J. Phys. Chem. A 2002, 106, 2489−2496

Theoretical Study on the Unimolecular Dissociation of CH_3SCH_3 and CH_3SCH_2

S. Hosein Mousavipour,* Lila Emad, and Sara Fakhraee

Department of Chemistry, Shiraz University, Shiraz, Iran

Received: March 15, 2001; In Final Form: December 19, 2001

We have studied the unimolecular dissociation reaction of CH_3SCH_3 (DMS) and CH_3SCH_2 radical theoretically. The structures of reactants, activated complexes, and products have been optimized at the MP2/6-311G(D,P) level. Energies have been derived from single point MP4SDTQ/6-311G(D,P) calculations at the MP2 geometries. The barrier height corrected for zero point energy for the unimolecular dissociation of DMS to CH_3 and SCH_3 in MP4SDTQ and CAS(2,2)MP2 calculations was found equal to 295.3 and 310.0 kJ mol^{-1}, respectively. The barrier height corrected for zero point energy for the dissociation reaction of CH_3SCH_2 radical to CH_3 and SCH_2 was calculated to be 135.5 kJ mol^{-1} at the MP4SDTQ level of theory. DMS is a C_{2v} molecule with two C_{3v} tops. The potential constants and barrier height for the torsional motion of methyl groups in DMS were also calculated. At the MP4SDTQ level of theory, the torsional barrier height for a methyl group was found to be 8.21 kJ mol^{-1}. Generalized transition state theory and RRKM method were employed to calculate the rate constants for the two reactions in the title in a temperature range of 300−3000 K. According to generalized transition state theory, we have found the Arrhenius parameters for the unimolecular dissociation reactions of DMS and CH_3SCH_2, $k_1 = 5.3 \times 10^{15}$ exp(−318.8 kJ mol^{-1}/RT) s^{-1} and $k_3 = 9.2 \times 10^{13}$ exp(−138.4 kJ mol^{-1}/RT) s^{-1}, respectively. According to RRKM method, we have found the high-pressure limiting rate constant values: $k_1 = 6.1 \times 10^{15} \exp(-317.2 \text{ kJ mol}^{-1}/RT)$ s^{-1} and $k_3 = 4.4 \times 10^{13} \exp(-138.0 \text{ kJ mol}^{-1}/RT)$ s^{-1}.

Introduction

It is believed that one of the responsible sources for the acidity of atmosphere and formation of cloud is organic sulfur compounds such as dimethyl sulfide (DMS).[1] One of the major natural sources for DMS is oceanic phytoplankton. Despite the intensive efforts on understanding the mechanism of reactions involving DMS in atmosphere, there are still some uncertainties about the mechanism of formation and consumption of key intermediates such as CH_2SCH_3 and SCH_3 radicals and active molecules such as SCH_2 in the pyrolysis or photolysis of DMS. One of the reactions that is not studied very well yet is the unimolecular dissociation reaction of DMS.[2] Nicholas and co-workers[3] have studied the decomposition of DMS in a radio frequency pulse discharge experiment. In their study, the absorption of transient species was measured by microdensitometry and end-product analyses were carried out by mass spectrometry. They have only reported a value of 500 kJ mol^{-1} for the enthalpy of overall reaction DMS→ S + $2CH_3$. In 1983, Benson has studied the unimolecular dissociation reaction of DMS experimentally[4]

$$(CH_3)_2S \rightarrow CH_3 + SCH_3 \tag{R1}$$

In his study, Benson followed the reaction by monitoring the total pressure changes in a static reactor. He reported the following Arrhenius parameters for reaction R1 as

$$k_1 = 5.0 \times 10^{16} \exp(-309 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1} \tag{1}$$

He calculated k_1 using k_{-1} equal to $10^{10.2}$ L $mol^{-1}s^{-1}$. In 1985, Shum and Benson[2] studied the pyrolysis of DMS in a temperature range of 681−723 K by monitoring the total pressure as a function of time. They proposed a chain reaction mechanism for the decomposition of DMS in the presence of SH_2

$$(CH_3)_2S \rightarrow CH_3 + SCH_3 \tag{R1}$$

$$CH_3 + (CH_3)_2S \rightarrow CH_4 + CH_2SCH_3 \tag{R2}$$

$$CH_2SCH_3 \rightarrow CH_3 + SCH_2 \tag{R3}$$

$$CH_3 + H_2S \rightarrow CH_4 + HS \tag{R4}$$

$$HS + (CH_3)_2S \rightarrow H_2S + CH_2SCH_3 \tag{R5}$$

$$CH_3 + SCH_2 \rightarrow C_2H_4 + SH \tag{R6}$$

$$CH_3 + SCH_2 \rightarrow C_2H_5S \tag{R7}$$

$$C_2H_5S + H_2S \rightarrow C_2H_5SH + HS \tag{R8}$$

$$2HS \rightarrow H_2S + S \tag{R9}$$

They have found that the rate of dissociation of DMS is accelerated in the presence of SH_2. In their paper, they have ignored reactions of CH_3S radicals. They have suggested this radical would produce negligible quantities of CH_3SH. This kind of behavior is also confirmed by our calculations. Our calculations predicts a relatively high activation energy for the unimolecular dissociation of S−CH_3 radical, which will be discussed later. This high activation energy decreases the rate of dissociation of S−CH_3 radical to S and CH_3.

10.1021/jp010990q CCC: $22.00

Shum and Benson in ref 2 have also reported the rate constant for the loss of DMS in a free radical mechanism as

$$k = 6 \pm 2 \times 10^{12} \exp(-196.5 \pm 6.3\ \text{kJ mol}^{-1}/RT)\ (\text{L/mol})^{1/2}\ \text{s}^{-1} \quad (2)$$

In 1985, Shum and Benson[5] studied the effect of presence of iodine on the pyrolysis of DMS at 644 K and in a pressure range of 0.1 to 6 Torr. They have reported a value of 1.3×10^5 L mol^{-1} s^{-1} for the bimolecular dissociation rate constant of CH_3SCH_2 radical (reaction R3).

Nourbakhsh and co-workers studied the laser photodissociation and photoionization of DMS and CH_3S radical.[6] In their study, they have used time-of-flight mass spectrometry to measure the thermochemical properties of molecular and radical ions. They have reported the zero point dissociation energy for reaction R1 equal to 313.1 ± 6.3 kJ mol^{-1}. In 1990, Nourbakhsh, Liao, and Ng[7] determined the time-of-flight spectra of SCH_3, CH_3, and $SSCH_3$ formed in the photodissociation process of CH_3SSCH_3. They have reported a value of 275.9 kJ mol^{-1} for the dissociation energy of S−C bond in SCH_3 radical at 298 K. Nicovich et al.,[8] in a temperature-dependent kinetics study of the reaction of Br with H_2S and CH_3SH, have performed a laser flash photolysis experiment for the initiation steps and monitored disappearance (or appearance) of Br ($^2P_{3/2}$) radicals using time-resolved resonance fluorescence detection technique. They have reported a value of 291.9 ± 3.3 kJ mol^{-1} at 0 K and 297.8 ± 2.9 kJ mol^{-1} at 298 K for the dissociation of S−C bond in $S{-}CH_3$ radical

$$CH_3S \rightarrow CH_3 + S \quad (R10)$$

They have also used the data from the literature and have calculated the bond strength of $H_3C{-}SCH_3$ as 307.5 ± 3.1 kJ mol^{-1} at 298 K and 301.6 ± 3.6 kJ mol^{-1} at 0 K. Benson[9] and McMillen and Golden[10] recommended values of 322 and 313 kJ mol^{-1} for $\Delta H°$ of reaction R1 at 298 K, respectively.

It is the goal of this paper to explore the potential energy surfaces for reactions R1, R3, and R10 and also to calculate the rate constants for reactions R1 and R3, theoretically. Reaction R1 is a unimolecular reaction with no saddle point. To calculate the rate constant for such reactions, people normally use the canonical or micro-canonical variational transition state or RRKM theories.[11] To find the minimum rate constant for such a reaction, one must perform calculations for a number of different distances along the reaction coordinate. Pacey applied canonical variational transition-state theory to a potential surface expressed in terms of tumbling and rocking force constants. To calculate the rate constant according to the method introduced by Pacey, one needs to know the exact shape of these tumbling and rocking potentials, which consists of at least a linear and a quadratic term. Here, we used simple collision theory to find the location of saddle point for reaction R1. After locating the position of transition state, the rate constants have been calculated by means of transition state theory and RRKM method.

DMS is a C_{2v} molecule with two C_{3v} tops. In 1977 Durig and Griffin[12] studied the torsional motion of DMS in a Raman spectroscopy experiment. They obtained the relevant potential constants for the torsional motion of methyl groups in DMS by fitting a potential function to the experimental data. We have also performed some ab initio calculations to acquire a physical understanding on the torsional interaction of two methyl tops in DMS.

Method of Calculations. In the present work, we used GAUSSIAN98−W program[13] to perform all related ab initio calculations. In the first stage, calculations were carried out at the HF/6-31G(D,P) level of theory to optimize the geometry of reactants, products, and also to explore the potential-energy surfaces along the minimum energy paths. For taking into account the effect of electron correlation, geometries of reactants, transition states, and products were optimized using second-order Moller−Plesset calculations, (P)MP2/6-311G(D,P) where P indicates that the effect of spin contamination has been projected out of the MP correlation energies.[14] Single point MP4SDTQ/6-311G(D,P),[15] means full MP4 calculation with single, double, triple, and quadruple substitutions, calculations at the MP2 geometries were done to obtain more accurate energies. To find the potential energy surface along the minimum energy path, one of the S−C bonds at different lengths was held fixed and the GAUSSIAN program was allowed to optimize the other parameters. At the HF level of theory, the potential energy surface for reaction R1 shows a maximum along the minimum energy path that could be an indication of the spin contamination. Also, the potential energy difference for reaction R1 was found to be too high at the MP2 level of calculations. Normally, it is not expected to find a saddle point for a reaction like R1. To annihilate the spin contamination, calculations along the reaction coordinate have repeated by using multi-configuration SCF (MCSCF) method.[16] In this kind of calculation, two electrons and two orbitals were specified in the active space as; CAS (2,2)MP2/6-31G(D,P). In the present study, vibrational term values were calculated at the HF/6-31G(D,P) level and scaled by 0.89. For the stationary points, there were no imaginary frequencies, whereas for the transition states, only one imaginary frequency was observed. Here, we used the vibrational term values from ref 12. In MCSCF calculations, spin contamination was not considered to be important because the expectation values of the S^2 operator was less than 0.76 for all radicals studied here.

The barrier height and the potential constants for the rotation of methyl groups in DMS were calculated at the HF level. To obtain more accurate energy values, single point MP4SDTQ/6-311G(D,P) calculations at the MP2 geometries were also performed.

Torsional Motion of DMS. DMS is a C_{2v} molecule with two internal C_{3v} rotors. The full optimized geometry of DMS indicates that the most stable configuration of DMS is the eclipse form. The potential function, $V(\gamma_1, \gamma_2)$, for a C_{2v} molecule with two equivalent C_{3v} tops could be written as[17]

$$V(\gamma_1, \gamma_2) = 1/2V_3(\cos 3\gamma_1 + \cos 3\gamma_2) + 1/2V_{33}(\cos 3\gamma_1 \cos 3\gamma_2) + 1/2V'_{33}(\sin 3\gamma_1 \sin 3\gamma_2) + 1/2V_6(\cos 6\gamma_1 + \cos 6\gamma_2) + \ldots\ldots \quad (3)$$

Here, V_3, V_{33}, V'_{33}, and V_6 are the potential constants and γ_1 and γ_2 are the dihedral angles between one of the C−H bonds in each CH_3 groups and the plane through C−S−C in the molecule. The three cosine terms in eq 3 describe the interaction of methyl rotors with the frame of the molecule and with each other leaving the two torsional fundamental frequencies equal. This degeneracy, however, is lifted by introducing the sine term, V'_{33}, which describes methyl−methyl interaction. In the present study, the total energy of DMS is calculated as a function of torsional angles of the two methyl groups. Figure 1 shows the potential energy as a function of torsional motion of methyl groups. The potential constants in eq 3 were found by nonlinear least-squares fitting of eq 3 to the calculated data for the rotation

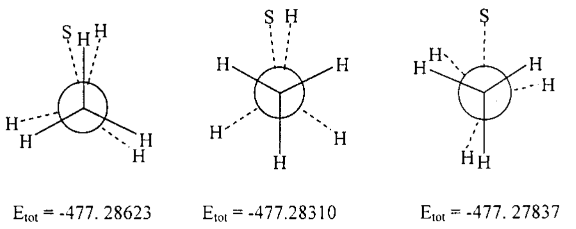

Figure 1. Calculated potential energy in hartree as a function of torsional motion of methyl tops in DMS at the MP4SDTQ/6-311G(D,P) level.

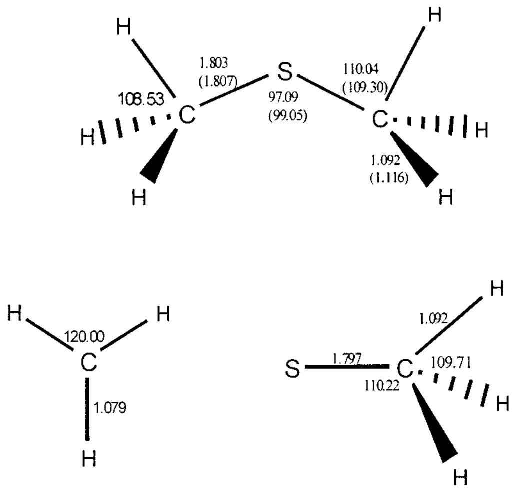

Figure 2. Optimized structures of DMS, CH_3S, and CH_3, at the MP2/6-311G(D,P) level. Numbers in parentheses are from ref 18. Distances are in Å and angles are in deg.

of two methyl groups. Values of V_3, V_{33}, V'_{33}, and V_6 were found to be 5.632, 3.546, 27.562, 9.041 kJ mol^{-1}, respectively. In this study, the torsional barrier of a methyl group about the C−S bond at the HF/6-31G(D,P) level was found to be 8.86kJ mol^{-1} and in MP4SDTQ/6-311G(D,P) calculations was equal to 8.21 kJ mol^{-1} in a good agreement with the experimental value of 8.12 kJ mol^{-1} reported by Durig and Griffin.[12] The overall torsional barrier height for simultaneous rotation of the two methyl groups was found to be 20.62 kJ mol^{-1}.

Unimolecular Dissociation of DMS, Reaction R1. Despite the importance of the presence of DMS and its role in the chemistry of atmosphere, thermal decomposition of this compound has not been studied very well yet. Figure 2 shows the structures of DMS molecule and SCH_3 and CH_3 radicals optimized at the MP2/6-311G(D,P) level. Numbers in parentheses are experimental values given in reference.[18] Vibrational term values of DMS from ref 12 and activated complex (we discuss about the position of transition state latter) for reaction R1 have been listed in Table 1. Figure 3 shows the energy profile for reaction R1 along the minimum energy path at the CAS(2,2)MP2/6-31G(D,P) level of theory. HF and MP2 calculations indicate some spin contamination at the S−C distances longer than 4.2 Å. As shown in Figure 3, there is no saddle point for the energy profile in CAS(2,2)MP2 calculations. In Figure 3 also, the Morse potential for CH_3S-CH_3 bond is compared with the theoretical results. Equation 4 has been used to calculate the Morse potential shown in Figure 3

$$V = D_o\,(1\text{-}\exp(-\beta(r - r_e))^2 - D_o \qquad (4)$$

Here, D_o was set equal to a value of 301.6 ± 3.5 kJ mol^{-1} reported by Nicovich et al. at 0 K.[8] The value of $\beta(= (k_e/2D_e)^{1/2})$ was found to be 1.79 $Å^{-1}$ and r_e is equal to 1.807 Å from ref 18. To calculate k_e, a value of 696 cm^{-1} was used for C−S−C stretching frequency, Table 1. For a better comparison, the total energies of separated CH_3 and SCH_3 were set equal to zero in Figure 3. In the present work, r_e from Figure 2 was found equal to 1.803 Å.

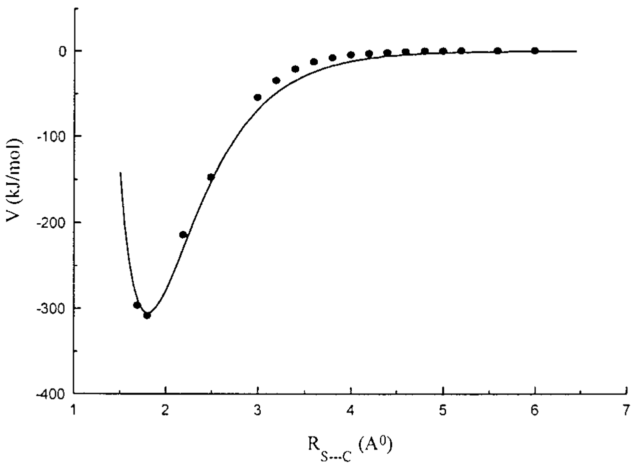

Figure 3. Potential energy surface for reaction DMS→CH_3+SCH_3. Solid line is the Morse potential and points are calculated at the CAS(2,2)MP2/6−31G (D,P) level.

TABLE 1: Vibrational Term Values of DMS from Ref 12, and the Activated Complex of Reaction R1 Calculated at the HF/6-31G(D,P) Level in cm^{-1} Scaled by 0.89 in Parenthesis

DMS	activated complex
2991	3270(2910)
2982	3269(2909)
2976	3193(2842)
2967	3179(2829)
2917	3119(2776)
2904	3108(2766)
1451	1606(1429)
1451	1593(1418)
1426	1568(1396)
1423	1565(1393)
1328	1488(1324)
1303	1197(1065)
1032	1076(958)
986	1015(903)
953	814(724)
910	495(441)
746	495(441)
696	268(239)
284	242(215)
271	77(69)
264	152i

We have found the value of ΔH^0_{298} for reaction R1 equal to 296.7 kJ mol^{-1} at the MP2/6-311G(D,P) level. The values of $\Delta_f H^0_{298}$ for CH_3S,[8] CH_3,[19] and DMS[6] are reported as 124.5 ± 1.8, 145.5 ± 1.3, and −37.6 ± 0.4 kJ mol^{-1}, respectively. These values lead to a value of 307.6 ± 3.5 kJ mol^{-1} for ΔH^0_{298} of the dissociation of DMS to CH_3 and SCH_3. Nicovich and coworkers[8] have earned values of 301.6 ± 3.6 kJ mol^{-1} at 0 K and 307.5 ± 3.6 kJ mol^{-1} at 298 K for the bond strength of S−C in DMS from heats of formation data. Nourbakhsh and co-workers[6] have reported values of 306.0 kJ mol^{-1} at 298 K and 313.1 ± 6.3 kJ mol^{-1} at 0 K for the dissociation energy of CH_3S-CH_3 bond in photodissociation experiment of DMS, see Table 2.

Table 3 shows the calculated energies of species at different levels of theory. Zero point energies at the MP2/6-311G(D,P) level of theory have also been shown in Table 3.

To locate the position of the transition state for reaction R1 along the reaction coordinate, it was assumed that there should

TABLE 2: Bond Dissociation Energies of CH_3S-CH_3 and CH_2S-CH_3 in kJ mol^{-1} at 298 K, ΔH^o, and 0 K, D_o

CH_3S-CH_3	D_o= 295.3 ΔH^o=296.7	this work
CH_3S-CH_3	D_o= 313.1 ± 6.3	ref 6
CH_3S-CH_3	ΔH^o=322	ref 9
CH_3S-CH_3	ΔH^o=312.7 ± 8.4	ref 10
CH_3S-CH_3	D_o= 301.6 ± 3.5 ΔH^o=307.5 ± 3.1	ref 8
CH_3-S	D_o= 291.9± 3.3 ΔH^o=297.8 ± 2.9	ref 8
CH_3-S	D_o= 267.4 ΔH^o=280.1	this work
CH_3-S	ΔH^o=276	ref 7
CH_3-S	ΔH^o=275.9 ± 6.3	ref 9
CH_2S-CH_3	D_o= 135.5 ΔH^o=109.2	this work

be a bottleneck along the reaction coordinate that limits the rate of the reaction.[20] The expression for the rate constant according to simple collision theory might be used to find the location of this bottleneck[20]

$$k(T,R) = p(R)\pi R^2 u_r \exp\left(\frac{-V(R)}{k_B T}\right) \tag{5}$$

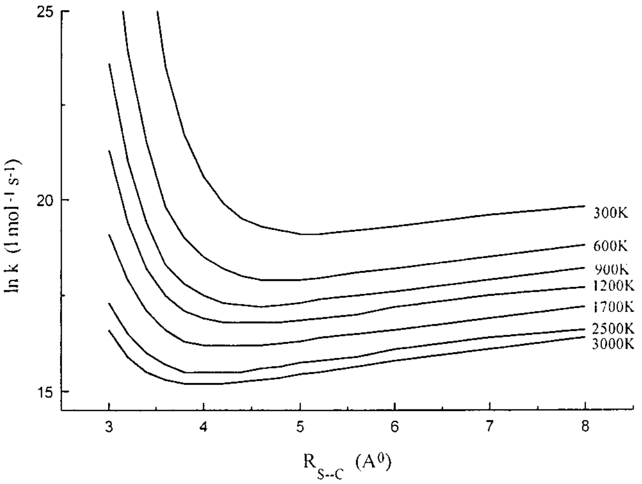

Figure 4. Calculated rate constant for the association reaction $CH_3S + CH_3 \rightarrow$DMS as a function of CH_3S- - -CH_3 distance at different temperatures (eq 5).

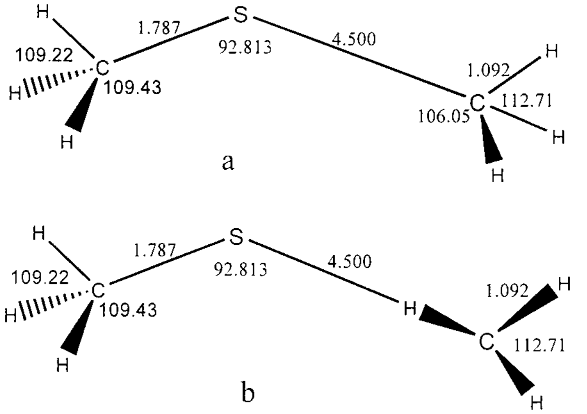

Figure 5. (a) Optimized structure of transition state for reaction R1 at the MP2/6-311G(D,P) level. (b) Structure of transition state, when the leaving CH_3group to be tilted around the axis perpendicular to the reaction coordinate (see the text). Distances are in Å and angles are in deg.

Here, $p(R)$ is the steric factor and might be calculated as the product of the quotient of electronic partition functions and the ratio of partition functions for hindered and free motions of the fragments with respect to the tumbling or rocking angles θ_i,[20] $p(R) = B_e B_\theta(R)$ ..., u_r is the relative velocity, R is the length of CH_3S- - - -CH_3 bond, and $V(R)$ is the potential energy along the reaction coordinate. Equation 5 was used to calculate the rate constant for reaction R1 as a function of CH_3S-CH_3 distance at different temperatures and the results have been shown in Figure (4). To find the location of saddle point, we calculated the rate of reverse reaction of R1 at different S−C distances along the reaction coordinate and different temperatures. To calculate the rate constant for the reverse reaction of R1 according to eq 5, $p(R)$ was calculated as the ratio of partition functions for hindered to free ($Q_{IR} = (8\pi^3 k_B T I_{IR})^{1/2}/h$) internal rotations of CH_3 group. We considered hindered rotations as harmonic vibrations. Value of B_e was set equal to unity. Value of $V(R)$ came from ab initio calculations in Figure 3. As shown in Figure 4, according to the microscopic reversibility principle, the bottleneck for the rate of reaction R1 was found at S−C bond distance of 5.0 Å at lower temperatures, which this value reaches to a value of 4.0 Å at temperatures close to 2500 K. Therefore, the location of transition state for reaction R1 was chosen when CH_3S-CH_3 bond was 4.5 Å long. Vibrational frequencies and moments of inertia for the activated complex of reaction R1 were calculated at this distance. Figure (5a) shows the structure of transition state. When CH_3S- - - -CH_3 bond is 4.5 Å apart the barrier height for the rotation of leaving methyl group around the reaction coordinate was found equal to zero and the barrier height for the rotation of leaving CH_3 group around the axes perpendicular to the reaction coordinate was found to be 2.1 kJ mol^{-1}, Figure 5b, at the MP4SDTQ level.

In the present study, after locating the position of transition state for reaction R1 as stated in the previous paragraph, the rate constant for the unimolecular reaction R1 was calculated by means of two methods. In the first method, the generalized transition state theory, eq 6, was used to calculate the rate constant[21]

$$k(T,s) = \frac{k_B T}{h}\sigma\frac{Q^{\neq}(T,s)}{Q_{DMS}(T)}\exp\left(\frac{-V_{MEP}(s)}{k_B T}\right) \tag{6}$$

TABLE 3: Calculated Total Energies and Zero Point Energies of All Species in Atomic Unit at Different Levels of Theory

species	(PU)HF	(P)MP2	CAS(2,2)MP2	MP4SDTQ	ZPE[a]
DMS	−476.780 49	−477.227 04	−477.377 38	−477.286 23	0.073 62
$[CH_3SCH_3]^{\#}$	−476.542 17	−477.061 96	−477.253 05	−477.214 03	0.067 47
CH_3S	437.135 04	−437.398 74		−437.436 74	0.035 16
CH_3	−39.575 90	−39.709 21		−39.730 77	0.030 12
S	−397.500 03	−397.581 58		−397.598 89	0.0
CH_3SCH_2	−476.155 90	−476.570 85		−476.626 10	0.06284
$[CH_3SCH_2]^{\#}$	−476.110 86	−476.521 71		−476.567 78	0.056 17
CH_2S	−436.540 13	−436.814 00		−436.851 07	0.025 17

[a] Zero point energies are calculated at the MP2/6-311G(D,P) level and scaled by 0.95.

TABLE 4: Calculated Activation Energies (corrected for zero point energies) for Reactions R1 and R2 at Different Levels of Theory, in KJ Mol^{-1}

reaction	(PU)HF	(P)MP2	CAS(2,2)MP2	MP4SDTQ
R1	166.3	296.3	310.0	295.3
R2	100.6	111.4		135.5

Here, k_B and h are Boltzmann's and Planck's constants, T is the temperature, σ is a symmetry factor (the ratio of symmetry numbers from the rotational partition functions), Q's are the product of rotational, vibrational, and translational partition functions for the transition state (numerator) and reactant (denominator), s is the distance along the reaction path, V_{MEP} is the potential energy corrected for zero point energy at the generalized transition state location s at zero degree. The vibrational partition function for each normal mode with a frequency of ν might be written as

$$Q_v = \frac{1}{1 - e^{-h\nu/k_BT}} \tag{7}$$

The rotational partition function for a nonlinear molecule is

$$Q_{rot} = \frac{8\pi^2(8\pi^3 I_a I_b I_c)^{1/2}(k_BT)^{3/2}}{\sigma h^3} \tag{8}$$

Here, I is the moment of inertia, and σ is the symmetry number. The translational partition function per unit volume of a molecule of mass m in three dimensions is

$$Q_{tr} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \tag{9}$$

According to Table 3, at the CAS(2,2)MP2/6-311G(D,P) level of theory, the potential energy difference between the transition state and DMS, V_{MEP} in eq 6, was found equal to 310.0 kJ mol^{-1}. This value was corrected for the zero point energy. As shown in Table 2, this difference at the HF (609.0 kJ mol^{-1}), MP2 (416.9 kJ mol^{-1}), and MP4SDTQ (173.3 kJ mol^{-1}) levels have not been realistic, probably due to the effect of spin contamination. Therefore, in these cases the value of V_{MEP} in eq 6 was calculated from the sum of energies of separated products, CH_3 and SCH_3, at infinite distances minus the total energy of DMS and shown in Table (4). These values of V_{MEP} are corrected for zero point energies. As shown in Table (4), the calculated value of V_{MEP} at CAS(2,2) level is about 15 kJ mol^{-1} higher than the values calculated at MP2 and MP4SDTQ levels.

To calculate the rate constant for reaction R1 the value of V_{MEP} in eq 6 was set equal to 310.0 kJ mol^{-1} from CAS(2,2) results.

To calculate the vibrational and rotational partition functions, eqs 7 and 8, we used the vibrational frequencies given in Table 1 and the moments of inertia, calculated by GAUSSIAN program, given in Table 5. A value of 2 was chosen for σ in eq 6. In these calculations, all the internal motions were considered as harmonic vibrations.

According to eq 6, the rate constant for reaction R1 was calculated and the results have been shown in Figure 6. According to generalized transition state theory the Arrhenius expression for reaction R1 was found, using Figure 6, as

$$k_1 = 5.3 \times 10^{15} \exp(-318.8 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1} \tag{10}$$

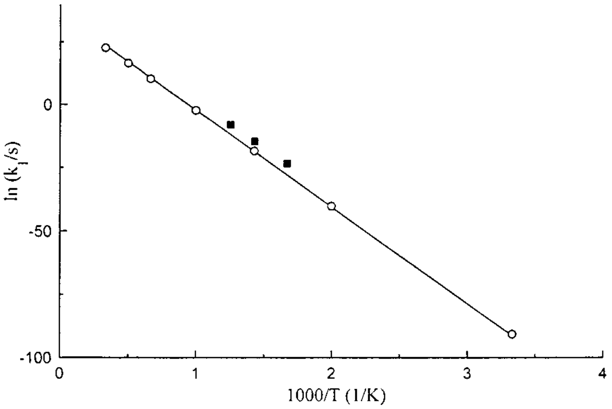

Figure 6. Arrhenius plot for reaction DMS→ $CH_3 + SCH_3$. Solid line is from generalized transition state theory (eq 6). Open circles are from RRKM method (eq 11) and squares are from ref 4.

TABLE 5: Parameters Used for RRKM Calculations for Reaction R1

threshold energy	310.0 kJ mol^{-1}	
moments of inertia of reactant	$I_c = 88.1$ amu Å^2	
	$I_b = 65.9$ amu Å^2	
	$I_a = 28.6$ amu Å^2	
moments of inertia of activated complex	$I_c = 282.8$ amu Å^2	
	$I_b = 250.1$ amu Å^2	
	$I_a = 39.4$ amu Å^2	
DMS reduced moment of inertia for	$I = 2.865$ amu Å^2	
internal rotations and symmetry number	$\sigma = 3$	
activated complex reduced moments of	$I = 2.991$ amu Å^2	$I = 2.865$ amu Å^2
inertia for internal rotations and symmetry numbers	$\sigma = 3$	$\sigma = 3$
collision efficiency β	0.05	

In the second method, RRKM calculations was performed to find the rate constant expression for reaction R1. For RRKM calculations a general RRKM program by Hase and Bunker was used[22] and modified to calculate the fall off region and high-pressure rate constant.[23] The following expression is used to calculate the unimolecular rate constant as a function of pressure[24]

$$k_{uni} = \frac{\sigma Q^{\neq}}{hQ_r}\exp\left(\frac{E_0}{RT}\right)\Delta E^{+}\sum\left[\frac{\{W(E^{+}_{vr})\}\exp\left(\frac{E^{+}}{RT}\right)}{1+\frac{k_a(E^{*})}{\beta_c Z[M]}}\right] \tag{11}$$

Here, E_0 is the zero point energy, E^+ is the total nonfixed energy of a given transition state, ΔE^+ is the energy increment, E^* is the energy of energized molecule. $W(E^+_{vr})$ is the sum of vibrational−rotational states, $k_a(E^*)$ is the rate constant for conversion of energized molecule to products, β_c is the collisional deactivation efficiency, Z is the collision number, and [M] is the concentration. The rate constant at infinite pressure is calculated according to the following equation[24]

$$k_{\infty} = \frac{\sigma Q^{\neq}}{hQ_r}\exp\left(\frac{E_0}{RT}\right)\int_{E^+=0}^{\infty}\{W(E^{+}_{vr})\}\exp\left(\frac{E^{+}}{RT}\right)dE^{+} \tag{12}$$

To calculate the rate constant for reaction R1 according to RRKM program, we have used the vibrational frequencies given in Table 1 and the other required input data given in Table 5. In our RRKM calculations, N_2 was chosen as bath gas and a value of 0.05 was selected for collision efficiency β_c from reference.[25] The reduced moments of inertia for internal rotations

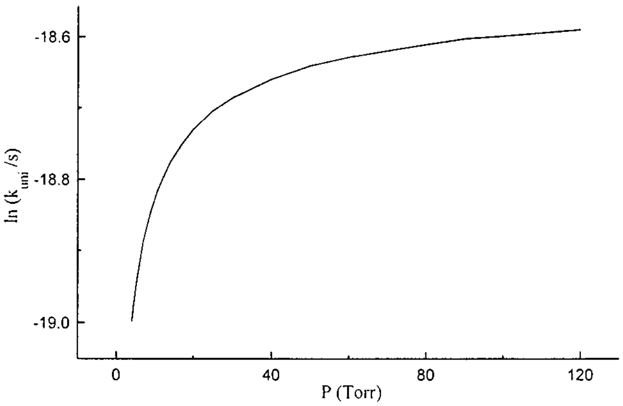

Figure 7. Fall off region of the unimolecular dissociation reaction rate constant of DMS at 700 K.

TABLE 6: Arrhanius Parameters for Reactions R1 and R3

	Ln (A/s^{-1})	E_a (kJ mol^{-1})
DMS→CH_3+SCH_3		
ref 4	38.5	309
transition state theory (eq 6)	36.2	318.8
RRKM (free rotation of leaving CH_3 in TS)	36.3	317.2
RRKM (free rotation of both CH_3 groups in reactant and TS)	34.6	317.5
CH_3SCH_2 → CH_3+SCH_2		
transition state theory (eq 6)	32.2	138.4
RRKM (free rotation of leaving CH_3 in TS)	31.4	138.0
RRKM (free rotation of leaving CH_3 in reactant and TS)	31.5	140.0

were calculated according to the method introduced by Pitzer.[26] In DMS molecule, the tumbling and rocking motions of the leaving methyl group in DMS would transform into the two hindered rotations around the axes perpendicular to the reaction coordinate axis as the transition state is approaching. In our calculations, these motions are considered as harmonic vibrations. The rotation around the C−S axis can be treated as a two-dimensional free internal rotation instead of harmonic vibrational motions. In our RRKM calculations, first we considered the rotation of leaving CH_3 group around the reaction coordinate as free rotation in the transition state and looked at this motion as harmonic vibration in the reactant. Arrhenius parameters according to this kind of calculations was found as

$$k_1 = 6.1 \times 10^{15} \exp(-317.2 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1} \quad (13)$$

Also, we considered the rotation of both methyl groups around the reaction coordinate as free rotations in the reactant and transition state. In this case, the Arrhenius parameters was found as

$$k_1 = 1.0 \times 10^{15} \exp(-317.5 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1} \quad (14)$$

The Arrhenius parameters for reaction R1 are summarized in Table 6. The high-pressure limiting values of the rate constant for reaction R1 have been shown in Figure 6 (as open circles) at different temperatures. The experimental results for k_1 from ref 4 has also been shown in Figure 6. Figure 7 shows the fall off region for the rate constant of reaction R1 as a function of pressure at 700 K.

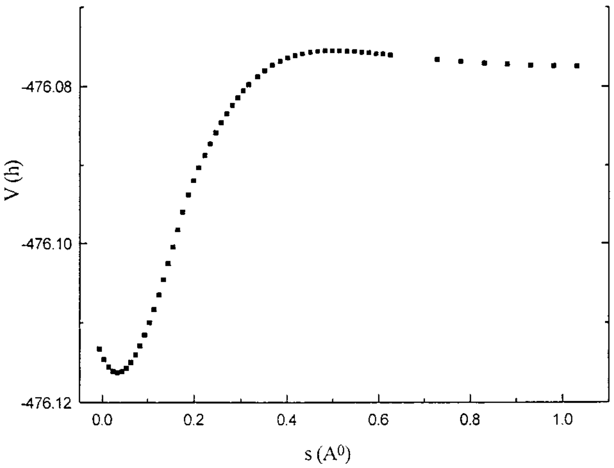

Figure 8. Potential energy surface as a function of reaction coordinate s for reaction $CH_3SCH_2 \rightarrow CH_3 + CH_2S$ at the HF/6-31G(D,P) level of theory.

Dissociation of CH_3S Radical, Reaction R10. Different organic sulfur compounds are able to produce SCH_3 radical in the atmosphere. SCH_3 radical could play an important role in atmospheric chemistry. This radical could react with different species present in troposphere like ozone, oxygen, or nitrogen dioxide.[8,27] Therefore, it would be interesting to examine the stability of this radical. In the present study, the total energy of one sulfur atom and one methyl radical in the gas phase was calculated to be 267.4 kJ mol^{-1} less than the total energy of SCH_3 radical at the MP4SDTQ/6-311G(D,P) level. This value was corrected for zero point energy, Table (3). We found the dissociation energy of S−CH_3 bond at 298 K as 280.1 kJ mol^{-1} at the MP2 level.

The value of heat of formation of S radical in the gas phase has been reported equal to 276.7 ± 0.3 kJ mol^{-1}.[8] Having the values of 124.5 ± 1.8 and 145.5 ± 0.8 kJ mol^{-1} for the heat of formation of CH_3S and CH_3,[8] respectively, the enthalpy change of unimolecular dissociation of SCH_3 radical was calculated as 297.7 ± 2.9 kJ mol^{-1} at 298 K. Nourbakhsh, Liao, and Ng reported a value of 275.9 kJ mol^{-1} for the bond dissociation energy of S−CH_3 at 298 K,[7] see Table 2. Therefore, it would be expected the SCH_3 radical gains a relatively stable structure and its unimolecular decomposition should comparatively be a slow process. This condition allows SCH_3 radical to be active toward reaction with other species in the atmosphere.

Unimolecular Dissociation of CH_3SCH_2 Radical, Reaction R3. CH_3SCH_2 radical could be produced by the reaction of DMS with some species in the atmosphere[27] or from decomposition of DMS, R2 and R5 reactions. Shum and Benson[5] studied the unimolecular decomposition of this radical at low pressures and suggested a value of 1.3×10^5 l mol^{-1}s^{-1} for the rate constant of reaction R3.

The potential energy surface along the minimum energy path was explored at the HF/6-31G(D,P) level of theory and has been shown in Figure 8. At this level of theory, the saddle point for reaction R3 is coincided with the bond distance of 2.66 Å for CH_3−SCH_2. These results have also been confirmed by MP2 calculations. The optimized structures of CH_3SCH_2 radical, the activated complex for reaction R3, and CH_2S at the MP2/6-311G(D,P) level of theory have been shown in Figure 9. Vibrational term values of CH_3SCH_2, activated complex for reaction R3, and CH_2S were listed in Table 7.

In the present work, the value of $\Delta H°$ at 298 K for reaction R3 was found equal to 109.2 kJ mol^{-1} at the MP2/6-311G(D,P) level. Unfortunately, the heat of formation of CH_3SCH_2

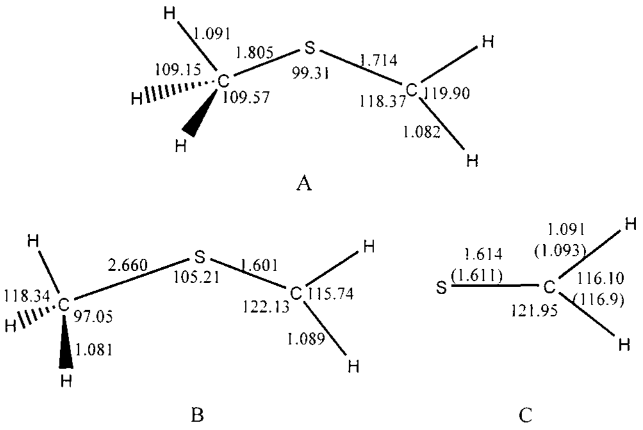

Figure 9. Optimized structures of CH_3SCH_2 (A), activated complex for reaction R3 (B), and CH_2S (C), at the MP2/6-311G(D,P) level of theory. Numbers in parentheses are from ref 18. Distances are in Å and angles are in deg.

TABLE 7: Vibrational Term Values of CH_3SCH_2, Activated Complex, and SCH_2 at Hf/6-31G(D,P) Level of Theory in cm^{-1}, Scaled by 0.89 in Parenthesis

CH_3SCH_2	activated complex	SCH_2
3429(3052)	3448(3069)	3363.9(2993.9)
3307(2943)	3441(3063)	3271.8(2911.9)
3304(2941)	3394(3021)	1642.8(1462.1)
3297(2934)	3297(2934)	1178.7(1049.0)
3208(2855)	3267(2908)	1157.0(1029.7)
1614(1436)	1551(1380)	1091.9(971.8)
1600(1424)	1545(1375)	
1542(1372)	1511(1345)	
1495(1331)	1038(924)	
1127(1003)	979(871)	
1074(956)	872(776)	
982(874)	870(774)	
859(765)	646(575)	
767(683)	559(498)	
503(448)	465(414)	
315(280)	222(198)	
231(206)	73(65)	
169(150)	171i	

radical at 298 K is not available in the literature. Heats of formation of CH_3SCH_2, CH_2S, and CH_3 at 0 K have been reported as 142.1 ± 10.5, 104.9, 148.8 ± 1.3 kJ mol^{-1}, respectively.[6] These values lead to a value of 111.6 ± 11.8 kJ mol^{-1} for $\Delta H°$ at zero Kelvin, see Table 2.

In the present study, we have calculated the rate constant of reaction R3 by means of generalized transition state theory, eq 6. Also we have applied RRKM method to calculate the fall of region and high-pressure limiting value of the rate constant for reaction R3, eqs 11 and 12.

According to Table 4 the barrier height, V_{MEP} in eq 6, corrected for zero point energies at the PMP2 and MP4SDTQ levels of theory was found equal to 111.4 and 135.5 kJ mol^{-1}, respectively. In our calculations, we used value of 135.5 kJ mol^{-1} for V_{MEP}. To calculate the vibrational and rotational partition functions, eqs 7 and 8, the vibrational frequencies given in Table 7 and the moments of inertia given in Table 8 calculated by GAUSSIAN program were used.

Arrhenius plot for reaction R3 has been shown in Figure 10 and the Arrhenius expression was found as

$$k_3 = 9.2 \times 10^{13} \exp(-138.4 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1} \quad (15)$$

For RRKM calculations, it was assumed that there are two hindered internal rotations for CH_3 and CH_2 groups around the S−C bonds. The internal rotation of CH_2 around the S−C bond transforming into a more hindered rotation, while the CH_3 internal rotation transforming into a more free rotation as the activated complex is approaching. In our RRKM calculations, we considered the rotation of CH_2 group around C−S bond as harmonic vibrational motion, but the rotation of CH_3 group around C−S bond could be treated as free rotation in both reactant and transition state or considered as harmonic vibrations in the reactant and free rotation in the transition state, see Table 6. The required input data for RRKM calculations have been listed in Table 8. The required vibrational frequencies were listed in Table 7. Figure 11 shows the fall off region of the rate constant for reaction R3 as a function of pressure at 300 K. High-pressure limiting values of the rate constant for reaction R3 at different temperatures have been shown as close circles in Figure 10. The Arrhenius parameters from RRKM calculations for reaction R3 were found as

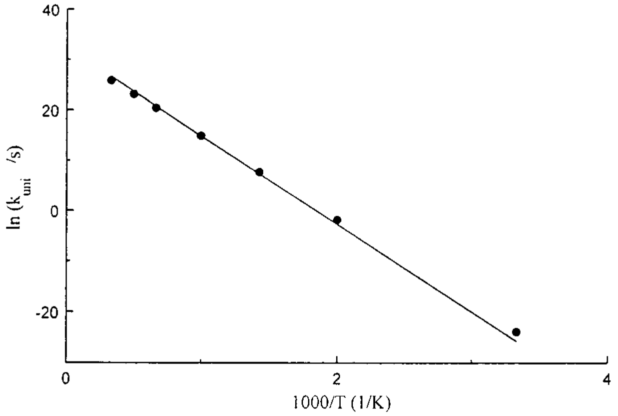

Figure 10. Arrhenius plot for the unimolecular dissociation of CH_3SCH_2 radical. Solid line from generalized transition state theory, (eq 6) and points are from RRKM method (eq 11).

TABLE 8: Parameters Used for RRKM Calculations for Reaction R3

threshold energy	135.5 kJ mol^{-1}	
moments of inertia of reactant	I_c =82.4 amu Å^2	
	I_b =60.7 amu Å^2	
	I_a =25.1 amu Å^2	
moments of inertia of activated complex	I_c =122.9 amu Å^2	
	I_b =103.2 amu Å^2	
	I_a =26.6 amu Å^2	
reduced moments of inertia for internal	I = 2.865 amu Å^2	I = 1.61 amu Å^2
rotations and symmetry numbers	$\sigma = 3$	$\sigma = 2$
activated complex reduced moments of	I = 2.991 amu Å^2	I = 1.61 amu Å^2
inertia for internal rotations and symmetry numbers	$\sigma = 3$	$\sigma = 2$
collision efficiency β	0.05	

$$k_3 = 4.4 \times 10^{13} \exp(-138.0 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1} \quad (16)$$

Conclusion

The unimolecular dissociation reaction of CH_3SCH_3 and CH_3SCH_2 radical has been studied theoretically. All the structures have been optimized at the MP2/6-311G(D,P) level of theory. DMS is a C_{2v} molecule with two C_{3v} rotors. The eclipsed form of DMS has been found to be more stable than the gauche form by a value of 8.21 kJ mol^{-1} in MP4SDTQ/6-311G(D,P) calculations. The potential constants for the torsional motion

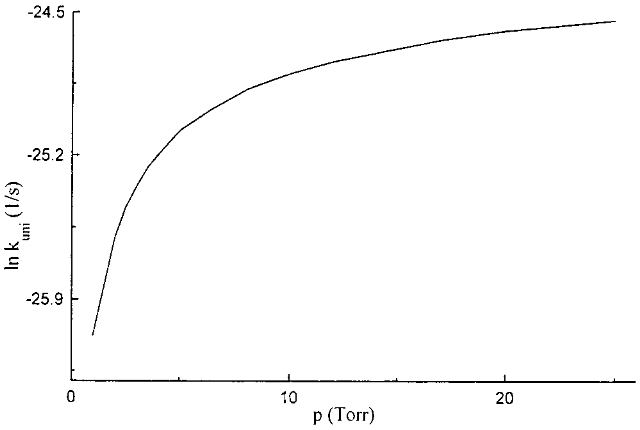

Figure 11. Fall off region of the unimolecular dissociation rate constant for reaction $CH_3SCH_2 \rightarrow CH_3 + SCH_2$ at 300 K.

of methyl groups were also calculated. The bond length of CH_3S-CH_2 has been found to be 0.089 Å less than the S−C bond length in DMS. According to simple collision theory the bottleneck for the dissociation rate of DMS to CH_3S and CH_3 was found when CH_3S-CH_3 bond is about 5.0 Å apart at lower temperatures and reaches to a value of 4.0 Å at temperatures close to 2500 K. The saddle point for reaction $CH_3SCH_2 \rightarrow CH_3 + SCH_2$ was found when H_3C-SCH_2 distance is 2.66 Å apart which shows an early transition state. At the MP4SDTQ/6-311G(D,P) level of theory, the barrier height for dissociation of DMS and CH_3SCH_2 were found equal to 295.3 kJ mol^{-1} and 135.5 kJ mol^{-1}, respectively. For reaction R1, this value was found equal to 310.0 kJ mol^{-1} at the CAS(2,2)MP2 level. The rate constants at infinite pressure for both reactions were calculated in a temperature range of 300 to 3000 K. The Arrhenius parameters for the unimolecular dissociation rate constant of DMS and CH_3SCH_2 radical, calculated by means of generalized transition state theory and RRKM theory. In our transition state theory calculations, we considered all internal motions as harmonic vibrations, whereas in our RRKM calculations, we considered the rotation of methyl groups around C−S bond as two-dimensional free internal rotation.

Acknowledgment. This work was supported by the Research Council of Shiraz University.

References and Notes

(1) Bates, T. S.; Lamb, B. K.; Guenther, A.; Dignon, J.; Stoiber, R. E. *J. Atmos. Chem.* **1992**, *14*, 315. Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; Wiley: New York, 1966. Thompson, S. D.; Carrol, D. G.; Watson, F.; O'Donnell, M.; McGlynn, S. P., *J. Chem. Phys.* **1966**, *45*, 1367.

(2) Shum, L. G.; Benson, S. W. *Int. J. Chem. Kinet.* **1985**, *17*, 749.

(3) Nicholas, J. E.; Amodio, C. A.; Baker, M. J. *J. Chem. Soc., Faraday Trans. 1*, **1979**, *75*, 1868.

(4) Benson, S. W. *Can. J. Chem.* **1983**, *61*, 881.

(5) Shum, L. G.; Benson, S. W. *Int. J. Chem. Kinet.* **1985**, *17*, 277.

(6) Nourbakhsh, S.; Norwood, K.; Yin, H.-M.; Liao, C.-L.; Ng, C. Y. *J. Chem. Phys.* **1991**, *95*, 5014.

(7) Nourbakhsh, S.; Liao, C.-L.; Ng, C. Y. *J. Chem. Phys.* **1990**, *92*, 6587.

(8) Nicovich, J. M.; Kreutter, K. D.; van Dijk, C. A.; Wine, P. H. *J. Phys. Chem.* **1992**, *96*, 2518.

(9) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.

(10) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(11) Forst, W. *J. Phys. Chem.* **1991**, *95*, 3620. Pilling, J. M.; Robertson, S. H.; Seakins, P. W. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 4179. Venkatesh, P. K.; Carr, R. W.; Cohen, M. H.; Dean, A. M. *J. Phys. Chem.* A **1998**, *102*, 8104. Hase, W. L. *Acc. Chem. Res.* **1983**, *16*, 258. Smith, S. C. *J. Phys. Chem.* **1993**, *97*, 7034. Klippenstein, S. J.; Marcus, R. A. *J. Phys. Chem.* **1988**, *92*, 3105. Truhlar, D. G.; Garrett, B. C.; Klippenstein, S. J. *J. Phys. Chem.* **1996**, *100*, 12 771.

(12) Durig, J. R.; Griffin, M. G. *J. Chem. Phys.* **1977**, *67*, 2220.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.3; Gaussian, Inc.: Pittsburgh, PA, 1998.

(14) Sosa, C.; Schlegel, H. B. *Int. J. Quantum Chem.* **1986**, *29*, 1001. Schlegel, H. B. *J. Chem. Phys.* **1986**, *84*, 4530.

(15) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91. Krishnan, R.; Frisch, M. J.; Pople J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(16) Yamamoto, N.; Vreven, T.; Robb, M. A.; Frisch, M. J.; Schlegel, J. B. *Chem. Phys. Lett.* **1996**, *250*, 373, and references therein.

(17) Ozkabak, A. G.; Philis, J. G.; Goodman L. *J. Am. Chem. Soc.* **1990**, *112*, 7854.

(18) *Handbook of Chemistry and Physics*, 80th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, 1999−2000, .

(19) Berkowitz, J.; Ellison, G. B.; Gutman, O. J. *J. Phys. Chem.* **1994**, *98*, 2744.

(20) Pacey, P. D. *J. Phys. Chem. A* **1998**, *102*, 8541 and references therein.

(21) Truhlar, D. G.; Isaacson, A. D.; Garrett, B. C. *Theory of Chemical Reaction Dynamics*; Baer, M., Ed., CRC Press: Boca Raton, FL, 1985.

(22) Hase, W. L.; Bunker, D. L. *QCPE Program 234*; Quantum Chemistry Program Exchange, Indiana University: Bloomington, IN.

(23) The RRKM program is modified by Dr. P. D. Pacey, Dalhousei University, Canada.

(24) Holbrook, K. A.; Pilling, M. J.; Robertson, S. H. *Unimolecular Reactions*, 2nd ed.; John Wiley & Sons Ltd: Chichester, England, 1996.

(25) Börjesson, L. E. B.; Nordholm, S. *J. Phys. Chem.* **1995**, *99*, 938.

(26) Pitzer, K. S. *J. Chem. Phys.* **1946**, *14*, 239.

(27) Tyndall G. S.; Ravishankara A. R. *J. Phys. Chem.* **1989**, *93*, 2426.