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The reaction between Si^+ and H_2O. Interstellar implications

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SUMMARY

Based on room temperature experiments and theoretical considerations, it has been determined that the reaction $Si^+ + H_2O \rightarrow SiOH^+ + H$ is rapid at temperatures down to 10 K. The low abundance of SiO in cool interstellar clouds such as TMC-1 is not a consequence of the slowness of this reaction.

1 INTRODUCTION

The ion–molecule reaction between Si^+ and H_2O is thought to lead to interstellar SiO via the reaction sequence (Herbst *et al.* 1989)

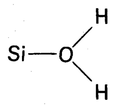
$$Si^+ + H_2O \rightarrow SiOH^+ + H \quad (1)$$

$$SiOH^+ + e \rightarrow SiO + H. \quad (2)$$

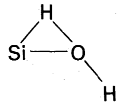
Reaction (1) has been studied in the laboratory at 300 K (Wlodek, Fox & Bohme 1987; Fahey *et al.* 1981) and found to proceed with rate coefficient 2.3×10^{-10} cm^3 s^{-1}. Since this rate coefficient is an order of magnitude below the collisional value, the possibility exists that there is an activation energy barrier which would render the $Si^+ + H_2O$ reaction unimportant at cool interstellar temperatures. Such a result might help to explain why SiO is not observed in cool sources such as TMC-1 (Ziurys, Friberg & Irvine 1989). In this source, Ziurys *et al.* (1989) found an upper limit for the fractional abundance of SiO of 2.4×10^{-12}. The recent gas phase model of Herbst *et al.* (1989), which contains reactions (1) and (2), predicts a fractional abundance for SiO four orders of magnitude greater. Accordingly, we have investigated reaction (1) by (i) calculating the potential surface on which the reaction occurs via *ab initio* methods, and (ii) using phase space theory (Bass *et al.* 1983; Herbst 1985a,b,c 1987) to determine the rate coefficient for the production of $SiOH^+ + H$ at room temperature and below based on the *ab initio* potential surface. Our results, discussed in Section 3, show that the rate of the $Si^+ + H_2O$ reaction actually increases as the temperature is lowered, reaching a value in excess of 10^{-9} cm^3 s^{-1} at 10 K.

2 THEORY

Fig. 1 shows the lowest energy pathways for production of $SiOH^+ + H$ products. The relative energies shown in this figure (taken from the tabulation in Table 1) have been calculated at the MP4(SDTQ)/6-31G**/MP2/6-31G** level of *ab initio* quantum chemical theory (Krishnan, Frisch & Pople 1980). Zero-point corrections, included in the energies shown in Fig. 1, were calculated at the MP2/6-31G** level (Moller & Plesset 1934; Pople, Binkley & Seeger 1976) and reduced by a factor of 0.90 (DeFrees & McLean 1985). Previous *ab initio* calculations on this system have been reported by Yanqui, Berthier & Pauzat (1984). It can be seen that the reaction between Si^+ and H_2O first passes through a deeply bound (bond energy = 2.08 eV) complex, of geometry



then must surmount a transition state (saddle point in the potential surface) of geometry



or one of even higher energy before forming products. The lower energy transition state actually leads to a second bound complex prior to product formation. A most important point is that the transition state energies lie below that of the reactants so that *there is no activation energy for the reaction.* On the other hand, the existence of energy barriers in the exit channel slows the decomposition of the $SiOH_2^+$ complex into products so that the overall rate coefficient for product formation is less than the collisional value and a significant fraction of collisions simply lead to the reformation of the $Si^+ + H_2O$ reactants.

The competition between complex redissociation and dissociation into products can be treated by the phase space theory (Bass *et al.* 1983; Herbst 1985a,b,c, 1987). In this treatment, we consider only the lower energy transition state

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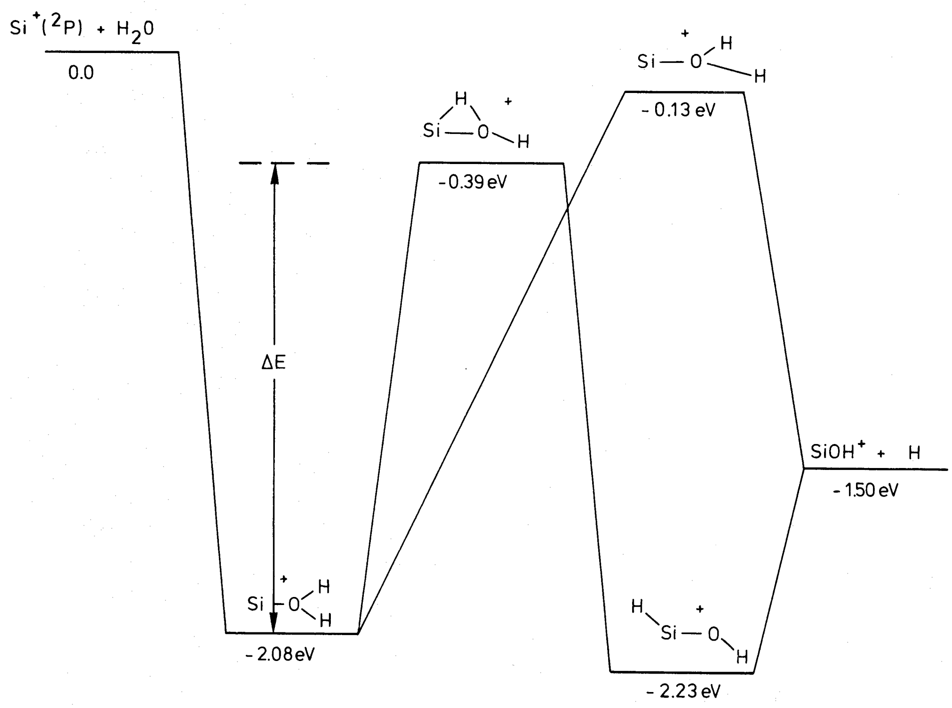
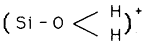
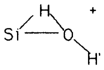
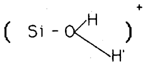
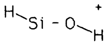


Figure 1. The calculated energies (eV; with zero-point corrections) along the two lowest energy reaction paths for $Si^+ + H_2O \rightarrow SiOH^+ + H$. The parameter ΔE, defined as the difference in energy between the lower energy transition state and the $SiOH_2^{+*}$ complex, is also shown.

Table 1. Calculated total energies, zero-point corrections, geometries, and harmonic frequencies for important species in the $Si^+ + H_2O$ reaction.

Species	State	Total Energy (a.u.; 1 a.u. = 27.2 eV)	Zero-point[a] (eV)	Geometry[b]	Harmonic Frequencies[a] (cm^{-1})
Si^+	^2P	-288.601227			
H_2O	$^1A_1$	-76.231244	0.54	OH = 0.96 <(HOH) = 103.9	3631, 3506, 1515
$SiOH^+$	$^1\Sigma^+$	-364.380067	0.33	SiO = 1.556 OH = 0.97	3507, 1026, 383(2)
	$^2B_2$ (C_{2v})	-364.911540	0.60	SiO = 1.92, OH = 0.97 <(SiOH) = 125.0	3463, 3359, 1507, 607, 426, 375
	$^2A'$ (C_s)	-364.841652	0.39	SiO = 1.71 OH = 1.29 OH' = 0.98 SiH = 1.71 <(SiOH) = 68.0 <(SiOH') = 154.7 <(HOH') = 137.3	3290, 1536, 801, 577, 153
	$^2A'$ (C_s)	-364.8320914	0.39	SiO = 1.65 OH = 0.97 OH' = 1.42 <(SiOH) = 130.4 <(SiOH') = 132.6	3418, 1077, 885, 569, 410
	$^2A'$ (C_s)	-364.913641	0.51	SiO = 1.59 OH = 0.97 SiH = 1.48 <(SiOH) = 131.5 <(HSiO) = 112.4	3470, 2032, 966, 689, 561, 531

[a] Calculated frequencies reduced by 10 per cent.
[b] Distances in Å, angles in degrees.

and neglect the possibility that once over the transition state barrier, the reaction system does not form products. These assumptions are discussed below. The reaction is thus modelled by the sequence

$$Si^+ + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} SiOH_2^{+*} \tag{3}$$

$$SiOH_2^{+*} \xrightarrow{k_4} SiHOH^{+\neq} \tag{4}$$

$$SiHOH^{+\neq} \longrightarrow SiOH^+ + H, \tag{5}$$

where * and ≠ refer to complex and transition state, respectively, k_3 is the rate coefficient for complex formation, k_{-3} the rate coefficient for complex redissociation into reactants and k_4 the rate coefficient for complex dissociation into products via the lower energy transition state structure. The overall rate coefficient k_1 for reaction (1) is given by the expression

$$k_1 = k_3 k_4/[k_{-3} + k_4] \qquad (6)$$

assuming the concentration of $SiOH_2^{+*}$ complex to be at steady state. There also exists the possibility of an association channel to form stable $SiOH_2^+$ via collisional and/or radiative stabilization of the complex. However, the small size of the reaction system renders this possibility unlikely (Bates & Herbst 1988). The association rate coefficient can be calculated by modifying the denominator of the right-hand side of expression (6) to incorporate a stabilization rate (Herbst 1985a,b,c) since the denominator contains all modes of complex depletion, and by replacing k_4 in the numerator on the right-hand side of equation (6) by the relevant stabilization rate. In addition, the overall rate coefficient for complex formation followed by redissociation into reactants can be obtained by replacing k_4 in the numerator by k_{-3}.

The partial rate coefficients shown in equation (6) refer to reactants in specific quantum states colliding with a known collisional energy to form a complex with known internal energy and angular momentum. The values of k_1 determined from equations (6) must therefore be summed over all possible angular momenta of the complex and then averaged over translational energy and reactant quantum state distributions (Herbst 1985c). The rate coefficients k_3, k_{-3} and k_4 for specific reactant quantum states, collisional energy and complex angular momentum are determined as follows. First, k_3 is obtained via the treatment of Bates (1982), which is one of several that yield the complex formation rate for systems in which the neutral reactant is polar. An additional assumption is made that only one-third of the orbiting collisions lead to complex formation due to the six-fold degeneracy of the Si^+ ^2P ground state (neglecting spin-orbit splitting) and the two-fold (doublet) degeneracy of the ground state of $SiOH_2^+$. It is assumed that there is no correlation between individual fine structure levels of Si^+ and potential surfaces of $SiOH_2^+$ and that the two excited state doublet potential surfaces of $SiOH_2^+$ correlating with ^2P Si^+ are repulsive and do not contribute to the reaction rate coefficient at thermal energies.

Once k_3 is determined, k_{-3} can then be obtained by microscopic reversibility (Herbst 1985a,b,c). The rate coefficient k_4 is handled by classical RRKM theory (Forst 1973) in which the effective transition state barrier as a function of angular momentum is utilized (Herbst 1985a). This barrier contains a centrifugal component and increases with increasing angular momentum. The result is that high angular momentum collisions experience a large effective transition state barrier and tend not to react.

Information necessary to determine k_{-3} and k_4 includes the structures, thermodynamics and vibrational frequencies of both complex and transition state. This information has been obtained by *an initio* calculation and is included in Table 1. Once k_3, k_{-3} and k_4 are determined for specific quantum states, collision energy and complex angular momentum, the summation and averaging discussed above can be undertaken. The assumption made in our treatment that the higher energy transition state can be neglected derives from RRKM theory (Forst 1973) in which it is shown that the higher density of vib-rotational states present in the lower energy transition state makes this the dominant one. (The calculated rate of reaction via the higher energy transition state is significantly smaller.) The assumption made that all reacting systems that pass over the lower energy transition structure continue on to produce products can be confirmed by calculating the rates of product formation and transition state reformation of the secondary complex $HSiOH^{+*}$. This complex dissociates into products much more rapidly than it reforms the $SiHOH^{+\neq}$ transition state structure due principally to the large exothermicity of the reaction.

3 RESULTS AND DISCUSSION

Our results for k_1 at 300 K are shown in Fig. 2 where they are plotted as a function of the energy difference ΔE between the transition state $SiHOH^{+\neq}$ and the complex $SiOH_2^{+*}$. Although this energy difference is calculated to be 1.69 eV via *ab initio* methods, it is known that *ab initio* procedures can overestimate the energies of transition states by as much as 0.50 eV (DeFrees, McLean & Herbst 1985). Therefore, we have varied ΔE to obtain Fig. 2. It can be seen in this figure that if the transition state energy ΔE is set at its theoretically determined value of 1.69 eV, then k_1 is calculated to be 1.3×10^{-10} cm^3 s^{-1}, which is somewhat below the experimental number of 2.3×10^{-10} cm^3 s^{-1} (Wlodek *et al.* 1987; Fahey *et al.* 1981). If, however, ΔE is reduced to 1.40 eV, the experimental value of k_1 is recovered. Use of this value for ΔE in our phase space treatment yields that k_1 at 10 K is 1.2×10^{-9} cm^3 s^{-1} while at 500 K k_1 has been reduced to 1.8×10^{-10} cm^3 s^{-1}. At 10 K, all Si^+ is essentially in its ground fine-structure state. If, contrary to our initial assumption, the ground fine-structure state correlates with the ground state of $SiOH_2^+$, then k_1 will be approximately three times as large as our calculated value at 10 K. In either case, the reaction between Si^+ and H_2O is calculated to be rapid at 10 K.

What is the importance of association reactions in this system? We calculate that the radiative association rate coefficient to form $SiOH_2^+$ is $\approx 10^{-14}$ cm^3 s^{-1} at 10 K if $\Delta E = 1.40$ eV. This value is insignificantly small for models of interstellar clouds. We calculate that the analogous ternary (collisionally induced) association rate is also very small; the

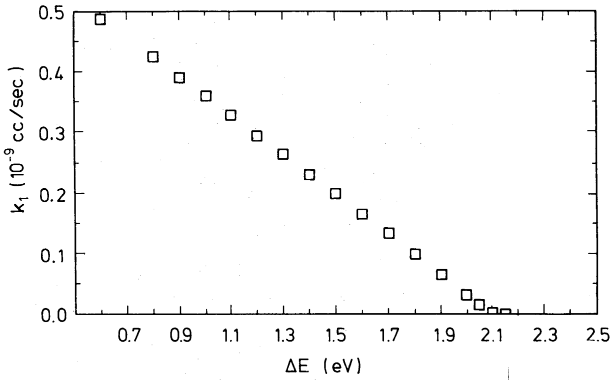


Figure 2. The calculated value for k_1 at 300 K is plotted as a function of ΔE (eV), the energy of the lower transition state structure compared with that of the complex $SiOH_2^{+*}$.

effective two-body rate coefficient at a helium number density of 10^{16} cm^{-3} and at 300 K is less than 10^{-13} cm^3 s^{-1}, a value too low for laboratory measurement.

In conclusion, it seems reasonably clear that the $Si^+ + H_2O \rightarrow SiOH^+ + H$ reaction occurs efficiently at low interstellar temperatures and that SiO is formed via this reaction and the subsequent dissociative recombination reaction. Herbst *et al.* (1989) have also recently shown that other gas phase pathways lead to SiO with only slightly smaller efficiencies although these reactions have not been studied in great detail. Even a large change in the rate of reaction (1) will have little effect on their results if these other pathways are correct. If the other pathways do not occur, however, our results show that reaction (1) leads by itself to large abundances of SiO in cold sources such as TMC-1, in contradiction to observations (Ziurys *et al.* 1989). The absence of SiO in this and other cold sources therefore cannot be explained by the slowness of reaction (1) but probably by a lack of elemental silicon in the gas phase (Herbst *et al.* 1989).

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