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A Gaussian-3 Study of the Photodissociation Channels of Propylene Sulfide

Justin Kai-Chi Lau and Wai-Kee Li*
Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

Fei Qi
Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, California 94720

Arthur G. Suits
Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794, and Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973

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Gaussian-3 (G3) calculations have been carried out to examine the photodissociation of propylene sulfide at 193 nm. On the basis of the good agreements between the G3 results and experimental measurements, three dissociation channels involving transition structures have been established. The sulfur-containing products of these three dissociation reactions are C_2H_3S, HS, and H_2S. Moreover, two channels leading to the loss of sulfur atom are observed experimentally and confirmed computationally. Furthermore, some additional elimination processes, also leading to the neutral fragments C_3H_6 and $S(^1D)$ or $S(^3P)$, and having exceedingly high experimental reaction barriers, are observed. These reactions are not likely to take place at the ground state of propylene sulfide. The experimentally measured high reaction barriers are in very good accord with our calculated excitation energies of propylene sulfide.

Introduction

Sulfur-containing hydrocarbons are important intermediates in combustion and atmospheric chemistry. These species may play important roles in the atmospheric sulfur cycle and contribute to acid rain and atmospheric aerosols.[1−7] Photodissociation of the sulfur compounds is an interesting topic from both theoretical and experimental perspectives. Using synchrotron radiation, we obtained five pairs of neutral photodissociation products of ethylene sulfide at the 193 nm region.[8] To interpret the results observed in these experiments, high-level theoretical methods were employed to establish the dissociation channels.[8]

Recently, we have studied the photodissociation of propylene sulfide (C_3H_6S) by also using the same synchrotron radiation technique. It is found that the observed neutral products[9] are similar to those from the dissociations of ethylene sulfide. In the present work, we apply the Gaussian-3 (G3)[10] method to examine the structures and energetics of the neutral photodissociation products of propylene sulfide. On the basis of the agreement between the estimated experimental reaction barriers (ΔE) and the G3 energies, three dissociation channels involving transition structures are established:

$$C_3H_6S \rightarrow CH_3 + C_2H_3S \qquad \Delta E = 111 \text{ kcal mol}^{-1} \quad (1)$$

$$C_3H_6S \rightarrow HS + C_3H_5 \qquad \Delta E = 74.5 \text{ kcal mol}^{-1} \quad (2)$$

$$C_3H_6S \rightarrow H_2S + C_3H_4 \qquad \Delta E = 44 \text{ kcal mol}^{-1} \quad (3)$$

In addition, two reactions leading to the loss of sulfur atom are observed:

$$C_3H_6S \rightarrow C_3H_6 + S(^1D) \qquad \Delta E = 98, 110, 126 \text{ kcal mol}^{-1} \quad (4)$$

$$C_3H_6S \rightarrow C_3H_6 + S(^3P) \qquad \Delta E = 73 \text{ kcal mol}^{-1} \quad (5)$$

It is found that the process to form $C_3H_6 + S(^1D)$ occurs via three different potential energy surfaces (PES), involving high experimental barriers. The elimination processes involving high-energy barriers are believed to take place at the excited states. To examine these channels, the energy profiles for the loss of sulfur atom via the ground and excited states of propylene sulfide are constructed. From these energy profiles, it is hoped that the elimination mechanisms of propylene sulfide can be understood.

Before proceeding to calculations, it is noted that the way the reaction barriers are derived from experimental data has been described in the ethylene sulfide paper,[8] and hence is not repeated here. Furthermore, as noted in that paper, the barriers so derived should be taken as estimates, instead of accurate measurements.

Methods of Calculations

All calculations were carried out on DEC 500au, XP900, and XP1000 workstations using the Gaussian 98 package of programs.[11] The computational model we employed was the aforementioned G3 level of theory.

In the G3 model, structures are optimized at the second-order Møller−Plesset theory (MP2) using the 6-31G(d) basis set with all electrons included, i.e., at the MP2(Full)/6-31G(d) level. On the basis of these optimized structures, five single-point calculations, namely, QCISD(T)/6-31G(d), MP4/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), and MP2(Full)/G3Large are carried out. Also, this model requires higher level correction (HLC) in the calculation of total electronic energies (E_e). The MP2(Full)/6-31G(d) harmonic vibrational frequencies, scaled by 0.9661, are applied for the zero-point vibrational energy (ZPVE) correction at 0 K ($E_0 = E_e +$ ZPVE).

For the dissociation involved in the excited states, the excitation energy (relative to the ground state) is calculated by

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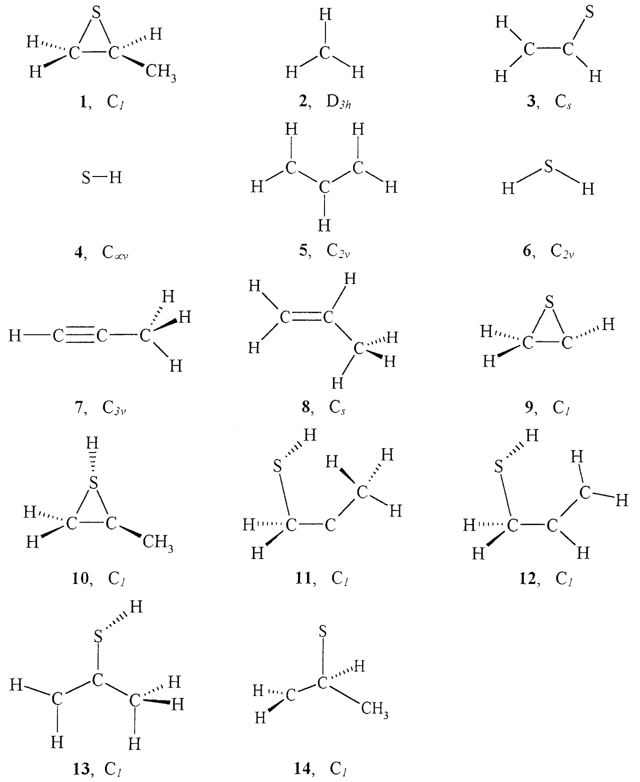

Figure 1. Structural formulas of the stable species involved in the dissociation of propylene disulfide, along with their symmetry point groups.

the time-dependent (TD) DFT method.[12] With this method, geometry is optimized at the B3LYP/6-31G(d) level.

The heats of formation at temperature T (ΔH°_{fT}) in this work were calculated in the following manner. For molecule AB, its G3 ΔH°_{fT} was calculated from the corresponding heat of reaction ΔH°_{rT} ($A + B \rightarrow AB$) and the respective experimental $\Delta H^\circ_{fT}(A)$ and $\Delta H^\circ_{fT}(B)$ for elements A and B. In addition, many transition structures (TSs) were located in this work. For each TS, the "reactant(s)" and "product(s)" were confirmed by intrinsic reaction coordinate calculation at the same level of theory at which the geometry of the TS was optimized.

Results and Discussion

The structural formulas of all the neutral stable species involved in this work, along with their symmetry point groups, are shown in Figure 1. The calculated G3 energies and standard heats of formation (ΔH°_f) at 0 and 298 K of various species involved in the dissociations of propylene sulfide (**1**) are summarized in Table 1. With the aid of these results, it is possible to establish the dissociation channels of propylene sulfide.

Dissociation Channels Involving Transition Structures. In this section, we consider the dissociation mechanisms of propylene sulfide, which involve one or more TSs.

$$C_3H_6S\ (\mathbf{1}) \rightarrow CH_3\ (\mathbf{2}) + C_2H_3S\ (\mathbf{3}) \qquad (1)$$

The potential energy surface for this dissociation is shown in Figure 2. It is seen that the reaction starts with **1** undergoing methyl group dissociation to form CH_3 (**2**) and *c*-CH_2CHS (**9**) via TS_a. Then, rearrangement of **9**, through TS_b, leads to the formation of CH_2CHS (**3**). The G3 overall barrier for this reaction is found to be 99.6 kcal mol^{-1}, which is lower than the experimental value of 111 kcal mol^{-1}. Bearing in mind that the experimental barrier is measured from the exit barrier plus the heats of reaction and it represents an upper bound, the G3 barrier as well as the proposed dissociation pathway are hence acceptable. On the other hand, kinetic shift may give rise to the discrepancy between the calculated and experimental reaction barriers. It should be noted that dissociation (1) is not observed in our previous study on ethylene sulfide,[8] as this compound does not have a methyl substituent.

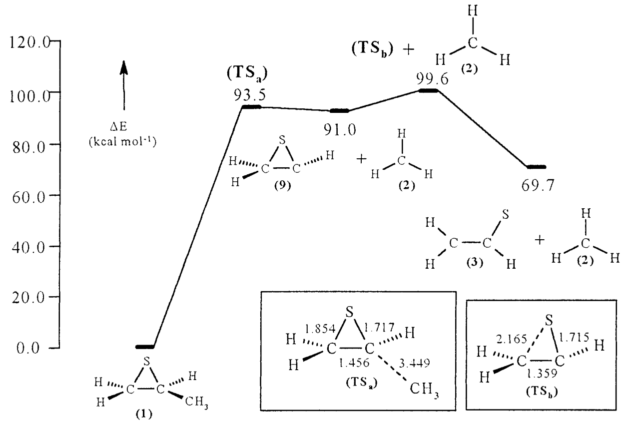

Figure 2. Potential energy surface showing the possible mechanism for dissociation $C_3H_6S \rightarrow CH_3 + C_2H_3S$.

TABLE 1: G3 Total Energies (E_0), Enthalpies (H_{298}), and Standard Heats of Formation at 0 K (ΔH°_{f0}) and 298 K (ΔH°_{f298}) of the Species Involved in the Dissociation of Propylene Sulfide (C_3H_6S)

species	E_0 (hartree)	H_{298} (hartree)	ΔH°_{f0} (kcal mol^{-1})	ΔH°_{f298} (kcal mol^{-1})
C_3H_6S (**1**)	−515.83519	−515.82960	16.3	12.4
CH_3 (**2**)	−39.79144	−39.78733	35.8	35.2
CH_2CHS (**3**)	−475.93261	−475.92810	50.3	48.9
HS (**4**)	−398.59510	−398.59180	33.8	34.0
CH_2CHCH_2 (**5**)	−117.14132	−117.13657	44.5	41.9
H_2S (**6**)	−399.23786	−399.23407	−3.5	−4.1
CH_3CCH (**7**)	−116.55517	−116.54984	46.3	45.1
CH_3CHCH_2 (**8**)	−117.77961	−117.77453	9.9	6.6
9	−475.89880	−475.89452	71.5	69.9
10	−515.73390	−515.72786	79.9	76.2
11	−515.72318	−515.71627	86.6	83.5
12	−515.82914	−515.82287	20.1	16.6
13	−515.83695	−515.83057	15.2	11.8
14	−515.74878	−515.74219	70.5	67.2
TS_a	−515.68626	−515.67821	109.8	107.4
TS_b	−475.88502	−475.88091	80.2	78.5
TS_c	−515.72872	−515.72275	83.1	79.4
TS_d	−515.72037	−515.71401	88.4	84.9
TS_e	−515.71412	−515.70792	92.3	88.7
TS_f	−515.73004	−515.72418	82.3	78.5
TS_g	−515.71332	−515.70626	92.8	89.8
TS_h	−515.73729	−515.73112	77.7	74.2

$$C_3H_6S\ (\mathbf{1}) \rightarrow HS\ (\mathbf{4}) + C_3H_5\ (\mathbf{5}) \qquad (2)$$

The energy profile for this reaction is given in Figure 3. Here, **1** first undergoes hydrogen shift via TS_c to form intermediate **10**, which then ring opens by breaking a S−C bond through TS_d to form **11**. Subsequently, **11** undergoes another hydrogen shift by way of TS_e to form intermediate **12**. Finally, cleavage of S−C bond in **12** produces HS (**4**) and C_3H_5 (**5**). The overall G3 barrier for this dissociation is 76.0 kcal mol^{-1}, which is in a very good agreement with experimental result of 74.5 kcal mol^{-1}. The dissociation of SH from ethylene sulfide (C_2H_4S), $C_2H_4S \rightarrow HS + C_2H_3$, was observed in our previous study.[8] The measured and G3 barriers for this reaction are 86 and 84.4

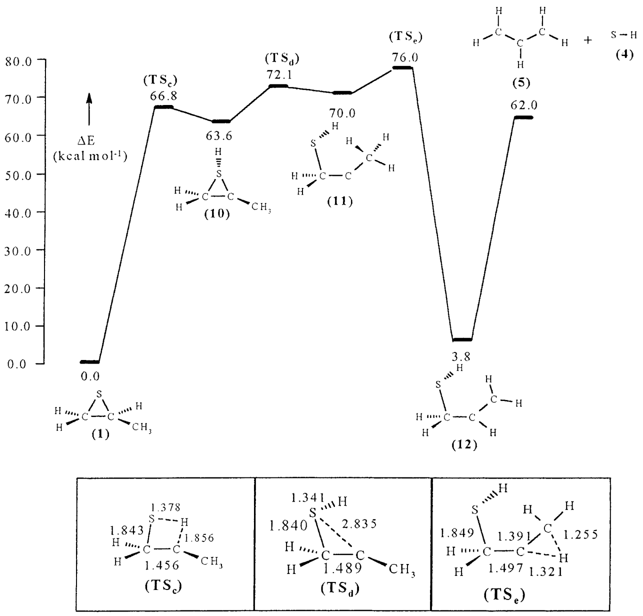

Figure 3. Potential energy surface showing the possible mechanism for dissociation $C_3H_6S \rightarrow HS + C_3H_5$.

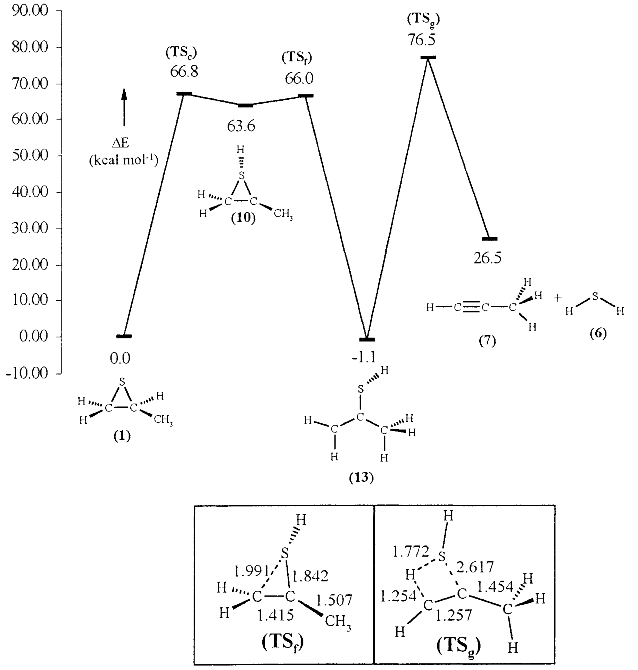

Figure 4. Potential energy surface showing the possible mechanism for dissociation $C_3H_6S \rightarrow H_2S + C_3H_4$. The geometry of transition structure TS_c is shown in Figure 3.

kcal mol^{-1}, respectively.

$$C_3H_6S\ (\mathbf{1}) \rightarrow H_2S\ (\mathbf{6}) + C_3H_4\ (\mathbf{7}) \qquad (3)$$

The energy profile for this reaction is displayed in Figure 4. It is seen that **1** forms **10** via the pathway described in Figure 3. Then **10** undergoes ring opening via TS_f to form **13**. Finally, the dissociation of H_2S (**6**) from **13** via TS_g produces propyne (**7**). The G3 overall barrier for this reaction is 76.5 kcal mol^{-1}, which is much higher than the experimental value of 44 kcal mol^{-1}. Such a large difference between experimental (35 kcal mol^{-1}) and G3 (81.4 kcal mol^{-1}) barriers[8] was also obtained for the dissociation $C_2H_4S \rightarrow H_2S + HCCH$. It is believed that the energy of a highly strained species (TS_g in this instance) is not likely to be available to translation as the system relaxes in the exit channel. Hence the experimental barrier is an underestimation of the true value. Experiment suggests, and calculations concur, that allene is unlikely to be the C_3H_4 isomer produced in this dissociation of propylene sulfide.[9]

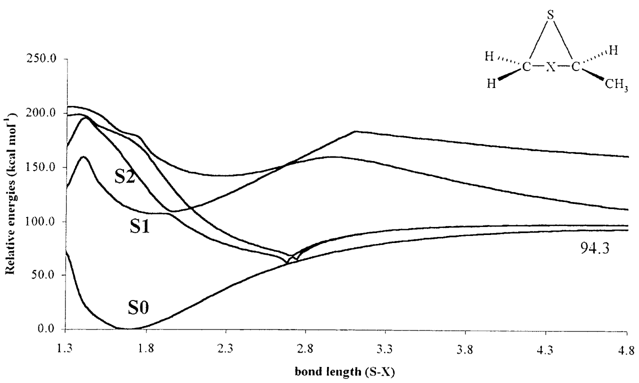

Figure 5. Singlet potential energy profiles for dissociation $C_3H_6S \rightarrow C_3H_6 + S(^1D)$.

Eliminations of Sulfur Atom. We have observed some reactions leading to the products of $S(^1D)$ or $S(^3P)$. Besides, some additional channels, involving high experimental barriers, but also leading to the neutral fragments C_3H_6 and $S(^1D)$, have been detected. We believe these processes involving high experimental barriers take place in excited states. To examine these channels, the energy profiles for the loss of sulfur atom via the ground and excited states of propylene sulfide have been constructed using the TD-DFT method. These profiles are shown in Figure 5. In this figure, energy is plotted against the S−X distance, where X is the midpoint of the C−C bond. Furthermore, to prevent the leaving S atom from drifting sideways, it was assumed that the S−X line was perpendicular to the C−C bond, whereas all remaining parameters were allowed to vary. Before discussing the results, it is noted that the treatment for propylene sulfide presented here follows closely to that for ethylene sulfide, whose photodissociation channels also include S atom detachment.[8]

Detachment of Singlet Sulfur Atom. There are three experimental barriers for the eliminations of singlet sulfur atom: 98, 110, and 126 kcal mol^{-1}.

$$C_3H_6S\ (\mathbf{1}) \rightarrow C_3H_6\ (\mathbf{8}) + S(^1D) \qquad (4)$$

From the S_0 curve shown in Figure 5, it is seen that the energy required for the loss of sulfur atom in the ground state is 94.3 kcal mol^{-1}, which is in fair agreement with the lowest measured barrier, 98 kcal mol^{-1}. For the corresponding reaction of ethylene sulfide, $C_2H_4S \rightarrow C_2H_4 + S(^1D)$, the experimental and G3 barriers are 88 and 85.1 kcal mol^{-1}, respectively.[8] For the eliminations of singlet sulfur atom via the excited states, it may be assumed that propylene sulfide is first excited to the second singlet excited state S_2, and then it undergoes three different processes on the singlet PES. First, direct elimination on the S_2 PES to form the fast $S(^1D)$ atoms (with excitation energy 126.9 kcal mol^{-1}); second, a coupling between S_2 and S_1 states gives the middle $S(^1D)$ fragment (with excitation energy 112.5 kcal mol^{-1}); last, the slow $S(^1D)$ atom comes from internal conversion on the ground state S_0 (with energy barrier 94.3 kcal mol^{-1}). The excited state propylene sulfide has a distorted structure, and the coupling between S_2 and S_1 becomes significant. From our previous work,[8] the loss of $S(^1D)$ from ethylene sulfide via excited states has experimental barriers of 107 and 123 kcal mol^{-1}.

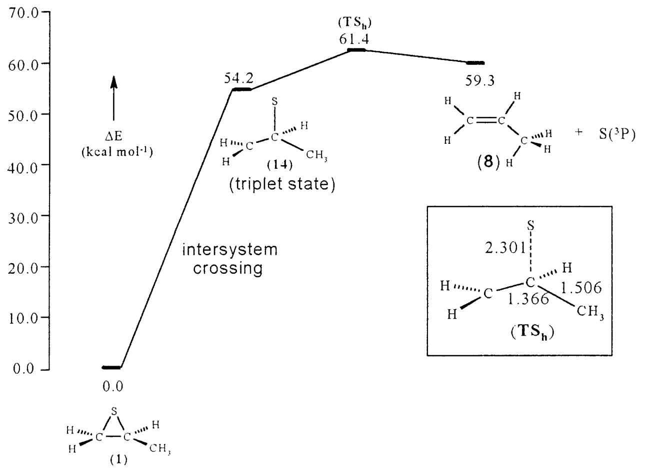

Figure 6. Potential energy surface showing the possible mechanism for dissociation $C_3H_6S \rightarrow C_3H_6S + S(^3P)$.

Detachment of Triplet Sulfur Atom. The experimental energy barrier for the elimination of triplet sulfur atom is 73 kcal mol^{-1}. This experiment confirms that the $S(^3P)$ is produced only at the ground state.[9]

$$C_3H_6S\ (\mathbf{1}) \rightarrow C_3H_6\ (\mathbf{8}) + S(^3P) \tag{5}$$

We now consider the loss of triplet sulfur atom taking place in the ground state. The energy profile for this process is given in Figure 6. It is seen that singlet C_3H_6S (**1**) first undergoes intersystem crossing to form triplet C_3H_6S (**14**). Note that **14** is no longer a cyclic species. Then the cleavage of the C−S bond leads to the formation of $S(^3P)$ and C_3H_6 (**8**). The energy required for this process is 61.4 kcal mol^{-1}, which is lower than the experimental result (73 kcal mol^{-1}). Because the experimental measurements represent the upper bound values, we believe the triplet sulfur dissociation is more likely to take place at the ground state. In our previous study on ethylene sulfide,[8] the corresponding loss of $S(^3P)$ was also observed. The measured and G3 barriers are 63 and 59.5 kcal mol^{-1}, respectively.

The general agreement between the TD-DFT and experimental results implies that, following the initial excitation to an excited electronic state, dissociation occurs on the initially prepared state, as well as by internal conversion and intersystem crossing to lower lying states and the ground state.

Conclusions

We have applied the G3 calculations to investigate the photodissociation of propylene sulfide. On the basis of the comparison between the G3 results and experimental measurements, three dissociation channels involving transition structures have been established. The sulfur-containing products of these three dissociations are C_2H_3S, HS, and H_2S. Also, two other channels leading to the dissociation of sulfur atom are observed experimentally and confirmed computationally. Furthermore, some additional dissociation processes, also leading to the neutral fragments C_3H_6 and $S(^1D)$ or $S(^3P)$, and having exceedingly high experimental reaction barriers, are observed. It is not likely that these reactions occur at the ground state of propylene sulfide. The measured high reaction barriers are in good agreement with the calculated excitation energies of propylene sulfide.

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