

WHY HOC^+ IS DETECTABLE IN INTERSTELLAR CLOUDS: THE RATE OF THE REACTION BETWEEN HOC^+ AND H_2

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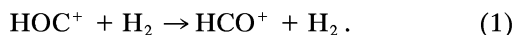
ABSTRACT

The recent confirmation by Ziurys and Apponi of the detection of HOC^+ toward Sgr B2 (OH), and their identification of the ion in Orion-KL and several other sources show that HOC^+ is far more abundant than predicted by previous ion-molecule models. In these models, the reaction $\text{HOC}^+ + \text{H}_2 \rightarrow \text{HCO}^+ + \text{H}_2$ is assumed to rapidly destroy HOC^+ , based on the results of a prior calculation. We have recalculated the rate of this reaction as a function of temperature using a new ab initio potential surface and a phase space approach to the dynamics which includes tunneling. The newly calculated rate is small ($\leq 1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) at temperatures under 100 K.

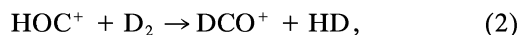
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1. INTRODUCTION

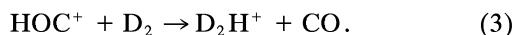
Recent observations by Ziurys & Apponi (1995) both confirm the original identification by Woods et al. (1983) that the metastable ion HOC^+ is present in dense interstellar clouds and show that ion-molecule models vastly underestimate its abundance (Jarrold et al. 1986). Although the formation mechanisms of the stable ion HCO^+ and its metastable counterpart HOC^+ by ion-molecule reactions are not identical (Jarrold et al. 1986; McEwan 1992), the major reason for the low calculated abundance of the metastable ion is the catalytic reaction



Although this reaction was first calculated to have a large transition state barrier in its potential surface and to be very slow at low temperatures (DeFrees, McLean, & Herbst 1984), subsequent calculations by Jarrold et al. (1986) showed a very small barrier of $(2 \pm 3) \text{ kcal mol}^{-1}$ including the contribution of zero-point energy ($1 \text{ kcal mol}^{-1} = 503 \text{ K}$). Jarrold et al. (1986) also reported the results of phase space dynamics calculations on reaction (1) undertaken with a transition state energy including zero-point energy of $0.7 \text{ kcal mol}^{-1}$ below the energy of the reactants. This energy, within the uncertainty of the ab initio calculations, was adopted to better fit nonthermal experiments on reaction (1), and its isotopic variant



as well as the slightly endothermic reaction



With the use of the lowered transition state energy, the phase space calculations yield a rate coefficient for reaction (1) that increases with decreasing temperature and reaches a value of $1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at 10 K. Subsequent to the calculations, McEwan (1992) measured a rate coefficient of $4.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for the disappearance of HOC^+ upon reaction with H_2 at room temperature, but there is evidence

that perhaps 50% of the reactions lead to the slightly endothermic products $\text{H}_3^+ + \text{CO}$ (McEwan 1992).

With a large rate coefficient for reaction (1) at low temperature, models of the gas phase chemistry show an $\text{HCO}^+/\text{HOC}^+$ abundance ratio of $\approx 10^5$ at standard gas densities of $10^4\text{--}10^5 \text{ cm}^{-3}$ (Jarrold et al. 1986; Lee, Bettens, & Herbst 1996). The observed ratio of Ziurys & Apponi (1995) is 140–360 toward Sgr B2 (OH) and 1800 toward Orion-KL. The discrepancy between observation and theory suggests two possibilities. First, the detected metastable ion is not found under normal low-temperature conditions but perhaps in high-density photon-dominated regions where the destruction rates of both stable and metastable ions are similar. Second, reaction (1) is not as rapid as the work of Jarrold et al. (1986) indicates. To explore the second possibility, we have both recalculated the potential energy surface for the destruction of HOC^+ by H_2 and have redone the phase space dynamics calculations to determine the rate coefficient of this reaction. Our results, discussed below, both fit the new thermal data at 300 K and show that the reaction is indeed slow at low temperatures, suggesting strongly that the second possibility is the correct one.

2. POTENTIAL ENERGY SURFACE CALCULATIONS

The new ab initio potential energy surface was generated¹ using triple zeta quality (correlation consistent polarized valence triple zeta [cc-pVTZ] on H and augmented cc-pVTZ on C and O) correlation consistent basis sets (Dunning 1989; Kendall, Dunning, & Harrison 1992) and the coupled cluster method CCSD(T) (Deegan & Knowles 1994). Separate surfaces were generated for the entrance and exit channel complexes, the transition state (TS), and the various species present in the reactant and product asymptotes, and fitted with

¹ All calculations were performed using the MOLPRO suite of ab initio programs written by H.-J. Werner and P. J. Knowles with contributions by J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. A. Peterson, R. M. Pitzer, A. J. Stone, and P. R. Taylor. Only valence electrons were correlated, and spherical contractions were used for *d* and *f* functions.

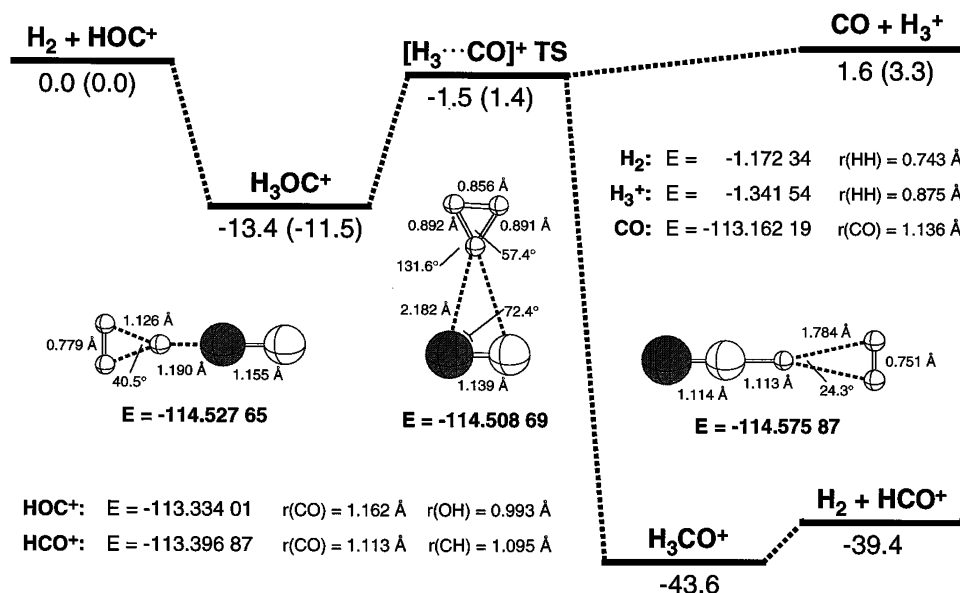


FIG. 1.—The minimum energy potential pathway from $\text{HOC}^+ + \text{H}_2$ reactants to two sets of products: $\text{HCO}^+ + \text{H}_2$ and $\text{CO} + \text{H}_3^+$. The computed relative energies (kcal mol^{-1}) listed for the stationary points (reactants, complexes, transition state, and products) are given without and with zero-point energy corrections. Corrected values are in parentheses. The structures of the two complexes and transition state are shown with bond lengths in angstroms (Å) and bond angles in degrees. Calculated absolute energies are in hartrees ($1 \text{ H} = 3.16 \times 10^5 \text{ K}$).

the SURVIBTM program (Harding & Ermler 1985). The use of large basis sets and a high level of correlated ab initio methodology makes it possible to put error bounds of about $\pm 0.5 \text{ kcal mol}^{-1}$ on the barrier height and $\pm 1 \text{ kcal mol}^{-1}$ on the ergicities of the $\text{H}_2 + \text{HCO}^+$ and $\text{CO} + \text{H}_3^+$ product asymptotes relative to reactants.

Figure 1 depicts the combined reaction path for reactions (1) and (3) with H_2 rather than D_2 and the structures of the three stationary points (two complexes and one TS) that are encountered upon it. Energy differences are relative to the reactants. The barrier height has the interesting property of changing sign when the zero-point energy correction is added to the equilibrium value. The values of the barrier height and other relative energies determined in the present study are not dramatically different from those reported in Jarrold et al. (1986), but the uncertainty in the barrier height is much less than the $\pm 3 \text{ kcal mol}^{-1}$ of that work.

Reaction (1) is aptly described as an escorted isomerization. The H_2 molecule catalytically decreases the energy barrier that must be surmounted to isomerize HOC^+ to HCO^+ . The computed barrier height for this process drops from almost 40 kcal mol^{-1} in isolated $\text{HOC}^+/\text{HCO}^+$ (Martin, Taylor, & Lee 1993) to almost zero in the present case. This dramatic change is due to a competition between CO and H_2 over possession of H^+ . In the entrance and exit channel complexes, H^+ is more closely bound to CO , but the transition state is essentially a weakly bound $[\text{H}_3\cdots\text{CO}]^+$ complex.

Various isotopic substitutions of H with D can significantly affect the barrier height of reaction (1) and the corresponding rate (Woon & Herbst 1996). Although of limited relevance in the present context of predicting the $\text{HCO}^+/\text{HOC}^+$ abundance ratio in cold interstellar clouds, an understanding of isotopic substitution is important for reconciling the astronomical observations with laboratory measurements at higher temperatures. Woon & Herbst (1996) also investigated a mechanism by which H/D exchange may occur, which is

critical for understanding the products of laboratory experiments with deuterated reactants.

3. CALCULATIONS OF THE REACTION DYNAMICS

The reaction dynamics have been treated by the phase space approach (Herbst 1996), which is a statistical method in which angular momentum is conserved rigorously. Our particular method, which has already been used for both ion-molecule (Herbst et al. 1991) and neutral-neutral (Herbst 1994) reactions, incorporates a tunneling algorithm first used by Miller (1979) and is optimized for low temperatures. Reactants in specific rotational-vibrational states collide with a specific collision energy to form a reaction complex with a range of possible angular momenta, constrained by the long-range potential, which is here assumed to be Langevin. The complex can then redissociate into reactants, stabilize itself via emission of radiation or collisions to form a stable entity, or dissociate into products. In the case studied here, stabilization of the complex is unimportant since it is not strongly bound. The dissociation of the complex to form products occurs via a transition state and leads to two sets of products: $\text{HCO}^+ + \text{H}_2$ and $\text{H}_3^+ + \text{CO}$, the latter being slightly endothermic. We have not attempted to calculate the branching ratio between the two sets of products; at low interstellar temperatures the endothermic channel is unimportant. Once the rate coefficient is calculated for the state-specific reactants, averaging is needed to obtain a thermal (canonical) rate coefficient for reaction.

The calculated rate coefficient as a function of temperature in the range 10–300 K is shown in Figure 2. The parameters used in the phase space calculations consist of the energies in Figure 1, the frequencies and rotational constants listed in Table 1, most of which have been calculated by the ab initio methods reported here, and the polarizability of H_2 . We have assumed the H_2 to exist in its equilibrium rotational modification rather than its normal one, but ortho/para effects have

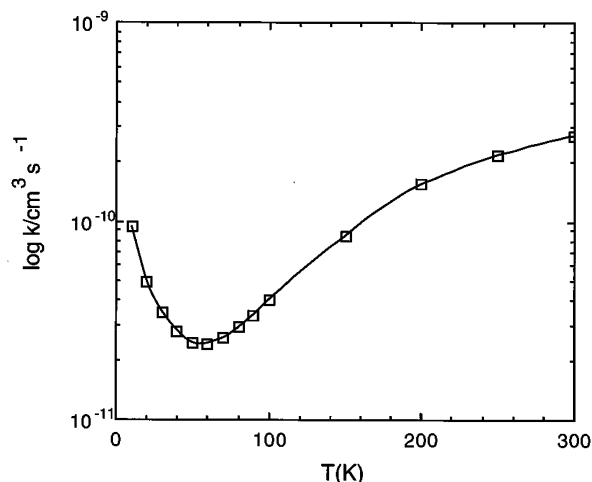


FIG. 2.—The rate coefficient k for the reaction between HOC^+ and H_2 is plotted vs. temperature. At low temperatures, the dominant exit channel is the exothermic one to form $\text{HCO}^+ + \text{H}_2$. Excited bending states of HOC^+ are assumed not to be thermally populated.

been found to be minimal at all temperatures studied. At the higher temperatures considered, a number of excited bending states of HOC^+ are populated in a thermal environment but not in the low-density interstellar medium. We have calculated rate coefficients with and without thermal excitation in the bending mode; the effect is always less than a factor of 2. At all temperatures studied, tunneling under the transition state has been found to be the dominant mechanism for reaction.

The calculated thermal rate coefficient at room temperature is $3.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, in reasonable agreement with the value of $4.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ obtained by McEwan (1992). With the exclusion of thermally excited bending states of HOC^+ , the calculated value drops to $2.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. As the temperature declines, the latter rate coefficient declines gradually, reaching a minimum of $2.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at 50 K and then begins to increase again as the temperature is further reduced. The unusual temperature dependence is similar to that measured and calculated for the $\text{NH}_3^+ + \text{H}_2$ system (Herbst et al. 1991). The rate coefficient for all temperatures in the range 10–100 K is considerably below the standard Langevin value of $1\text{--}2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

4. DISCUSSION

Our results differ significantly from those of Jarrold et al. (1986), who also used the phase space technique, mainly because we use the ab initio result that a transition state of positive energy with respect to reactants exists when zero-point energy is included, and we consider tunneling under that transition state. The refined nature of our ab initio calculations

TABLE 1
MOLECULAR PARAMETERS USED IN CALCULATIONS

Species	Rotation Constant (cm^{-1})	σ^a	Vibrational Frequencies (cm^{-1})		
Reactants: $\text{HOC}^+ \dots\dots\dots$	1.4754	1	3468	1932	81(2)
$\text{H}_2 \dots\dots\dots$	59.32		$\alpha = 0.8023 \text{ \AA}^3$		
Entrance channel complex: $\text{H}_3\text{OC}^+ \dots\dots\dots$	2.8770 ^b	2	4005	2027	1589
			1097	1075	635
			619	121	117
Transitionstate: $(\text{H}_3\text{CO})^+ \dots$	0.9913 ^b	1	3422	2654	2629
			2120	403	295
			266	150	285i

^a The classical symmetry number. A symmetry number analysis is not used for molecular hydrogen; the ortho and para spin modifications are treated exactly.

^b Geometric mean of three rotational constants used in spherical top approximation.

leaves little doubt that the barrier exists. We have not attempted to redo the nonthermal calculations of Jarrold et al. (1986) since our technique is not feasible at high energies and since the agreement between our results and the truly thermal 300 K experimental results of McEwan (1992) confirms the correctness of our approach.

The calculated interstellar abundance ratio for the $\text{HCO}^+/\text{HOC}^+$ ratio depends somewhat on the uncertain branching ratios of assorted reactions to form these ions, as well as the rate of reaction (1). Use of our “new standard model” (Bettens, Lee, & Herbst 1995; Lee et al. 1996) at a temperature of 50 K and at “early” time ($10^{4.5}\text{--}10^5 \text{ yr}$) with our newly computed rate for reaction (1) yields $\text{HCO}^+/\text{HOC}^+$ abundance ratios of 1500–4000 depending on the gas density. This range of values reproduces the value of 1800 obtained by Ziurys & Apponi (1995) toward Orion-KL, although it is somewhat high compared with observations of Sgr B2 (OH). In addition to the uncertainties in the formation rates of the two ions, the computed rate coefficient for reaction (1) at low temperature is highly dependent on the barrier height, the imaginary vibrational frequency of the transition state structure, and the approximate nature of the tunneling correction. A factor of 3 diminution in this rate, which would fit the range of astronomical data better, is entirely possible given the uncertainties in its calculation.

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