193 nm Photodissociation of Ethylene Sulfide Probe via Synchrotron Radiation

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INTRODUCTION

Ethylene sulfide, *c*-C_2H_4S, is a three-membered heterocycle with a sulfur atom. Photodissociation studies of ethylene sulfide at 193 nm have shown the importance of a process yielding electronically excited sulfur atoms (^1D) and the ground electronic state (^1A_g) of ethylene using photofragmental translational spectroscopy (PTS)[1] and Doppler broadened laser induced fluorescence spectra.[2] Previous studies showed that the sulfur atoms were produced mostly at excited state ^1D, although the ground state sulfur is allowed energetically. Chin and coworkers detected S, C_2H_4, CS_2 and H_2S as major products in the thermal decomposition study of *c*-C_2H_4S. Some minor products, C_2H_2 and thiophene, were also observed.[3] Ethylene, one of photoproducts from *c*-C_2H_4S photodissociation at 193 nm, is a molecule of broad fundamental and practical importance. It is a central species in hydrocarbon combustion and in interstellar chemistry, a key hormone in biological systems, and a synthetic precursor to vast array of commercial products.

The following channels are energetically accessible via photodissociation at 193 nm:

c-$C_2H_4S + h\nu_{193nm} \rightarrow C_2H_4\ (^1A_g) + S\ (^1D)$	ΔH_{avai} = 65 kcal/mol	(**1**)
c-$C_2H_4S + h\nu_{193nm} \rightarrow C_2H_4\ (^1A_g) + S\ (^3P)$	ΔH_{avai} = 92 kcal/mol	(**2**)
c-$C_2H_4S + h\nu_{193nm} \rightarrow C_2H_4\ (^3B_{1u}) + S\ (^3P)$	ΔH_{avai} = 28 kcal/mol	(**3**)
c-$C_2H_4S + h\nu_{193nm} \rightarrow H_2CCH + HS$	ΔH_{avai} = 66 kcal/mol	(**4**)
c-$C_2H_4S + h\nu_{193nm} \rightarrow HCCH + H_2S$	ΔH_{avai} = 121 kcal/mol	(**5**)
c-$C_2H_4S + h\nu_{193nm} \rightarrow C_2H_3S + H$	ΔH_{avai} = ~43 kcal/mol	(**6**)

The PTS experiments of Felder and coworkers identified channels **1**, **4** and **6** as primary processes in the 193 nm photodissociation. We have revisited this system using PTS, but with product detection employing soft photoionization using tunable vacuum ultraviolet (VUV) light rather than electron impact ionization, allowing us to identify additional channels not apparent in the previous work. The results demonstrate the presence of a channel giving S(^3P) in conjunction with *triplet* ethylene C_2H_4 ($^3B_{1u}$), and allow for the first experimental measure of the energy of the latter species near the equilibrium geometry, in which the two methyl groups occupy perpendicular planes. Another new channel representing the production of H_2S with acetylene was observed at 193 nm photodissociation of *c*-C_2H_4S in this study (process **5**).

EXPERIMANTAL

The experiment was performed at Beamline 9.0.2.1 of the Advanced Light Source using a rotatable source molecular beam apparatus described in detail elsewhere.[4] Helium was bubbled through an ethylene sulfide sample held at 0°C. The total pressure was about 800 Torr, thus yielding an about 10% mixture of *c*-C_2H_4S balance in He. The pulse molecular beam was skimmed twice and intersected at 90° with the 193 nm photolysis laser. Photofragments formed by 193 nm photodissociation entered the detector chamber region, and were photoionized using tunable synchrotron radiation. The tunability of the light source allows for selective ionization of

products and very low background counts, and also allows for measuring the photoionization efficiency (PIE) spectra of photoproducts. The photoionized products were mass selected by using a quadrupole mass filter, and the ions were counted with a Daly ion counter. Ethylene sulfide (>98%) was obtained from Aldrich and used without further purification.

RESULTS AND DISCUSSION

TOF spectra of photofragments from photodissociation of *c*-C_2H_4S at 193 nm have been measured at several angles from 10° to 40°. Signals at m/e = 59, 58, 34, 33, 32, 28, 27 and 26 were detected. These correspond to C_2H_3S, C_2H_2S, H_2S, HS, S, C_2H_4, C_2H_3 and HCCH respectively. In all the TOF spectra presented here, the open circles represent the experimental data, the dash lines, the dot lines and the dash-dot lines are single channel contributions to the forward convolution fit, and the solid lines are the overall fit to the data. A forward convolution method was used to get center-of-mass translational energy distributions, P(E).[5]

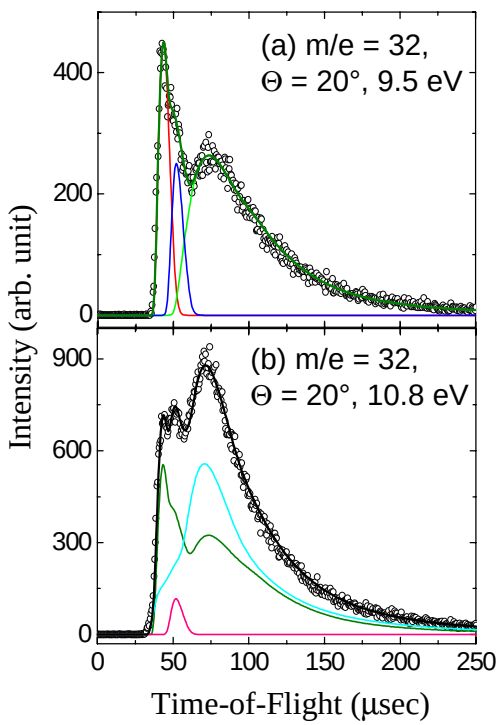

Fig. 1 TOF spectra of m/e = 32 at the indicated scattering angles and photon energies. The open circles are experimental data, the colored lines are single channel contribution to the forward convolution fit.

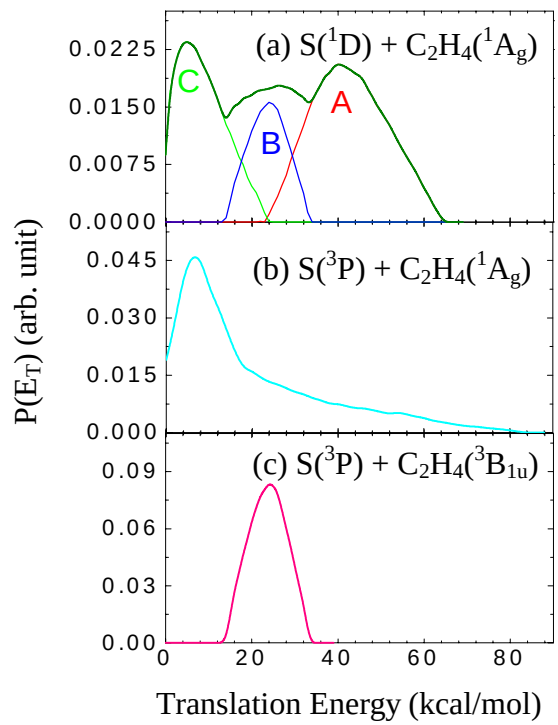

Fig. 2 Translational energy distributions, $P(E_T)$s, for the indicated dissociation channels from ethylene sulfide at 193 nm photoexcitation.

In this report, we mainly describe the C_2H_4 + S channel. Fig.1 shows TOF spectra of the S atom at a laboratory angle of 20° with photon energy at 9.5 and 10.8 eV respectively. Two peaks are readily apparent in the TOF spectra of Fig.1(a). Three translational energy distributions, $P(E_T)$s, shown in Fig. 2(a) were used to fit these data (Fig. 1(a)). They correspond to a channel producing excited state sulfur (^1D) and ground state ethylene (^1A_g), because photoionization energies used here are below the ionization potential of ground state sulfur (10.36 eV), and a MgF_2 filter was used to eliminate high-order scattering radiation. Three peaks are clearly observed in the TOF spectra at the scattering angle of 20° and the probe energy of 10.8 eV. Two additional translational energy distributions shown in Fig. 2(b) and 2(c) were used to fit the 10.8 eV data (Fig. 1(b)). The maximum translational energy of the distribution shown in Fig. 2(b) exceeds the

available energy for the $S(^1D) + C_2H_4(^1A_g)$ and the $S(^3P) + C_2H_4(^3B_{1u})$ channels. However, this limit is very close to the available energy for the spin-forbidden $S(^3P) + C_2H_4(^1A_g)$ channel. On the other hand, comparing the TOF spectra of mass 32 obtained below and above the IP of the ground state atom, the *second* peak (~52 μs) of the S atoms actually corresponds partly to the production of ground state sulfur atoms. These ground state (^3P) sulfur atoms are formed at energies near that anticipated for the production of the excited *triplet* state ($^3B_{1u}$) of ethylene (process **3**).

Three components were observed for the $S(^1D) + C_2H_4(^1A_g)$ channel. In each case, it originated from different potential energy surface. The detailed dissociation mechanisms have been discussed in our full paper.[6] Furthermore, the heat of formation can be derived to be 72±3 kcal/mol. It is in good agreement with theoretical predication.[7] The energetics for process **3** can be used to provide the first experimental insight into the properties of triplet ethylene near its equilibrium geometry. Ethylene sulfide can be thought as a suitable precursor to produce the *triplet* ethylene near its equilibrium geometry by "photochemistry" method.

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