

Theoretical studies of hypervalent silicic acid compounds



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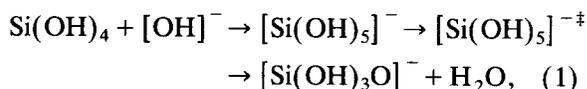
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Hypervalent silicon compounds play a vital role in polymerization and sol–gel processes. Ab initio all electron calculations are performed to characterize the nature of the species involved in the reaction $\text{Si}(\text{OH})_4 + [\text{OH}]^- \rightarrow [\text{Si}(\text{OH})_5]^- \rightarrow [\text{Si}(\text{OH})_5]^{-\ddagger} \rightarrow [\text{Si}(\text{OH})_3\text{O}]^- + \text{H}_2\text{O}$. Since the hydration of the reactants may aid in the polymerization process, we have determined both minima and transition state structures for the complexes between $\text{Si}(\text{OH})_4$ and H_2O . An effective drying agent in the sol–gel process involves the formation of a complex between $\text{Si}(\text{OH})_4$ and HF and we have performed ab initio calculations on this system. Finally, the energetics and bonding between $\text{Si}(\text{OH})_4$ and NH_3 is examined.

1. Introduction

The formation, properties and reactions of hypervalent silicon compounds have received considerable experimental and theoretical attention [1]. It has been suggested that these compounds play key roles in polymerization and sol–gel processes [2]. The purpose of the present paper is twofold:

1) The mechanism and energetics of the reaction:



believed to be an important step in the polymerization of silanols to silicas, are examined using ab initio electronic structure theory calculations to determine the pertinent points on the potential energy surface. The quantum theory of atoms in molecules (AIM) is used to gain a further understanding of the bonding in the compounds [3].

2) Semi-empirical calculations [4] have suggested that reaction (1) above is aided by hydration of the reactant molecules. To assess this possibility, it is essential to characterize the energetic mini-



Table A.1 of this article is to be found in the CMS electronic Bulletin Board, see inside back cover.

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imum and other stationary points of the silicic acid–water potential energy surface. This characterization is performed using ab initio electronic structure theory calculations.

Experimental studies of sol–gels have suggested that hydrogen fluoride acts as an effective drying agent [5]. Therefore, the silicic acid–hydrogen fluoride complex is examined, as well as the isoelectronic silicic acid–ammonia complex. Once again, the AIM analysis is used to provide an understanding of the bonding in these compounds.

2. Computational methods

Ab initio all electron calculations were performed using the electronic structure program GAMESS [6]. All geometries were optimized in C_1 symmetry using the restricted Hartree–Fock (RHF) method and the 6-31(d) basis set [7]. At this level of theory, an analytic hessian (matrix of energy second derivatives) corresponding to each optimized structure was calculated and diagonalized, to determine whether the structure is a minimum (positive definite hessian) or n th order saddle point (n negative eigenvalues). Zero-point vibrational energy corrections, needed in the determination of the reaction enthalpy, ΔH_{rxn} , are also calculated from the hessian. The computed frequencies are scaled by 0.89 to correct for the overestimation made when using an RHF wavefunction [8]. Several different starting geometries were employed to maximize the likelihood that all local minima have been detected.

To obtain reliable relative energies, second order perturbation theory (MP2 [9]) is used with the 6-31++ G(d, p) basis set [10] at the RHF/6-31G(d) geometry. This is denoted MP2/6-31++ G(d)/RHF/6-31G(d) (hereafter referred to as Scheme B; RHF/6-31G(d)//RHF/6-31G(d) is referred to as scheme A).

The critical points in the RHF/6-31++ G(d, p)//RHF/6-31G(d) total electron density were calculated using AIMPACK. According to AIM, a bond critical point (r_b) exists between two atoms if there is a saddle point in the total electron density between the two atoms. At the

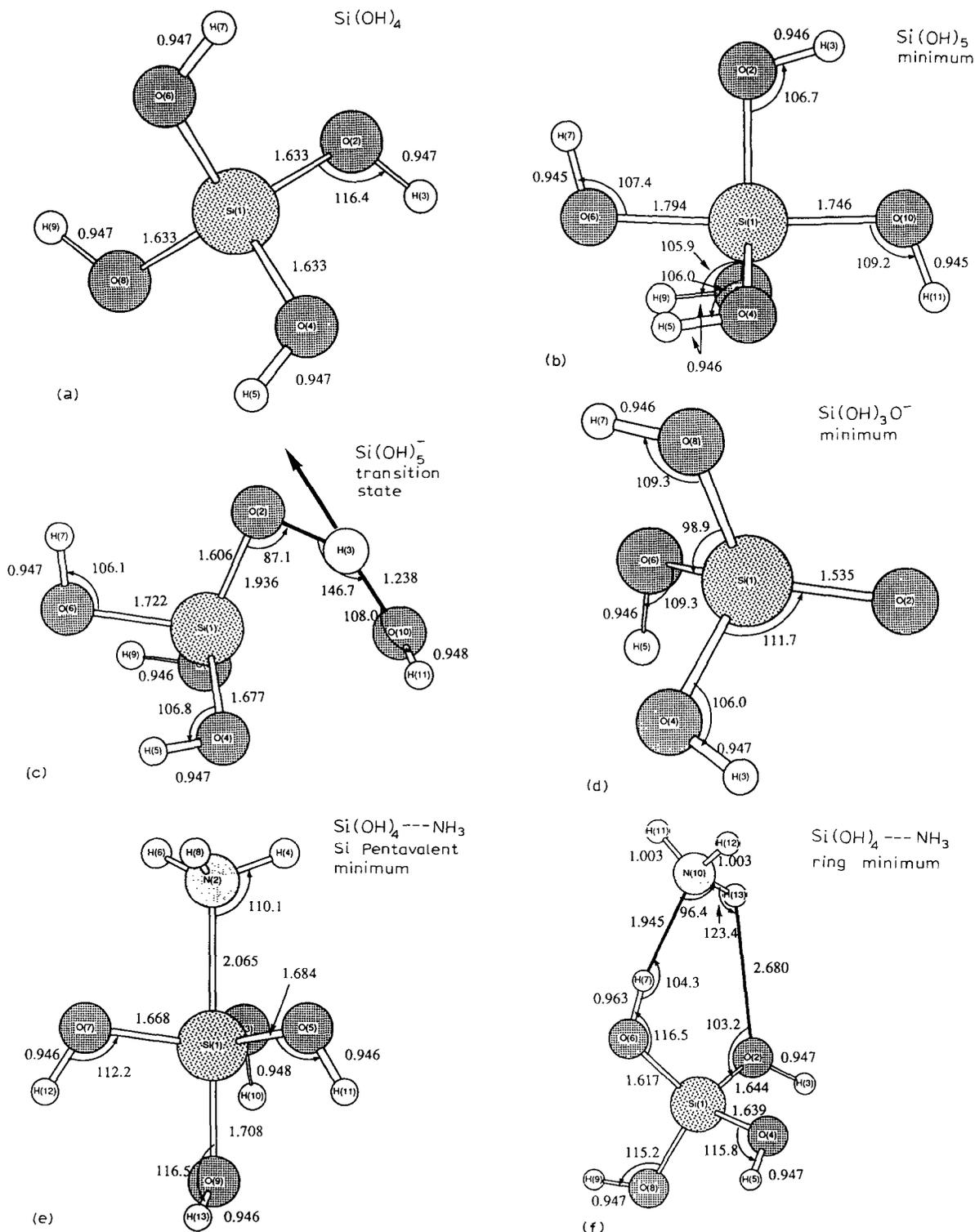
bond critical point, the gradient of the total electron density vanishes ($\nabla\rho(\mathbf{r}) = 0$ at $\mathbf{r} = \mathbf{r}_b$), and the second derivative matrix of the electron density has one positive eigenvalue corresponding to the bond axis and two negative eigenvalues corresponding to the perpendicular transverse axes. The existence of a bond critical point implies the existence of a bond path (the path of maximum electron density with respect to any lateral displacement passing through \mathbf{r}_b .) The reader is referred to ref. [3] for a detailed discussion of AIM.

3. Results and discussion

3.1. Geometries

The structures and most pertinent geometrical parameters of the optimized structures are displayed in fig. 1. (A complete set of cartesian coordinates are given in table A.1 to be found in the CMS electronic Bulletin Board). The bonds drawn between atoms correspond qualitatively with the AIM bond paths. All of the structures possess definite Hessians with the exception of two silicic acid–water complexes (figs. 1(j) and 1(k)) and $[\text{Si}(\text{OH})_5]^{-\ddagger}$ (fig. 1(c)). These three transition state structures each contain exactly one negative eigenvalue. The imaginary frequency for $[\text{Si}(\text{OH})_5]^{-\ddagger}$ has a magnitude of $1484i \text{ cm}^{-1}$ and corresponds mainly to the vibrational motion of H_3 as H_3 becomes bonded to O_{10} . This is clearly the transition state for the elimination of water from $\text{Si}(\text{OH})_5^-$ to yield $\text{Si}(\text{OH})_3\text{O}^-$.

The apparent transition state in fig. 1(j) (the single hydrogen-bonded structure), with an imaginary frequency of $191i \text{ cm}^{-1}$, actually corresponds to a rotation of the hydrogen-bonded water molecule. Similarly, the imaginary mode (frequency = $101i \text{ cm}^{-1}$) for the pentacoordinated silicon structure in fig. 1(k) corresponds mainly to OH group rotations. Extensive efforts to remove the imaginary frequency of the latter by rotating the OH_2 group reduced the frequency to the value quoted above, but did not entirely remove it. This is a result of the very flat nature of the potential energy surface. It is expected



Figs. 1(a)–(k). Geometries of the structures numbered in tables 1 and 2. Pertinent distances are labelled in ångströms and angles are in degrees. The bonds drawn correspond to the predicted AIM structures.

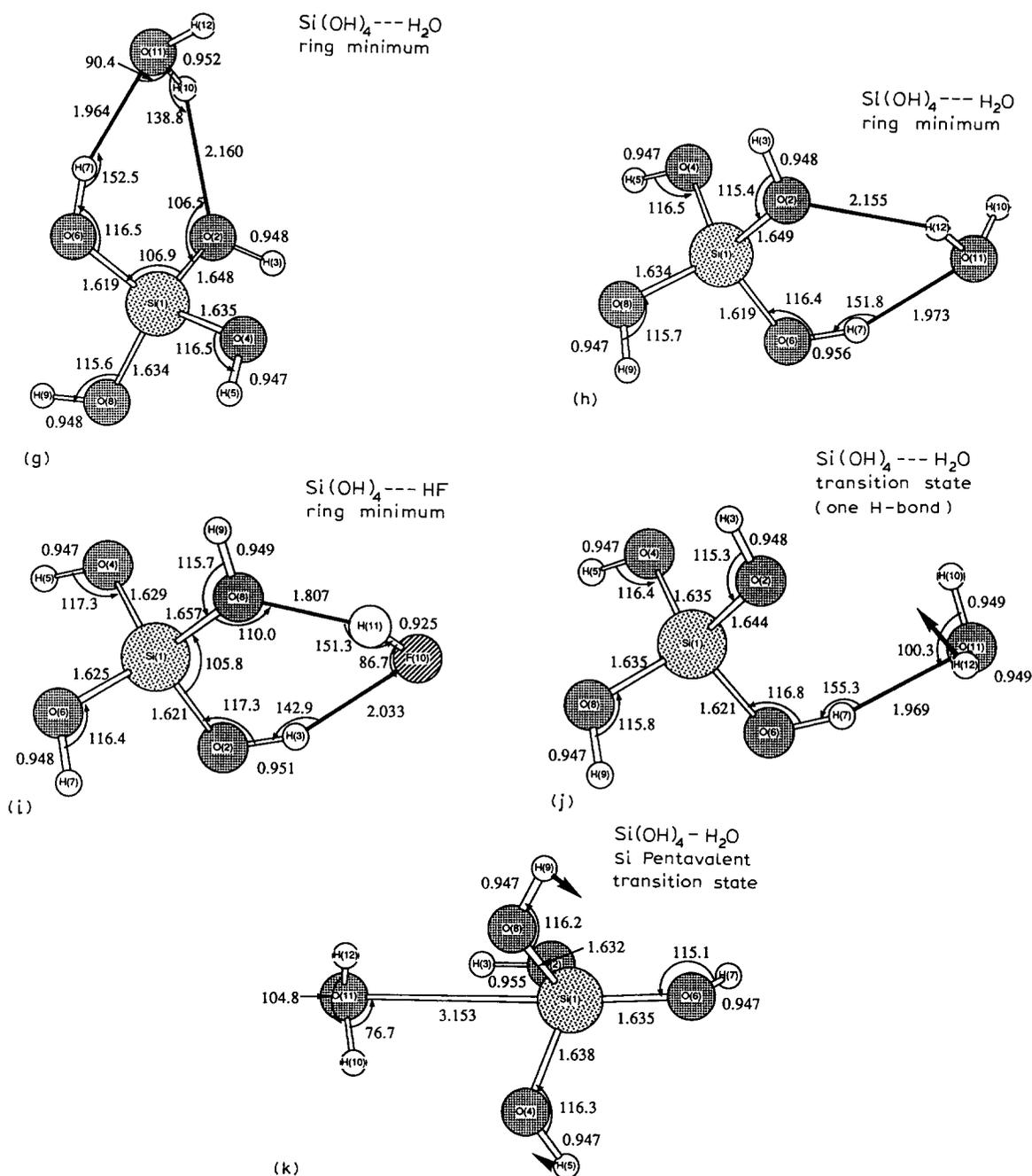


Fig. 1. Continued.

that, aside from minor changes in (O)H positions, this structure will correspond to a local minimum on the potential energy surface. The energetics discussed in the following section supports this view.

3.2. Energies

3.2.1. Water elimination reaction

The energies of the species involved in reaction (1) are compiled in table 1. The reaction is

Table 1
Energies of the systems involved with the reaction of Si(OH)₄ with OH⁻

System	Method	E_{system} (hartrees)	Zero point energy (kcal/mol)	Figure
Si(OH) ₄	A	-590.88542	34.5	1(a)
	B	-591.71406	34.5	
[OH] ⁻	A	-75.32660	4.7	-
	B	-75.58869	4.7	
[Si(OH) ₅] ⁻	A	-666.33852	44.2	1(b)
	B	-667.40390	44.2	
[Si(OH) ₅] ^{-‡}	A	-666.28885	40.9	1(c)
	B	-667.36296	40.9	
[Si(OH) ₃ O] ⁻	A	-590.29300	27.7	1(d)
	B	-591.15761	27.7	
H ₂ O	A	-76.01075	12.8	-
	B	-76.20904	12.8	

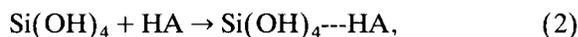
The ΔE and H values in kcal/mol for computational method B for each step in the reaction are given below:

i) Si(OH) ₄ + [OH] ⁻ → [Si(OH) ₅] ⁻	$\Delta E = -63.5$ $\Delta H = -58.5$
ii) [Si(OH) ₅] ⁻ → [Si(OH) ₅] ^{-‡}	$\Delta E = +25.7$ $\Delta H = +22.3$
iii) [Si(OH) ₅] ^{-‡} → [Si(OH) ₃ O] ⁻ + H ₂ O	$\Delta E = -2.3$ $\Delta H = -2.6$
iv) Si(OH) ₄ + [OH] ⁻ → [Si(OH) ₃ O] ⁻ + H ₂ O	$\Delta E = -40.1$ $\Delta H = -38.8$

predicted at the MP2/6-31++ G(d, p) level of theory to be exothermic overall by about 39 kcal/mol. This is in reasonable agreement with the semi-empirical AM1 prediction of an exothermicity of 27 kcal/mol [4]. Both ab initio and semi-empirical calculations predict the [Si(OH)₅]⁻ structure shown in fig. 1(b) to be the global minimum on the potential energy surface. This global minimum is found to be 58 and 76 kcal/mol, respectively, more stable than the isolated reactants at the ab initio and semi-empirical levels of theory. The MP2/6-31++ G(d, p) potential energy curve is depicted in fig. 2. The energy barrier separating the global minimum from the products is predicted to be 22.3 kcal/mol; however, the transition state (fig. 1(c)) is itself 36 kcal/mol below the separated reactants. So, there will be sufficient energy available for the overall reaction to occur.

3.2.2. Association reactions

The total and relative energies for the association reactions



with HA = H₃N, H₂O, HF, are compiled in table 2. For HA = NH₃, two adduct structures have been found. One of these (fig. 1(e)) contains a pentacoordinated silicon bonded directly to axial N, as well as to the four OH groups. The second structure (fig. 1(f): more stable by 4 kcal/mol) is a 6-membered ring (6mr) with two (N-H---O and O-H---N) hydrogen bonds. The calculated ΔH is negative in both cases.

For HA = H₂O, three adduct structures are found. The pentacoordinated structure with the oxygen of the water molecule directly bound to silicon (fig. 1(k)) has a slightly larger binding

Table 2
Energies of the systems involved with the reaction of Si(OH)₄ with NH₃, H₂O and HF

System	Method	E_{system} (hartrees)	Zero point energy (kcal/mol)	ΔH ^{a)} (kcal/ mol)	Fig
<i>Reactants</i>					
Si(OH) ₄	A	-590.88542	34.5		1(a)
	B	-591.71406	34.5	n/a	
H ₂ O	A	-76.01075	12.8		-
	B	-76.20904	12.8	n/a	
NH ₃	A	-66.18436	20.7		-
	B	-56.36324	20.7	n/a	
HF	A	-100.00291	5.5		-
	B	-100.20209	5.5	n/a	
<i>Product minima</i> ^{b)}					
Si(OH) ₄ NH ₃	A	-647.07313	59.7		1(e)
	{one SiN bond} B	-648.09423	59.7	-6.1	
Si(OH) ₄ NH ₃	A	-647.08489	57.3		1(f)
	{6mr} B	-648.09702	57.23	-10.3	
Si(OH) ₄ H ₂ O	A	-666.91108	49.8		1(g)
	{6mr} B	-667.94105	49.8	-8.8	
Si(OH) ₄ H ₂ O ^{c)}	A	-666.90920	49.4		1(j)
	{one H-bond} B	-667.93811	49.4	-7.4	
Si(OH) ₄ H ₂ O ^{c)}	A	-666.90820	49.1		1(k)
	{pentavalent Si} B	-667.93782	49.1	-7.4	
Si(OH) ₄ HF	A	-690.90622	42.5		1(i)
	{6mr} B	-691.93488	42.5	-9.3	

^{a)} Relative to reactants.

^{b)} 6mr = 6-membered ring.

^{c)} These structures have one small imaginary frequency. See text.

energy than its NH_3 counterpart, despite the fact that one expects nitrogen to be a better lone pair donor. The single hydrogen bond structure in fig. 1(j) probably corresponds to an internal rotation transition state, with the corresponding minimum being the structure shown in different perspectives in figs. 1(g) and 1(h). The energy difference between these structures is only 1.4 kcal/mol. The 6-membered ring (fig. 1(g)) is not quite as stable in the case of water as it is for ammonia.

For $\text{HA} = \text{HF}$, only one minimum is found on the silicic acid--- HA potential energy surface, corresponding to the double hydrogen bond 6mr species shown in fig. 1(l). The ring structure ΔH values all fall within 1.5 kcal/mol of each other. This is an interesting result as it represents the energetic compromises made between strong/weak acids and weak/strong bases, respectively.

3.3. Electron density analysis

3.3.1. Water elimination reaction

The AIM analysis is particularly useful for exploration of that part of the potential energy curve (fig. 2) connecting the global minimum $[\text{Si}(\text{OH})_5]^-$ with the transition state $[\text{Si}(\text{OH})_5]^{-\ddagger}$ (accompanied by an increase in energy). Analysis of the total electron density, ρ , of $[\text{Si}(\text{OH})_5]^-$, shown in fig. 3 (see also the structure illustrated in fig. 1(b)), reveals no bond critical point be-

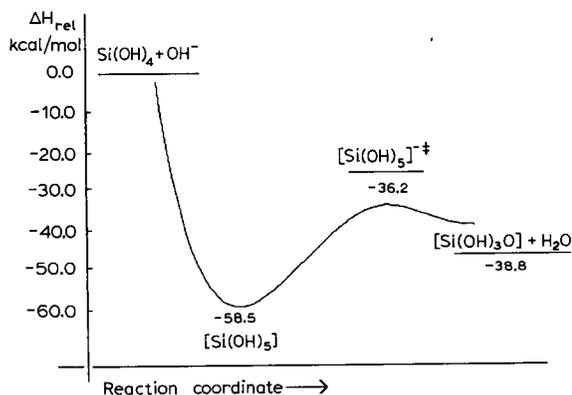


Fig. 2. Potential energy curve for the reaction $\text{Si}(\text{OH})_4 + [\text{OH}]^- \rightarrow [\text{Si}(\text{OH})_5]^- \rightarrow [\text{Si}(\text{OH})_5]^{-\ddagger} \rightarrow [\text{Si}(\text{OH})_3\text{O}]^- + \text{H}_2\text{O}$. The numerical values are calculated using the MP2/6-31++G(d)//RHF/6-31G(d) scheme.

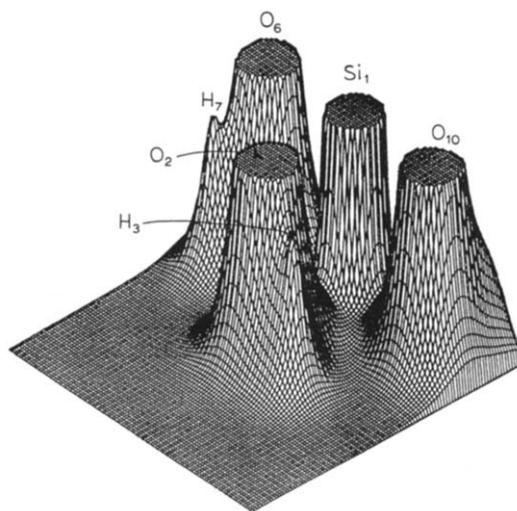


Fig. 3. Total density contour map for $[\text{Si}(\text{OH})_5]^-$ minimum.

tween H_3 and O_{10} , even though the $\text{H}_3\text{---O}_{10}$ distance of 2.109 Å is not so great as to preclude intramolecular hydrogen bonding.

When the transition state forms (fig. 1(c)), the topological analysis of the electron density (fig. 4) reveals a bond critical point between H_3 and O_{10} . The $\text{H}_3\text{---O}_{10}$ distance is 1.238 Å (0.871 Å less than the corresponding distance in the minimum energy structure). Further, there is no bond critical point between Si_1 and H_3 in the transition state, so H_3 is bound only to O_{10} at this point on the reaction path. In addition, the $\text{Si}_1\text{---O}_{10}$ bond apparent at the minimum energy structure (fig. 3) is broken in the transition state, as no bond critical point is found between these atoms (fig. 4). The $\text{Si}_1\text{---O}_{10}$ internuclear separation in the transition state is 2.312 Å. This is 0.566 Å greater than the corresponding distance in the minimum energy structure. This analysis illustrates how formation of the transition state leads to eventual elimination of a water molecule. The vibrational mode with imaginary frequency of $1484.2i \text{ cm}^{-1}$ is concentrated on H_3 and suggests (see fig. 1(c)) that H_3 will move so as to decrease the $\text{H}_3\text{---O}_{10}\text{---H}_{11}$ angle. Simultaneously, the $\text{H}_3\text{---O}_{10}$ distance will decrease and the O_2H_3 distance will increase.

It is instructive to quantify the hydrogen-bonded region of the transition state. Since the

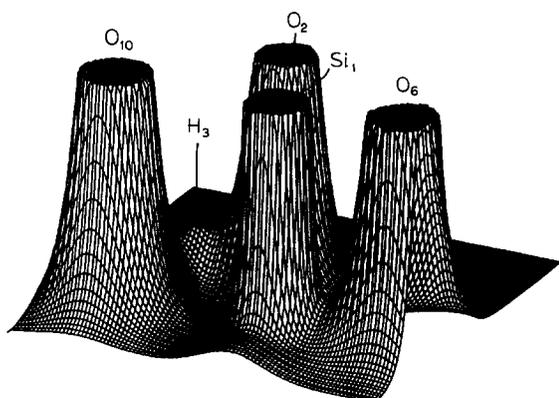


Fig. 4. Total density contour map for Si(OH)_5^- transition state.

$\text{O}_2\text{-H}_3$ distance (1.167 Å) is less than the $\text{H}_3\text{-O}_{10}$ distance (1.238 Å), O_2 is the acidic oxygen, H_3 is the acidic hydrogen and O_{10} is the basic oxygen. The values (in a.u.) of ρ at the corresponding bond critical points are 0.178 for the $\text{O}_2\text{-H}_3$ bond and 0.146 for the $\text{H}_3\text{-O}_{10}$ bond. The longer bond has less electron density at its bond critical point than the shorter bond, an observation consistent with previous studies of hydrogen-bonded systems.

3.3.2. Association reactions

(a) $\text{Si(OH)}_4\text{-NH}_3$ complexes (figs. 1(e) and 1(f))

The ring structure 1(f) is energetically more stable than the pentavalent Si structure 1(e) by $\Delta H = 4.2$ kcal/mol. Even though the $\text{O}_2\text{-H}_{13}$ distance is very long in the ring structure (2.680 Å), a bond critical point is found between the two atoms. Thus, H_{13} (of the ammonia fragment) is acting as an acidic hydrogen, and O_2 is acting as a base in the formation of this hydrogen bond. The second hydrogen bond has H_7 (of silicic acid) acting as the acidic hydrogen and N_{10} acting as a base. The result of the formation of the two hydrogen-bonds (verified by the AIM analysis) is the creation of a six-membered ring consisting of $\text{Si}_1\text{-O}_2\text{-H}_{13}\text{-N}_{10}\text{-H}_7\text{-O}_6$. In structure 1(e), the amphoteric characteristics of the two interacting molecules are not exploited. Only the fact that N_2 acts as a base is used. Thus, this structure is less stable than 1(f).

(b) $\text{Si(OH)}_4\text{-OH}_2$ complexes (figs. 1(g)–1(k))

The six-membered ring structure (fig. 1(g)), in which two hydrogen bonds are formed, has a positive definite hessian. One hydrogen bond has H_{10} (of the water fragment) acting as an acidic hydrogen, with O_2 of the silicic acid fragment acting as a base. The other hydrogen bond has H_7 of silicic acid acting as the acidic hydrogen and O_{11} of water acting as the base. The structures shown in figs. 1(j) and 1(k) have already been discussed.

(c) $\text{Si(OH)}_4\text{-FH}$ complex (fig. 1(i))

In this structure, containing a six-membered ring and two hydrogen bonds, H_{11} of the hydrogen fluoride fragment acts as the acidic hydrogen, while O_8 of silicic acid acts as the corresponding base in the formation of the first hydrogen bond. In the formation of the second hydrogen bond, H_3 of silicic acid acts as the acidic H and F_{10} of hydrogen fluoride acts as the base.

4. Conclusions

The major findings of this study are the following:

- 1) The formation of the pentacoordinated anion is quite exothermic, so that the transition state for the subsequent elimination of water is well below the energy of the separated reactants. The overall reaction is exothermic as well. The potential energy curve for the reaction of silicic acid with water, determined using MP2/6-31++G(d, p)//RHF/6-31G(d) energies, has the same qualitative features as the curve determined using semi-empirical AM1 wavefunctions [2].

- 2) The AIM analysis is especially useful in characterizing bond-breaking and bond-forming as the reaction proceeds from $[\text{Si(OH)}_5]^- \rightarrow [\text{Si(OH)}_5]^{-\ddagger}$, as it illustrates that proton abstraction from the second OH group is the final step in the process.

- 3) Ring structures appear to be the most consistently favored species when silicic acid bonds with ammonia, water and hydrogen fluoride. The stabilization energies of these complexes are quite similar: the most stable of the three ring com-

plexes is $\text{Si(OH)}_4\text{---NH}_3$ (fig. 1(f)) with $\Delta H = -10.3$ kcal/mol; the least stable is $\text{Si(OH)}_4\text{---H}_2\text{O}$ (fig. 1(g)) with $\Delta H = -8.8$ kcal/mol.

4) The potential energy surface for the $\text{Si(OH)}_4\text{---H}_2\text{O}$ system is extremely flat. The pentacoordinated and transition state structures (figs. 1(j) and 1(k)) are just over a kcal/mol less stable than the six-membered ring structure.

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