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Exclusive Production of Excited State Sulfur (^{1}D) from 193 nm Photolysis of Thietane

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Spin conservation is rarely expected in chemical reactions of large molecular systems and is only occasionally observed even in small molecules. This is particularly the case for the dissociation of large molecules in which potential energy surfaces are often strongly coupled. It is thus of considerable surprise to find that the loss of a sulfur atom from thietane, (*c*-C_3H_6S) a four-membered ring compound, generates exclusively the spin allowed, but excited state of the sulfur atom, (^{1}D). As shown in Table 1, the photodissociation of most sulfides produces a mixture of S(^{3}P) and S(^{1}D), presumably because the heavy sulfur atom increases the probability for intersystem crossing. In all these cases the starting compounds are singlet states and the products are also singlet states plus a sulfur atom that can be either in the ground ^{3}P or in the excited ^{1}D state. Thus the spin conserved path in all cases should produce the excited state. The most nearly spin-conserved reaction is the S atom loss from OCS. On the other hand, thiophene produces exclusively the ground state even though there is more than sufficient energy to generate the spin allowed excited state of sulfur. To our knowledge, there is no known reaction that produces exclusively S(^{1}D).

Table 1 The Branching Ratio of S(^{3}P):S(^{1}D)from Various Sulfides

Species	S(^{3}P)/S(^{1}D)	Wavelength
H_2S	0.87/0.13 [1]	193 nm
CS_2	0.75/0.25 [2]	193 nm
OCS	0.05/0.95 [3]	223 nm
CH_3S	0.15/0.85 [4]	193 nm
C_2H_4S (ethylene sulfide)	0.59/0.41 [5a]	193 nm
C_3H_6S (propylene sulfide)	0.28/0.72 [5b]	193 nm
C_4H_4S (thiophene)	1.0/0.0 [5c]	193 nm

The results in Table 1 give some indication of the difficulty in producing pure excited state sulfur atoms for use in subsequent chemical reactions. While the photoabsorption and photoionization of ground state sulfur atoms S(^{3}P) have been the subject of numerous theoretical and experimental investigations,[6] few studies have focused on the first excited state, (^{1}D), of the sulfur atom.[7]

Previous photolysis studies in which thietane was excited at 313 nm and 254 nm have been carried out by several groups in low pressure reaction cells using GC product analysis. The only direct dissociation products formed were C_2H_4 + CH_2S, and no evidence for S atom production was noted even though there is sufficient energy to produce C_3H_6 + S, the latter in both ground or excited states.[8] At these photolysis energies, the initial step appears to be the breaking of the C-S bond and the formation of a diradical followed by rearrangement to form ethylene and thioformaldehyde. However, as the excitation energy is increased to 214 nm, the production of C_3H_6 becomes important.[9,10] On the basis of an RRKM theory analysis of the ratio of collisionally stabilized cyclopropane to ring opened propene products as a function of the inert gas pressure, Dorer et al [9] concluded that the sulfur atom is formed predominantly in the ^{3}P ground state.

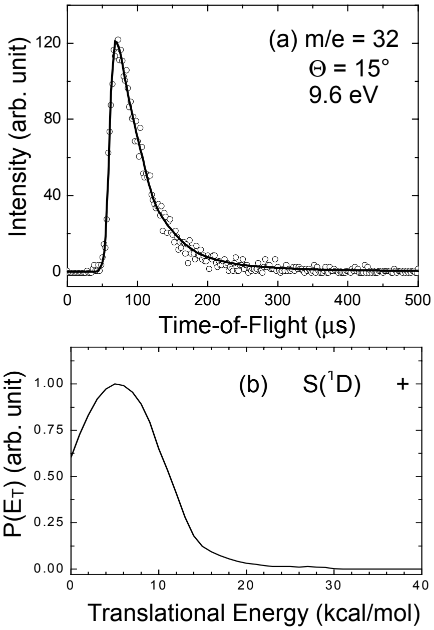

Figure 1. (a) TOF spectrum of the S atom (m/e = 32) at a scattering angle of 15°. The photon energy used to ionize the products was 9.6 eV. The open circles are experimental data, while the solid line is the calculated TOF distribution using the total translational energy distribution, P(E_T), for the S + C_3H_6 reaction as shown in Figure 1(b).

We report here the use of tunable (6 to 20 eV) synchrotron undulator radiation, to probe the sulfur and C_3H_6 products, as well as the molecular channels of the photodissociation of thietane at 193nm. These experiments permit not only the determination of the product translational energy in a collisionless environment, but also their internal energy. The experiments were performed at the Chemical Dynamics beamline 9.0.2 of the Advanced Light Source using a rotatable source molecular beam apparatus described in detail elsewhere.[11,12] A 7.5% thietane sample in 700 Torr of He,

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introduced as a pulsed and skimmed molecular beam, was photolyzed by a 193 nm ArF excimer laser. The small fraction of the dissociation products that scatters toward the detection region some 15.2 cm from the photolysis point, was photoionized using undulator radiation from the synchrotron. Time-of-Flight (TOF) spectra of neutral photofragments were measured at several scattering angles for the following ions: CH_2S^+, $C_3H_6^+$, $C_3H_5^+$, $C_3H_4^+$, H_2S^+, HS^+, S^+, and $C_2H_4^+$. In this communication, we describe only the results for the S + C_3H_6 reaction, which is a major channel for the dissociation at this photolysis wavelength.

One of the unique features of detecting products by tunable photoionization is the ability to distinguish products that have different ionization energies. Photolysis at 193 nm permits sulfur atoms to be formed in any of three electronic states, whose ionization energies are: 10.36 eV (^3P), 9.21 eV (^1D), and 7.61 eV (^1S). Photon energies between 7.61 and 9.21 eV will ionize only the ^1S state, while energies between 9.21 and 10.36 eV will ionize only the two excited states. Finally, above 10.36 eV, all three states can be ionized. We have successfully applied this method to selectively probe S(^3P) and S(^1D) from photodissociations of CS_2[2], ethylene sulfide[5a] and propylene sulfide.[5b]

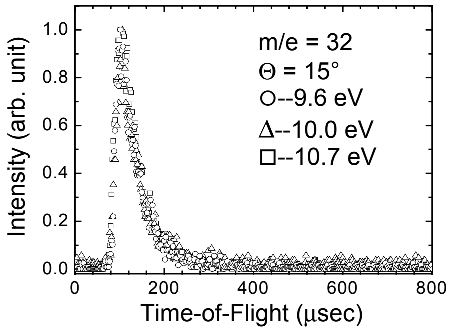

Figure 2. TOF spectra of S (m/e = 32) at the three indicated probe photon energies.

Figure 1(a) shows a TOF spectrum of the m/e = 32 (S^+), signal from the photoionization of sulfur atoms, at a scattering angle of 15°. The photon energy for this spectrum was 9.6 eV, which is below the IE of the ground state S(^3P). Hence, only excited state S(^1D) and/or S(^1S) species contribute to the data in Figure 1. However, as will be shown, the latter does not contribute. The translational energy distribution shown in Figure 1(b) was used to fit the data by convolution with the instrumental function. The maximum translational energy, peaks at approximately 5 kcal/mol, extends to about 30 kcal/mol, and has an average energy of 6.8 kcal/mol. The C_3H_6 fragment TOF distribution (not shown here) was measured as well, and its distribution was fitted with the same P(E_T) distribution shown in Figure 1b. Because the two fragments have the same momentum (but in opposite directions), the same P(E_T) distribution must fit the two sets of data.

Figure 2 shows the normalized TOF spectra of S^+ at a scattering angle of 15° at photon energies of 9.6, 10.0, and 10.7 eV. These three distributions are identical. If more than one electronic state had produced these signals, the TOF distributions should have been different. Because no signal is produced below 9.3 eV, where S(^1S) atoms would ionize, these results indicate that the sulfur atom is produced exclusively in the excited ^1D state. This is entirely different from the S atoms produced from photolysis of other organo-sulfur compounds, as well as the simplest sulfides such as H_2S^1 and CS_2,[2] which all produce mixtures of ground and excited state sulfur atoms that are easily distinguished by their different TOF distributions.

Because the C_3H_6 product is a singlet, spin conservation demands that the sulfur be produced in the singlet state. However, previously mentioned studies at lower photolysis energies indicate that excited thietane breaks up by the initial formation of the diradical, $^{\bullet}CH_2CH_2CH_2S^{\bullet}$, which at lower energies has sufficient time to fragment to ethylene and CH_2S. Under these circumstances it would seem that intersystem crossing to the triplet surface should be possible. Because we see no evidence of S(^3P) production, the production of S atoms at 193 nm must involve a concerted release of the S atom and a simultaneous formation of the three membered hydrocarbon ring. It thus remains rigorously on the singlet surface. If a diradical were initially produced, then the lower energy ethylene plus CH_2S reaction channel would dominate. In fact, just the opposite is observed with the S release being the dominant dissociation channel.

The ability to produce a pure excited state of the S atom, makes the 193 nm photodissociation of thietane a very important method for producing such atoms for spectroscopic or dynamical studies. A rough photoionization efficiency (PIE) spectrum of the S(^1D), obtained by scanning the undulator with its resolution of about 0.2 eV, is shown in Figure 3. The onset at about 9.2 eV is close to the IP of S(^1D). Three obvious peaks at 9.6, 10.7, and 11.9 eV, are due to autoionizing Rydberg states that are only partially resolved in our spectrum. They approximately coincidence with previously measured S(^3P)[6d,6f] states if one shifts the spectrum to lower energies by the energy difference of 1.15 eV between the S(^1D) and S(^3P) states. Such a shift is expected (although the intensities will vary greatly) since the Rydberg states converge to the same final ion states, $S^+(^2D^0)$ at 11.05 eV, and $S^+(^2P^0)$ at 12.25 eV. These limits are indicated in the Figure. Plans are presently underway to measure a high resolution photoionization efficiency spectrum of the S(^1D) state using a 6.65 m monochromators that will yield a resolution of 0.5 meV. Such a study will be complementary to both the one photon spectrum of S(^3P) of Gibson et al.[6d] and the two-photon experiment on S(^1D) reported by Pratt.[7]

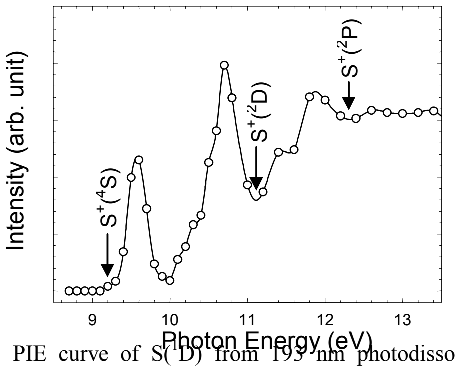

Figure 3. PIE curve of S(^1D) from 193 nm photodissociation of thietane at the scattering angle of 15°.

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