u. With the monitor gas pulse, due to the high number density, CH$_5^+$ products are formed within a few milliseconds via the exothermic reaction (4a) (*lower two curves*). The gas pulse is sufficiently intense that nearly all HOC$^+$ ions are converted into CH$_5^+$ during this process. The two sets of data points marked with $m = 29$ u are the combined HOC$^+$ and HCO$^+$ products without (upper trace) and with (lower trace) injection of the CH$_4$ monitor gas pulse. The early $m = 29$ u products represent the total initial HOC$^+$ and HCO$^+$ population, while the late-time $m = 29$ u products are almost exclusively ground-state HCO$^+$ isomers. As the CH$_4$ gas pulse is further delayed relative to the CO$^+$ injection, the HOC$^+$ concentration at the time of the CH$_4$ pulse decays as a result of the H$_2$ quenching process, reaction (1). This behavior is evident from the reduction of the maximum
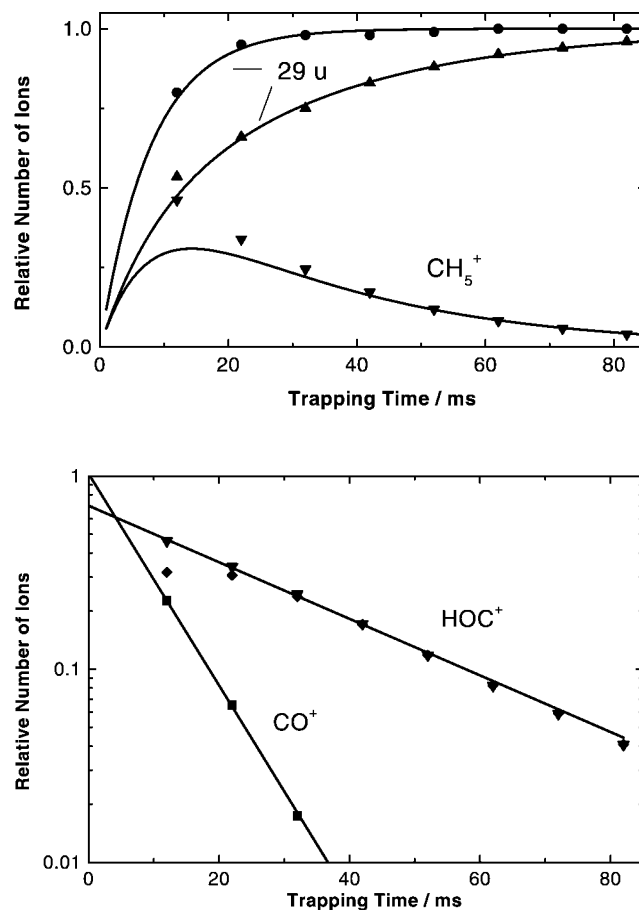

Fig. 1.—Time dependence of the indicated product ions with and without chemical probing by CH$_4$ at 25 K and with [H$_2$] = 6 × 10^{10} cm^{-3}. In the top panel, the upper data points marked with $m = 29$ u (*filled circles*, no probing gas) show the sum of both isomers, HCO$^+$ and HOC$^+$. The normal upward-pointing filled triangles are exclusively HCO$^+$ ions after removing HOC$^+$ with CH$_4$. As can be concluded from the solid line that shows the solution of a simple kinetic equation, the CH$_5^+$ products (*downward-pointing filled triangles*) are predominantly formed via reaction (4a). Deviations at short times are due to parasitic reactions of CO$^+$ with methane. After 40 ms, the decrease of the number of CH$_5^+$ ions is predominantly due to the quenching reaction (1). *Bottom panel*: Semilogarithmic plot of the decay of CO$^+$ due to reactions (2a) and (2b) (*solid squares*) and of HOC$^+$ due to reaction (1). The number of HOC$^+$ has been determined indirectly in two ways. The downward-pointing triangles show the number of CH$_5^+$ ($\propto$HOC$^+$); the filled diamonds show the difference of the mass 29 u intensities from the top panel.

CH$_5^+$ number with increasing time. After 40 ms, the CH$_5^+$ signal becomes a simple first-order exponential decay governed by the isomerization rate k_1 times the H$_2$ density as displayed in the bottom panel of Figure 1. The solid lines represent a simulation of the CH$_5^+$ and $m = 29$ u products.

At the low temperature of the experiment, no evidence of the slightly endoergic proton transfer reaction of HOC$^+$ + H$_2 \rightarrow$ H$_3^+$ + CO is observed, which argues strongly that the HOC$^+$ studied in this apparatus is predominantly thermalized to the trap temperature. Further evidence for internally cold ions under the present circumstance is no indication of the formation of HNO$^+$ and CH$_5^+$ in collisions with potentially vibrationally hot HCO$^+$. The surest sign that the measurements are not perturbed by a cooling HOC$^+$ reagent is that the number of HOC$^+$ products measured via the CH$_5^+$ quenching channel decays monoexponentially. Details of the analysis will be given in a forthcoming publication focusing on the kinetics involved in the procedure of chemically probing metastable ion con-

centrations (S. Schlemmer, M. A. Smith, & D. Gerlich 2002, in preparation).

The value of k_1 is found, within the error of the experiment, to be independent of the quenching agent employed (CH_4 or NO). The isomerization rates derived from studies with CH_4 vary between 3.3 and 4, the results with NO between 3.5 and 4.2 (in units of 10^{-10} cm^3 s^{-1}). The final result is presented in Table 1. Comparison of this result with the 300 K rate coefficient from Freeman et al. (1987) allows for the conclusion that reaction (1) is not significantly temperature dependent between 25 and 300 K.

In order to give an upper limit of a possible barrier for the isomerization reaction, other factors aside from the collision temperature have to be taken into account. At 25 K, the normal H_2 employed in this study consists of approximately 75% ortho-H_2 ($J = 1$) and 25% para-H_2 ($J = 0$). Scrambling of all three points in the HOC^+ + ortho-H_2 collision can lead to the incorporation of rotational energy into the reaction. Since ortho-H_2 is the dominant species in the present study, the barrier could be substantially higher than 50 K (0.4 kJ mol^{-1}). In order to obtain a reliable upper bound for the barrier height, measurements employing para-H_2 are necessary.

An interesting experiment that provides important information on the chemical equivalence of the three hydrogen atoms in the H_3CO^+ collision complex is the H-D isotope exchange in collisions with HD or D_2. In addition, such low-temperature experiments are urgently needed for providing reliable data for the astrophysically important process of isotope enrichment as recently discussed by Gerlich & Schlemmer (2002). Reactions (2a) and (2b) have been performed with natural hydrogen containing 3×10^{-3} parts HD, leading to the formation of a small amount of DOC^+ and DCO^+. The actually measured fraction of 5×10^{-3} is less than twice the HD abundance. No conversion is observable when most ions have been converted into HCO^+. This allows for the conclusion that the ground-state isomer HCO^+ does not undergo H-D exchange with HD. A more detailed analysis of the ion temporal profiles in CO^+ + H_2/HD collisions at 25 K suggests that the reaction HOC^+ + HD → DOC^+/DCO^+ + H_2 is at least as fast as reaction (1). In addition, a certain amount of DCO^+ also can be formed in collisions of HOC^+ with HD if, in the course of isomerization, proton-deuteron scrambling is possible. In summary, the experiment allows one to conclude that under the conditions of the ISM, CO^+ ions can only produce a DCO^+/HCO^+ ratio that is twice as large as the prevailing HD/H_2 ratio. Of course, other reactions such as H_2D^+ + CO also lead to DCO^+.

In another set of measurements, HCO^+ and HOC^+ have been produced in the ion source and then injected into the trap at 20 K, containing pure D_2 target gas with a number density of 4×10^{11} cm^{-3}. From the results, it could be concluded that

$$HOC^+ + D_2 \rightarrow DOC^+/DCO^+ + HD \qquad (5)$$

proceeds at a rate coefficient of $(2.0 \pm 0.4) \times 10^{-10}$ cm^3 s^{-1} and that isotopic fractionation of HCO^+ via

$$HCO^+ + D_2 \rightarrow DCO^+ + HD \qquad (6)$$
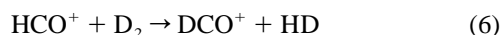
is not happening. An upper boundary derived from the experimental results is $k_6 \leq 3 \times 10^{-12}$ cm^3 s^{-1}. These findings are consistent with the picture of the H_3OC^+ transition state that consists of a H_3^+ fixed to CO. A more accurate picture of the role of the activation barrier and the rate of isomerization comes only from more detailed phase-space calculations and further

TABLE 1
RATE COEFFICIENTS FOR ASSOCIATED HOC^+/HCO^+ REACTIONS

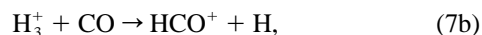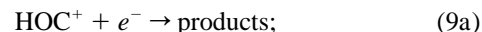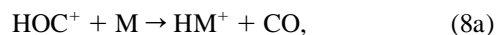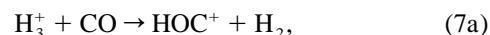| Reaction	T (K)	k ($\times 10^{-10}$ cm^3 s^{-1})
$CO^+ + H_2 \rightarrow HOC^+/HCO^+ + H$	...	15.3[a]
	20–300	15.5 ± 1.6
$H_3^+ + CO \rightarrow HOC^+/HCO^+ + H_2$	80	20 ± 2
$HOC^+ + H_2 \rightarrow HCO^+ + H_2$	300	4.7 ± 1.9[b]
	25	3.8 ± 0.5
$HOC^+ + D_2 \rightarrow DOC^+/DCO^+ + HD$	20	2.0 ± 0.4
$HCO^+ + D_2 \rightarrow DCO^+ + HD$	20	<0.03

[a] Langevin.
[b] Freeman et al. 1987.

experiments involving para-H_2 and pure HD as the isomerization agent.

From the work of Herbst & Woon (1996), one would predict that a negative barrier height (purely attractive) reaction surface is required for reaction (1), most likely with a late transition state characterized by a slightly less negative barrier than -0.7 kcal mol^{-1} (-350 K), if an agreement is to be made with the current 25 K experimental result. This leaves the situation such that reaction (1) remains fast across the temperature range of interest in the ISM ($T > 10$ K), with a rate coefficient approximately $\frac{1}{5}$ that of the Langevin capture value. With the assumption of similarly rapid isomerization rates, Jarrold et al. (1986) concluded earlier that [HCO^+]/[HOC^+] ratios should exceed 10^5–10^6. In order to shed light on the low values of [HCO^+]/[HOC^+] recently detected, the processes associated with the production and destruction of these ions should be reexamined.

The production of HOC^+ is believed to be dominated, in the various interstellar environments, by the proton transfer reaction of H_3^+ with CO, reactions (7a) and (7b):

$$H_3^+ + CO \rightarrow HOC^+ + H_2, \qquad (7a)$$

$$HOC^+ + M \rightarrow HM^+ + CO, \qquad (8a)$$

$$HOC^+ + e^- \rightarrow products; \qquad (9a)$$

$$H_3^+ + CO \rightarrow HCO^+ + H, \qquad (7b)$$

$$HCO^+ + M \rightarrow HM^+ + CO, \qquad (8b)$$

$$HCO^+ + e^- \rightarrow products. \qquad (9b)$$
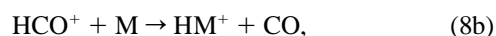
Other possibly important sources of HOC^+ might also be reactions (2a) and (2b) and the reaction of C^+ with H_2O depending on the relative ion and neutral molecule abundances. Loss of HOC^+ comes via the competition between hydrogen-catalyzed isomerization, reaction (1), and chemical removal channels. The chemical removal processes would include proton transfer to molecules M with greater proton affinities than those for CO, reactions (8a) and (8b), and electron-ion recombination, reactions (9a) and (9b).

Simple steady state analysis for the above reaction scheme leads to the following relationship between chemical rate processes and the [HCO^+]/[HOC^+] ratios:

$$[HCO^+]/[HOC^+] = (k_1 n_{H_2})/[\alpha(k_{(8b)} n_M + k_{(9b)} n_e)]. \qquad (10)$$

The branching ratio for the net production of nascent HOC^+ in the object under observation is given by α. In the simplest case of a single reaction yielding the majority of both isomers,

such as reactions (7a) and (7b), α simply becomes the branching ratio, $k_{(7a)}/(k_{(7a)} + k_{(7b)})$. The major approximation going into equation (10) is that the rate of isomerization, $k_1 n_{H_2}$, greatly exceeds the rates for reactions (8a) and (9a), $k_{(8a)} n_M$ and $k_{(9a)} n_e$. With the current 25 K value for k_1, this would appear to be a generally good approximation applied to the objects for which HOC$^+$ is being observed. In order to explain ratios of 300–6000 for [HCO$^+$]/[HOC$^+$], it is necessary to have conditions such that the HCO$^+$ loss rate approaches a fraction of the HOC$^+$ quenching rate given by $\alpha/([HCO^+]/[HOC^+])$. The value of α for the most important source reaction varies between 0.06 (for reactions [7a] and [7b]) up to possibly 0.8 for C$^+$ + H$_2$O. For reactions (2a) and (2b), α is reported to be 0.48 (Freeman et al. 1987). This value is in good agreement with our results for CH$_4$ as the probing agent assuming that CH$_4$ does not isomerize HOC$^+$. For the question of ion-molecule removal, even the fastest proton transfer reactions would be expected to have rate coefficients comparable to or less than 10^{-8} cm^3 s^{-1} and at least an order of magnitude lower for nonpolar molecules, M. In this case, relative abundances of M compared with H$_2$ would need to be in the range of 10^{-3} to 10^{-4} in order to explain the [HCO$^+$]/[HOC$^+$] ratios. Electron-ion recombination rate coefficients are typically at least 1 order of magnitude larger than ion-molecule rate coefficients values. For reaction (9b), the rate coefficient has been predicted to be 1.3×10^{-6} cm^3 s^{-1} near 25 K (Le Teuff, Millar, & Markwick 2000). Use of this value (ignoring reaction [8b]) and the observed [HCO$^+$]/[HOC$^+$] ratios would require a relative electron density approximately equal to 1.4×10^{-5} to 5×10^{-8} depending on source branching into HOC$^+$. These values of fractional ionization required to explain the HOC$^+$ abundance appear much more likely than the neutral M abundances necessary for reaction (8b) to dominate the HCO$^+$ loss. Although this precise relationship between the [HCO$^+$]/[HOC$^+$] ratios and the HCO$^+$ dissociative recombination rate needs to be con-

firmed by the global reaction models employing these new results with all reaction networks, it would imply that the most sensitive indicator of HOC$^+$ presence in interstellar media may well be fractional ionization. At high electron densities, the HCO$^+$ destruction rate becomes comparable to the isomerization rate of HCO$^+$. In this instance, the [HCO$^+$]/[HOC$^+$] ratio approaches that nascent to the net HCO$^+$ + HOC$^+$ production process branching. These nascent branching ratios are expected to initially result in [HCO$^+$]/[HOC$^+$] ratios less than 100 even in the presence of several active source reactions. Competition between HOC$^+$ isomerization and HCO$^+$ destruction through mechanisms like electron-ion recombination then increases this steady state ratio upward.

4. CONCLUSIONS

Uncertainty regarding the rate of the HOC$^+$ + H$_2$ isomerization reaction at interstellar temperatures has been removed. The reaction is observed to be rapid with a 25 K rate coefficient approximately $\frac{1}{5}$ that of the Langevin capture value. This observation requires reanalysis of the reaction sequences predominantly governing HCO$^+$ (and to a lesser extent HOC$^+$) chemical destruction. It is proposed that electron-ion recombination is the most likely reaction governing this loss and that [HCO$^+$]/[HOC$^+$] ratios may be a valid indicator of fractional ionization in the local environment.

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