Molecular Structure of Cyclopentanone by Gas-Phase Electron Diffraction

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Abstract: The molecular structure of cyclopentanone has been investigated by combined analysis of electron diffraction and microwave spectroscopic data. The results are consistent with a twisted (half-chair) conformation and a rather high potential barrier. The more important bond lengths (r_g) and valence angles (θ_α) obtained from the least-squares analysis are $r_g(C_1—C_2) = 1.531$ (4) Å, $r_g(C_2—C_3) = r_g(C_3—C_4) = 1.542$ (3) Å, $r_g(C—H) = 1.104$ (4) Å, $r_g(C{=}O) = 1.213$ (4) Å, $\angle C_2C_1C_5 = 108.6$ (2)°, $\angle HCH_{av} = 107.5$ (8)°, and τ (the angle between the $C_2C_1C_5$ plane and the $C_3—C_4$ line) = 24.7 (4)°.

The notion of pseudorotation was first introduced by Kilpatrick et al.[1] in order to explain the unexpectedly high entropy of cyclopentane. A five-membered ring can distort from a planar configuration in two ways. It can either be twisted, retaining C_2 symmetry, or it can be bent, retaining C_s symmetry. In cyclopentane the twisted and bent ring conformations have essentially identical energy, and as a result the barrier to pseudorotation is effectively zero. Pitzer and Donath[2] have shown, by examining and comparing torsional barriers of different compounds, that the pseudorotational motion of substituted cyclopentanes should be more restricted since the energies of the twisted and bent forms were no longer identical. For example, both chlorocyclopentane[3] and cyanocyclopentane[4] have hindered pseudorotational barriers. The stability of the twist and bent forms depends on the torsional barriers of the C–C bond and the bonds involving the substituted atom. In their original publication,[2] Pitzer and Donath predicted cyclopentanone to have a twist form and a rather high barrier to pseudorotation.

Kim and Gwinn[5] have studied the microwave spectra of some deuteriated isomers of cyclopentanone and concluded that cyclopentanone has the twisted equilibrium conformation predicted by Pitzer and Donath. Durig et al.[6] and Carreira and Lord[7] fitted the observed far-infrared frequencies to different periodic potential functions and estimated the pseudorotational barrier heights of 940 and 1303 cm^{-1}, respectively. It appeared that although it was possible to reproduce the frequencies, the barrier heights were function dependent. A more conclusive study of the far-infrared spectrum of cyclopentanone has been carried out by Ikeda and Lord.[8] They observed the far-infrared spectra of the parent compound and its α-d_4, β-d_4, and d_8 derivatives and determined the potential surface by fitting the data using a two-dimensional Hamiltonian. They concluded that the stable conformation is twist and the interconversion between two twist forms occurs through the planar ring form with a barrier of 750 cm^{-1}.

The molecular structure of cyclopentanone has so far been studied both by microwave spectroscopy[5,9] and electron diffraction.[10] There are, however, large discrepancies in some of the important geometrical parameters. For example, the reported values for the C=O bond ranged from 1.24 to 1.21 Å. For the purpose of determining the unambiguous structure, we undertook a combined ED/SP investigation of cyclopentanone.

Experimental Section

A sample of cyclopentanone was obtained from Aldrich Chemical Co. and was used without further purification. Electron diffraction data were collected on 4 × 5 in. Kodak electron image plates, at room temperature (298 K), on the North Dakota State University electron diffraction instrument with nozzle-to-plate distances of 245 and 92 mm. Exposure times were 50–60 s for the long camera and 120–150 s for the short camera plates with an accelerating voltage of 40 keV and a beam current of 0.55 μA. The ambient pressure was maintained at 2×10^{-5} torr with the aid of a liquid nitrogen trap. Benzene plates, obtained under operating conditions identical with those used for the sample, were used for the final voltage/distance calibrations.

Table I. Force Field Used for Cyclopentanone[a]

force const	value	force const	value
$C_\beta—H$	4.694[b]	$\angle CCO$	0.905
$C_\gamma—H$	4.645	$\angle C—CO—C$	0.341
$C{=}O$	10.149	$\tau C_\alpha—C_\beta$	0.032[c]
$C_\alpha—C_\beta$	4.252	$\tau C_\beta—C_\gamma$	0.089
$C_\beta—C_\gamma$	4.144	$\tau C_\gamma—C_\gamma$	0.089
$C_\gamma—C_\gamma$	4.144	C—H, C—H	0.006[d]
$\angle HC_\beta H$	0.495[c]	C—C, C—C	0.101
$\angle HC_\gamma H$	0.520	$C'—C''$, $\angle HC'C''$	0.328[e]
$\angle HC_\beta C$	0.601	$C'—C''$, $\angle HCC'$	0.079
$\angle HC_\gamma C$	0.677	C—C, $\angle CCC$	0.417
$\angle CC_\beta C$	1.012	C—C, $\angle CCO$	0.417
$\angle CC_\gamma C$	0.878	$\angle HCC$, H′CC	−0.021[f]
$\angle CC_\alpha C$	1.111	$\angle HCC$, $\angle CCC$	−0.031

[a] The force constants are taken from ref 13. [b] In mdyn/Å. [c] In mdyn Å. [d] In mdyn/Å. [e] In mdyn. [f] In mdyn Å.

Table II. Calculated Mean Amplitudes and Shrinkage Corrections for Cyclopentanone[a]

distance[b]	l_{ij}[c]	K_{ij}[c]	$r_\alpha(0) - r_\alpha(T)$[c]
$C_1—C_2$	518	24	−3
$C_2—C_3$	530	16	−2
$C_3—C_4$	530	16	−2
C—H	788	149	7
C=O	390	37	8
$C\cdots C_3$	633	13	
$C_2\cdots C_4$	644	9	
$C_2\cdots C_5$	618	8	
$O\cdots C_2$	629	9	
$O\cdots C_3$	651	4	
$C\cdots H_{gem}$	1087	68	

[a] Atomic numbering employed is illustrated in Figure 1. [b] Only calculated values for prominent distances in the radial distribution curve are shown. [c] Values multiplied by 10^4.

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Table III. Observed and Calculated Rotational Constants for Cyclopentanone[a]

	B_0, MHz	B_z^{obsd}, MHz	B_z^{calcd}, MHz	error, MHz
parent	6620.06	6624.1	6623.76	0.33
	3351.53	3352.2	3352.75	−0.55
	2410.42	2410.0	2410.38	−0.38
$^{13}C_1$	6620.1	6624.2	6623.75	0.45
	3335.99	3336.6	3336.58	0.02
	2402.45	2402.0	2402.01	−0.01
$^{13}C_2$	6490.5	6494.4	6494.56	−0.16
	3351.2	3351.9	3351.53	0.37
	2393.28	2392.9	2392.83	0.07
$^{13}C_3$	6571.0	6574.9	6575.37	−0.46
	3304.43	3305.1	3304.76	0.34
	2380.76	2380.3	2380.44	−0.14
2-d_a	6309.5	6313.4	6313.53	−0.13
	3322.44	3323.2	3323.38	−0.18
	2382.82	2382.4	2381.92	0.48
2-d_b	6258.0	6261.9	6261.93	−0.03
	3344.54	3345.3	3345.28	0.02
	2361.96	2361.6	2361.63	−0.03

[a] B_0 rotational constants taken from ref 5 and 9. $B_z - B_0$ corrections calculated from the molecular force field in ref 13. B_z^{calcd} is calculated from the least-squares r_z structure for cyclopentanone. $2 - d_a$ and $2 - d_b$ are isotopic species where one of the hydrogens on the C_2 carbon has been deuteriated.

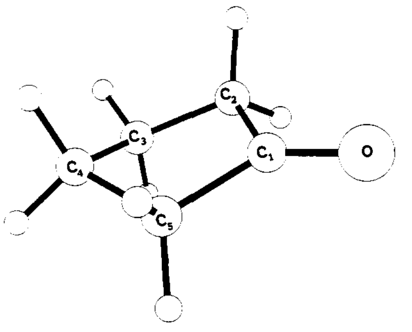

Figure 1. Atomic numbering used in defining structural parameters for cyclopentanone.

Table IV. Structural Parameters for Cyclopentanone Obtained from Least-Squares Analysis[a]

parameters	models rigid ED	 rigid ED + MW	 dynamic
$C_1—C_2$	1.529 (6)	1.531 (4)	1.526 (6)
$C_2—C_3$	1.544 (5)	1.542 (3)	1.546 (5)
C=O	1.213 (3)	1.213 (4)	1.213 (3)
$C—H_{av}$	1.104 (5)	1.104 (4)	1.105 (5)
$\angle C_2C_1C_5$	108.6 (6)	108.6 (2)	109.1 (5)
$\angle HCH_{av}$	110.2 (30)	107.5 (8)	110.4 (27)
τ^c	23.7 (23)	24.7 (4)	24.0 (1)
l_{C-C}	0.055 (2)	0.056 (2)	0.054 (2)
$l_{C_1\cdots C_4}$	0.090 (9)	0.086 (10)	0.080 (9)
$l_{C=O}$	0.038 (3)	0.040 (4)	0.038 (3)
$l_{C_2\cdots O}$	0.056 (6)	0.056 (7)	0.055 (6)
$l_{C_3\cdots O}$	0.088 (9)	0.092 (15)	0.092 (9)
l_{C-H}	0.069 (5)	0.069 (7)	0.069 (5)
$l_{C\cdots H_{gem}}$	0.104 (8)	0.099 (11)	0.103 (8)
dependent[d]			
$\angle C_1C_2C_3$	104.7 (8)	104.2 (1)	
$\angle C_2C_3C_4$	103.7 (10)	103.4 (2)	
$\tau(C_5C_1C_2C_3)$	12.0 (12)	12.4 (2)	
$\tau(C_1C_2C_3C_4)$	31.3 (29)	32.5 (5)	
$\tau(C_2C_3C_4C_5)$	38.9 (35)	40.5 (6)	
R^e	0.059	0.057	0.060

[a] Distances (Å) are reported as r_g parameters; angles (deg) are reported as r_α parameters. Quoted errors are 3σ values obtained from least-squares analysis. [b] $C_2—C_3 = C_3—C_4$ is assumed. [c] τ is the angle between the $\angle C_2C_1C_5$ plane and the $C_3—C_4$ bond. [d] Dependent parameters were calculated from the final results, and the reported errors were calculated from errors in the independent parameters by transforming the elements of the error matrix. [e] R factors are defined as $R = [(\sum W_i(I_{(\mathrm{obsd})} - I_{(\mathrm{calcd})})^2)/(\sum W_i I_{(\mathrm{obsd})}^2)]^{1/2}$.

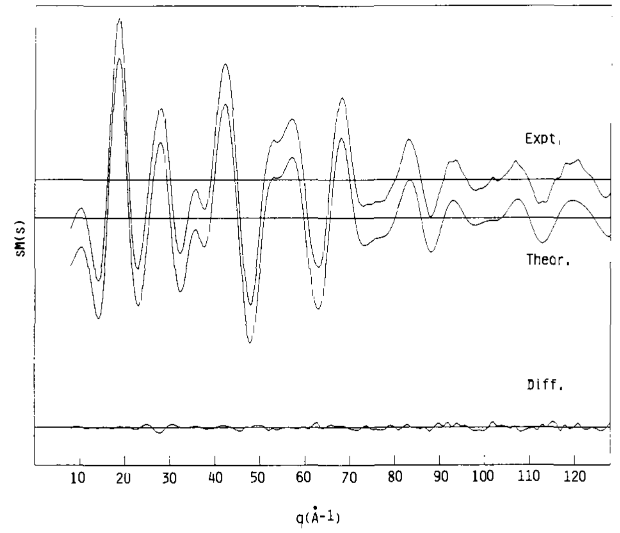

Figure 2. Leveled experimental and theoretical intensity curves for cyclopentanone.

Four plates each from the long and short camera distances were selected and traced on the NDSU microcomputer-controlled microdensitometer for analysis. The optical densities were obtained at intervals of 0.15 mm for the short and 0.20 mm for the long camera plates. After corrections for plate flatness, sector imperfections and emulsion saturation, the data were interpolated at integral $q = [40/\lambda(\sin(\theta/2))]$ intervals and averaged to form two curves for least-squares analysis. Least-squares procedures outlined by Gundersen and Hedberg[11] were followed by using elastic scattering factors and phase shifts calculated by Schafer et al.[12]

Analysis

Normal Coordinate Analysis. Vibrational amplitudes and shrinkage corrections were calculated from the valence force field which was determined and reported by Kartha.[13] The force constants used are summarized in Table I. Table II lists the calculated vibrational amplitudes and shrinkage corrections for some of the more important distances in the radial distribution curve. All the $r_\alpha(0)$ extrapolations and B_z to B_0 corrections necessary for the combined ED/MW analysis were calculated using this valence force field.

Electron Diffraction Analysis. 1. Rigid Model Analysis. The following assumptions were introduced in the construction of the model: (a) The molecule has C_2 symmetry. (b) The C_2–C_3 and C_3–C_4 bond lengths are equal. (c) All C–H bond lengths are equal. (d) All ∠HCH valence angles are equal. (e) The ∠HCH planes are the perpendicular bisector of the respective ∠CCC planes and vice verse. The geometrical parameters chosen to specify the structure are (a) the $C_1—C_2$ bond length, (b) the $C_2—C_3$ bond length, (c) the C=O bond length, (d) the C—H bond length. (e) the $\angle C_2C_1C_5$ valence angle, (f) the ∠HCH valence angle, and (g) τ, the angle between the $C_2C_1C_5$ plane and the $C_3—C_4$ bond. τ has the value one-half of the $C_2C_3C_4C_5$ torsional angle. The atomic numbering used in defining the structural parameters for cyclopentanone is shown in Figure 1.

Initially only electron diffraction data were used in the analysis and a rigid twist model was assumed. The agreement between the data and model was excellent. In the final refinement seven geometrical parameters and seven amplitudes were refined simultaneously. Table IV indicates the best results obtained from this model.

Rotational constants for cyclopentanone and five isotopically substituted isomers are available from microwave spectroscopic studies.[5,9] These 18 constants were included in the least-squares

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Table V. Comparison of Some Geometrical Parameters of Related Molecules[a]

molecules	C_1—C_2	C_2—C_3	C=O	$\angle CC_1C$	methods	ref
acetone	1.520 (3)		1.213 (4)	116.0 (3)	ED + MW	15
cyclopropanone	1.475 (19)	1.575 (12)	1.191 (20)	64.6 (9)	MW	20
cyclobutanone	1.534 (3)	1.567 (5)	1.202 (2)	92.8 (3)	ED + MW	16
cyclopentan-3-one	1.509 (8)	1.524 (8)	1.210 (2)	109.2 (10)	MW	21
cyclopentanone	1.529 (1)	1.529 (1)	1.230 (4)	112.4 (3)	ED	10
	1.504 (10)	1.557 (7)	1.215 (5)	110.5 (7)	MW	5
	1.512	1.542	1.241	110.3	MW	13
	1.5223	1.5375 (20)	1.5315 (20)	109.1	MW	9
	1.531 (4)	1.542 (3)	1.213 (4)	108.6 (2)	ED + MW	this work
cyclohexanone	1.503 (4)	1.544 (4)	1.229 (3)	115.4 (4)	ED + MW	17
cycloheptanone	1.517	1.536 (2)	1.219 (12)	117.3 (18)	ED	18

[a] Distances in Å, and angles in deg. Values from different methods might have different meaning. Parenthesized values are the quoted errors.

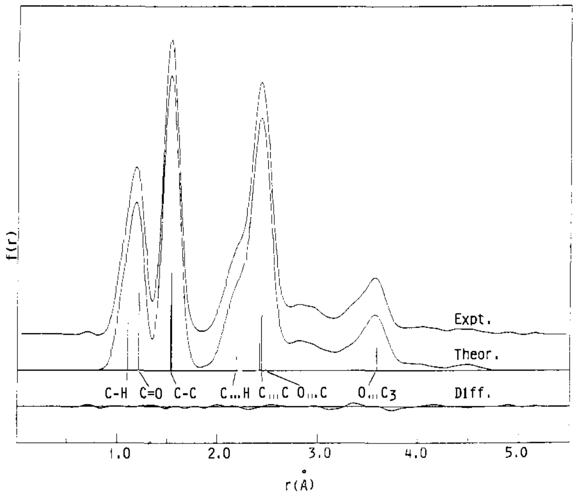

Figure 3. Experimental and theoretical radial distribution curves for cyclopentanone. Only the principal peaks are labeled.

analysis after appropriate B_z to B_0 corrections,[14] and the correction terms to extrapolate the room-temperature r_α to 0 K were made. Table III shows the experimental rotational constant values, the corrected values, and the calculated values obtained from the combined ED/MW analysis. Figures 2 and 3 show the final intensity and radial distribution curves from the combined analysis.

In the most general model of cyclopentanone, there are three different C–C bond lengths in cyclopentanone, and with the presence of 18 rotational constants we decided to try to resolve these distances. Refinements with the removal of assumption (b) resulted in the following C—C and C—O bond lengths: $r(C_1—C_2) = 1.533$ (5) Å, $r(C_2—C_3) = 1.538$ (4) Å, $r(C_3—C_4) = 1.543$ (7) Å, and $r(C=O) = 1.213$ (4) Å. All the other parameters obtained were essentially identical with the previous model. There were no significant differences between the models with two and three different C–C bonds.

2. Dynamic Model Analysis. A dynamic model with a double minimum potential function was also analyzed. A potential function of the form

$$V(x) = V_0[1 + (x/x_0)^4 - 2(x/x_0)^2]$$

$$x = \sin\tau \qquad x_0 = \sin\tau_0$$

was employed where V_0 is the magnitude of the potential energy hump at $\tau = 0$ and τ_0 represents the location of the two minima in the ring twisting potential energy function. This model is an oversimplification of the true two-dimensional pseudorotational motion. It is justified in the present case on the basis of previously obtained far-infrared results which indicate that the pseudorotation is highly restricted. This one-dimensional model mimics the dynamic behavior near the two potential minima corresponding to the twist forms of the molecule.

A total of eight pseudoconformers were included in the analysis between $\tau = 0$ and 40°. The weight assigned to each pseudoconformer was determined by using the classical Boltzmann weighting scheme as

$$W_i(x_i) = \frac{\exp(-V(x_i)/RT)}{\sum \exp(-V(x_i)/RT)}$$

In this model the O···C_3 and C_1···C_4 amplitudes of vibration were allowed to vary as a function of τ as defined by

$$l_{O\cdots C_3} = l^0_{O\cdots C_3} + 0.000177\tau + 0.00005\tau^2$$

$$l_{C_1\cdots C_4} = l^0_{C_1\cdots C_4} + 0.00031\tau + 0.000002\tau^2$$

These were used to take into account the large variations in these parameters with the ring twisting angle τ.

Since the potential barrier, V_0, could not be determined well in the least-squares analysis, several least-squares refinements were run by setting V_0 to different values in the range between V_0 = 2000 and 7000 cal/mol. The R factors from these refinements suggested the barrier height to be over 2 kcal/mol and that the value of τ_0 be 24°. Table IV summarizes the results obtained from the dynamic model.

Discussion

Table V summarizes the important geometrical parameters for cyclopentanone from several structural investigations and the parameters of some related molecules. The C=O bond length from this study is 0.017 Å shorter than the previous ED work. Our value (1.213 (4) Å) is identical with that reported for acetone[15] and is 0.01 Å longer than the value reported for cyclobutanone.[16] However, the value reported for cyclohexanone[17] is long (1.229 (3) Å) and for cycloheptanone[18] is 1.219 (12) Å. The value reported for 2-chlorocyclohexanone is 1.211 (4) Å.[19]

The C_1—C_2 bond length is of interest, and many values have been reported. The length of this carbonyl sp^3–sp^2 bond is 1.520 (3) Å in acetone, 1.534 (3) Å in cyclobutanone and 1.531 (4) Å in cyclopentanone. It is lengthened in the formation of strained rings like cyclobutane and cyclopentane. The value reported for cyclohexanone (1.503 (4) Å) appears to be inconsistent with these other results. It is unlikely that the C_1—C_2 bond in cyclohexanone should be shorter than the corresponding bond in acetone in view of the results for cyclobutanone, cyclopentanone, and cycloheptanone.

The ∠CCC valence angle of the carbonyl moiety increases from cyclobutanone to cycloheptanone where the value of 115.4° is close to the value for acetone, 116.0°. This trend simply reflects the geometrical requirement for the closure of the four-, five-, six-, and seven-membered rings. In cycloheptane the ring is flexible

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enough to maintain the "normal" carbonyl base angle.

The C_2–C_3 bond length in cyclobutanone (1.567 (5) Å) is longer than the average sp^3–sp^3 C–C bonds in the five-, six-, and seven-membered rings. This long bond length in cyclobutanone reflects the strain of the ring system and is released as the rings get larger and larger. The results for cyclopropanone are included in the table for completeness; however, the special bonding environment in cyclopropane makes comparison with the other cyclic systems impossible.

The dynamic model analysis of the electron diffraction data indicates that for cyclopentanone the barrier to the conversion between the two twist forms is about 2 kcal/mol which is in good agreement with the results reported by Ikeda and Lord.[8] We do not wish to place too much emphasis on the results obtained for the dynamic model. For molecules such as cyclopentanone, where the barrier to interconversion is high, the electron diffraction analysis is simply not sensitive enough to determine good values for such energy parameters. The far-infrared data and its analysis by Ikeda and Lord provide a much better physical picture of the molecular dynamics than provided in this paper by electron diffraction.

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Supplementary Material Available: Correlation matrix and long and short camera distance data for cyclopentanone (4 pages). Ordering information is given on any current masthead page.

Tunneling Reaction Path for the Interaction of Silicon Atom and Water

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Abstract: Ab initio molecular orbital (MO) calculations are carried out for the reaction path of a silicon atom and a water molecule. An intrinsic reaction coordinate (IRC) analysis for the potential energy surface reveals the following reaction mechanism. First a triplet silicon atom forms a triplet silicon–water adduct. Then a hydrogen of water in the adduct migrates to silicon to form the triplet HSiOH through proton tunneling. This migrated species may be converted to the singlet state by intersystem crossing. This picture is in close agreement with matrix isolation experiments.

I. Introduction

Recently, interactions and reactions of silicon-containing compounds have received much attention from both experimental and theoretical viewpoints.[1] In particular, the characteristic reaction pathway of silanone $H_2Si{=}O$ is a typical case study in silicon chemistry as a counterpart of formaldehyde H_2CO in hydrocarbon chemistry.[2–6] A variety of rearrangement channels both in the ground and excited states is available. Recent experimental study has proven that *trans*-HSiOH is the most stable species of the $[H_2SiO]$ system.[2,3] This is in accordance with predictions from previous theoretical studies.[4–6]

The rearrangement channel from silicon atom and water molecule is also interesting, because it is a model surface water reaction which may occur in the preparation of semiconductor or amorphous silicon devices in the electronics industry. In this direction of research, Ismail et al. carried out the experiment of the addition reaction of a silicon atom with water in an argon matrix and traced the IR spectra.[2] The mixture containing silicon, of which the ratio to water (H_2O + D_2O) and argon was 9:1:3300, immediately gave silicon–water adducts $Si{:}OH_2$, Si:OHD, and $Si{:}OD_2$ at 15 K. The IR spectra measured 7 h later for this mixture indicated the formation of insertion products HSiOH and HSiOD but no formation of DSiOH and DSiOD. The D_2O only formed the adduct $Si{:}OD_2$ upon thermal interaction with silicon. Photolysis using light of a wavelength greater than 400 nm was necessary for the formation of DSiOD. The thermal reaction rate of Si atom insertion into the OH bond, which is also regarded as the migration of hydrogen from water to silicon, is not affected by temperature. This suggests that the rate-determining step contains a tunneling process. Consequently, the following mechanism has been suggested: the ground state of atomic silicon, the triplet $Si(^3P)$, forms the silicon–water triplet adduct ($^3A''$). It rearranges to HSiOH (triplet) through a hydrogen atom tunneling maintaining the spin multiplicity. This is finally converted to the ground singlet state HSiOH ($^1A'$). Irradiation of the matrix causes the dissociation of HSiOH, HSiOD, and DSiOD to form silicon monoxide and molecular hydrogen or two hydrogen atoms.

In this paper, we study the following reaction processes of the silicon–water system, possessing these characteristic isotope effects mentioned above, by use of an ab initio molecular orbital (MO) method. The terms in parentheses after species indicate electronic

$$Si(^3P) + H_2O \rightarrow Si{:}OH_2(^3A'')(SiW(^3A'')) \quad (1)$$

$$Si(^1D) + H_2O \rightarrow Si{:}OH_2(^1A'')(SiW(^1A'')) \quad (2)$$

$$Si(^1S) + H_2O \rightarrow Si{:}OH_2(^1A')(SiW(^1A')) \quad (3)$$

$$SiW(^3A'') \rightarrow TS(triplet) \rightarrow HSiOH(triplet) \quad (4)$$

$$SiW(^1A'') \rightarrow TS(open\ singlet) \rightarrow HSiOH(open\ singlet) \quad (5)$$

$$SiW(^1A') \rightarrow TS(closed\ singlet) \rightarrow HSiOH(^1A') \quad (6)$$

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