Photoionization Study of the Sulfur Monoxide Radical Produced by Pyrolysis of Ethylene Sulfoxide

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Sulfur monoxide (SO) radical has been produced in the gas phase by pyrolysis of ethylene sulfoxide (C_2H_4=SO) at 510 °C. The vacuum ultraviolet photoionization efficiency curve between 915 and 1220 Å has been obtained for the first time. Several thermodynamic data about C_2H_4=SO have also been obtained from direct photoionization. The values of the bond energies of $D_0(C_2H_4=SO)$ and $D_0(C_2H_4=SO^+)$ are 4640±30 and 5160±30 cm^{-1} respectively. Ionization potentials (IP) of the $SO(X^3\Sigma^-)$ radical and C_2H_4=SO, and the appearance potential (AP) of SO^+ fragment ion from C_2H_4=SO are 10.28±0.01, 9.49±0.02, and 10.13±0.01 eV. In the system of C_2H_4=SO, the AP is lower than the IP and this phenomenon has only been found in this system.

The sulfur monoxide (SO) radical has been studied as an important intermediate in reactions involving oxygen atoms and molecules containing sulfur. It has also been found in interstellar space by radio telescopes.[1] In addition, the SO radical is a very interesting radical from the point of electronic structure because of the isoelectronic species of diatomic sulfur (S_2) and molecular oxygen (O_2). In contrast to the large amount of spectroscopic data obtained for O_2, SO, and S_2 in several low-lying electronic states,[2] our current knowledge concerning the SO radical in the vacuum ultraviolet region is very limited. Though autoionization in radicals has been rarely observed in this region so far, it is expected that the autoionization peaks might appear in the SO radical because of the similarity to O_2.

Since the far ultraviolet absorption spectrum of O_2 was observed by Price and Collins in 1935,[3] absorption spectra, the photoionization efficiency curves and photoelectron spectra of O_2 have been intensively studied. A high resolution (FWHM 0.07 Å) photoionization study of O_2 has been carried out by Dehmer and Chupka.[4] For the S_2 radical, the relative photoionization efficiency curve has been observed by Berkowitz *et al.*[5] in the gas phase by thermal vaporization of HgS. They found that an autoionization structure emerged, but the peak shapes were not clear enough to allow spectroscopic studies.

Compared to the study of these species, at the present stage, very few works have been carried out on the SO radical in the vacuum ultraviolet region. Donovan *et al.*[6] have obtained the absorption spectrum of the SO radical and studied the Rydberg series (The $D^3\Pi$ and $E^3\Pi$ states) converging to the $X^2\Pi$ state of SO^+. The photoelectron spectrum of the SO radical produced by discharge of CS_2 and O_2 was also observed by Jonathan *et al.* in 1974.[7]

The present work reports the first mass spectrometric analysis of the relative photoionization efficiency curve of the SO radical produced by pyrolysis of ethylene sulfoxide (C_2H_4=SO). The synthesis of C_2H_4=SO[8] and production of the SO radical by its pyrolysis has been reported.[9] Also the $a^1\Delta$ state of the SO radical produced by pyrolysis of C_2H_4=SO was analyzed from the microwave spectrum by Saito in 1970.[10]

The pyrolysis and photoionization in the present system are described below:

$$C_2H_4{=}SO \xrightarrow{\Delta} C_2H_4(X^1A_{1g}) + SO(a^1\Delta)$$

$$SO(a^1\Delta) + M \longrightarrow SO(X^3\textstyle\sum^-) + M$$

$$SO(X^3\textstyle\sum^-) + h\nu \longrightarrow SO^+(X^2\Pi) + e \quad \text{(IP)} \quad (1)$$

$$C_2H_4{=}SO + h\nu \longrightarrow C_2H_4{=}SO^+ + e \quad \text{(IP)} \quad (2)$$

$$C_2H_4{=}SO + h\nu \longrightarrow C_2H_4(X^1A_{1g}) + SO^+(X^2\Pi) + e \quad \text{(AP)} \quad (3)$$

From the threshold energies for above processes, the bond energies of $D_0(C_2H_4=SO)$ and $D_0(C_2H_4=SO^+)$ were determined. The IP of the SO radical in process (1) obtained from mass spectrometric photoionization is in excellent agreement with the results of photoelectron studies[7] and photofragmentation studies of sulfur dioxide.[11] The IP of C_2H_4=SO in process (2) and the AP of SO^+ from C_2H_4=SO in process (3) were obtained. Thus, these threshold energies indicate that the AP of SO^+ from C_2H_4=SO should be lower than the IP of the SO radical. This unique phenomenon was first observed in the system of C_2H_4=SO.

On the other hand, in process (1) the relative photoionization efficiency curve of the SO radical was obtained by scanning the excitation wavelength. Rather strong autoionization peaks were observed on this curve. But these peaks could not be assigned due to the lack of strong vibrational progressions such as are found for O_2^+.

Experimental

The experimental arrangement is shown in Fig. 1. The apparatus consisted of a hydrogen discharge light source operated at 0.4 A dc with about 700 V across the tube, a 50 cm Seya-Namioka type vacuum monochromator with a resolution of 2.3 Å (FWHM) which dispersed and refocused the monochromatic light into the ionization chamber, a set of

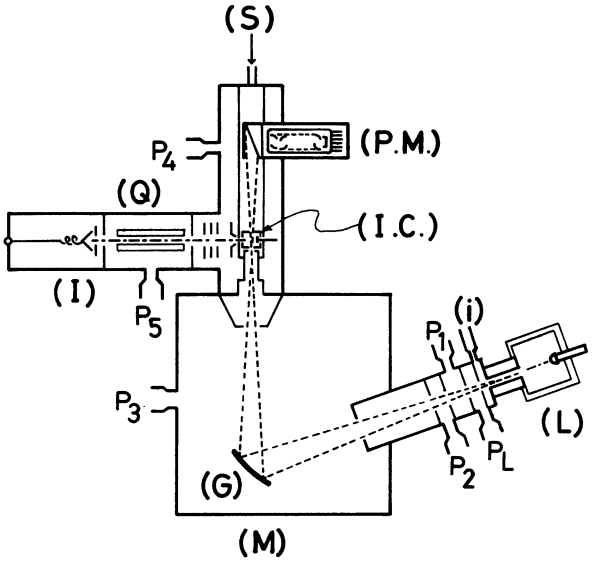

Fig. 1. Schematic diagram of the experimental apparatus. L; light source, i; gas inlet, G; grating, M; monochromator, I.C.; ionization chamber, Q; quadrupole mass filter, P.M.; photon monitor, I; ion multiplier, S; sample gas inlet, P_L, P_1—P_5; differential pumping system.

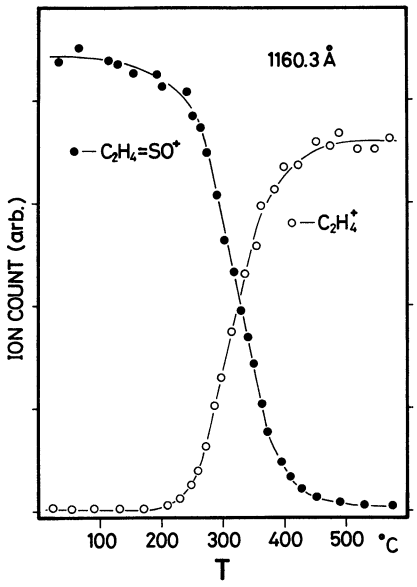

Fig. 2. Temperature variation of the ion counts of C_2H_4=SO and C_2H_4.
● denotes the ion counts of C_2H_4=SO, ○ denotes the ion counts of C_2H_4 produced by pyrolysis from C_2H_4=SO.

ion extraction and focusing lenses, and a quadrupole mass spectrometer (NEVA NAG-520) for ion detection.

Ion counts were measured by an electronmultiplier (Murata EMS-6081B), and photon counts were measured by the scintillation counter of a photomultiplier (HTV R-268) coated with sodium salicylate. After each signal had been amplified and identified by a fast pre-amplifier (ORTEC 9301) and an amplifier-discriminator (ORTEC 9302), it was integrated by the counter (ORTEC 9315). The accumulation of signals and control of the experimental apparatus were regulated by a microcomputer (NEC PC-9801). The relative photoionization efficiency was derived by the normalization method, dividing the ion counts by the photon counts.

In order to obtain radicals by pyrolysis, a tape-heater wrapped around a 10 mm diameter quartz tube was used at about 20 cm upstream from the ionization chamber. The temperature was varied in the region between room temperature and 580 °C. The total pressure was measured by a capacitance manometer (MKS-Baratoron). The sample pressure was typically about 0.6 m Torr in the ionization chamber.

In order to investigate the temperature dependence of pyrolysis of C_2H_4=SO, ion counts for several species were measured in the range, room temperature to 580 °C. The sample was irradiated by light at 1160.3 Å, whose energy is higher than either of the IPs of the parent molecule or ethylene produced by pyrolysis, but it was lower than the AP of the fragment ethylene ion from the parent molecules. The SO^+ radical ion could not be used for monitoring the pyrolysis because its IP is higher than the AP of the SO^+ fragment ion from the parent molecules. The temperature dependence of ion counts produced by irradiation at 1160.3 Å is shown in Fig. 2. At 300 °C, the ion counts of C_2H_4=SO^+ were reduced to one-half of those at room temperature. With a further rise in the temperature, they were rarely observed. On the other hand, ion counts of ethylene increased up to 500 °C, and above 500 °C they remained stationary. Thus, the temperature of the pyrolysis was maintained at 510 °C throughout this experiment.

Results and Discussion

The relative photoionization efficiency curve of SO^+ from the SO radical for the wavelength region 915—1220 Å, is shown in Fig. 3, where the hydrogen discharge lamp was used as a source at a wavelength resolution (FWHM) of 2.3 Å. In the present experiment, the accuracy of the wavelength was determined to be within about 0.5 Å from H Lyman-α and H Lyman-β in the light source. For excited $O_2(a^1\Delta_g)$, Jonathan *et al.*[13] examined the photoelectron spectrum of the ($^2\Delta_g \leftarrow {}^1\Delta_g$ and $^2\Phi_u \leftarrow {}^1\Delta_g$) ionization transition using phase-sensitive detection. These transitions from the $a^1\Delta$ state could not be being observed in the present photoionization efficiency curve, the reason that the excited $SO(a^1\Delta)$ may have almost completely been deactivated. The photoionization efficiency rises sharply at 1206.3±0.5 Å (=10.28±0.01 eV), and above this threshold there is a gradual increase in ionization cross section. Somewhat strong peaks, assigned to autoionization structures, have been detected between 1010 and 920 Å from which the autoionization structures have been determined. But along the SO^+ photoionization curve there are no very strong vibrational progressions like O_2^+ between 1005 Å (the threshold of IP) and 850 Å.[4] Therefore, spectroscopic studies could not be done as successfully of the autoionization peaks in SO^+ as those of the broad ones S_2^+.[5]

Furthermore, to obtain various thermodynamic data

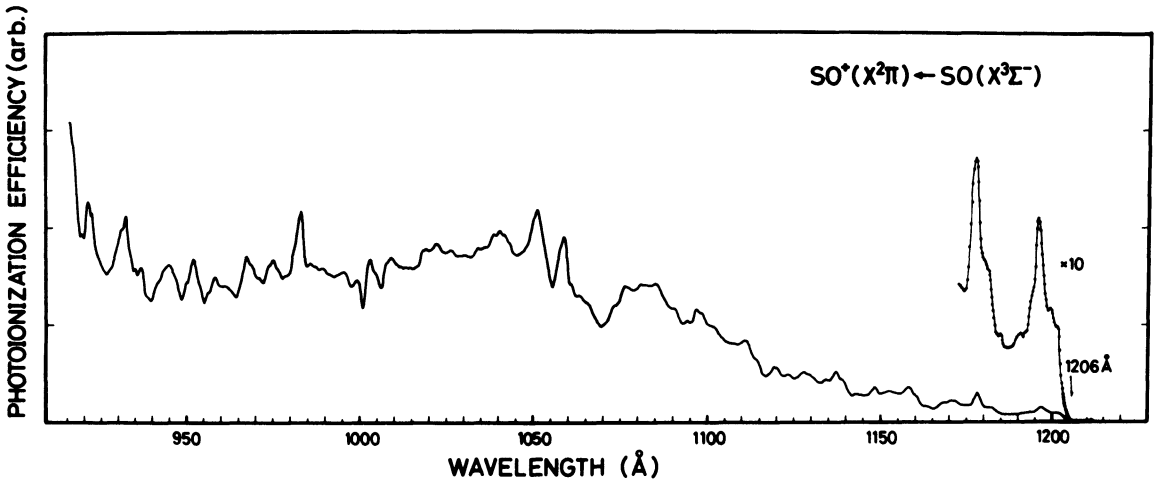

Fig. 3. Photoionization efficiency curve for SO^+ from the SO radical taken between 1220 and 915 Å at a wavelength resolution (FWHM) of 2.3 Å at 510 °C.

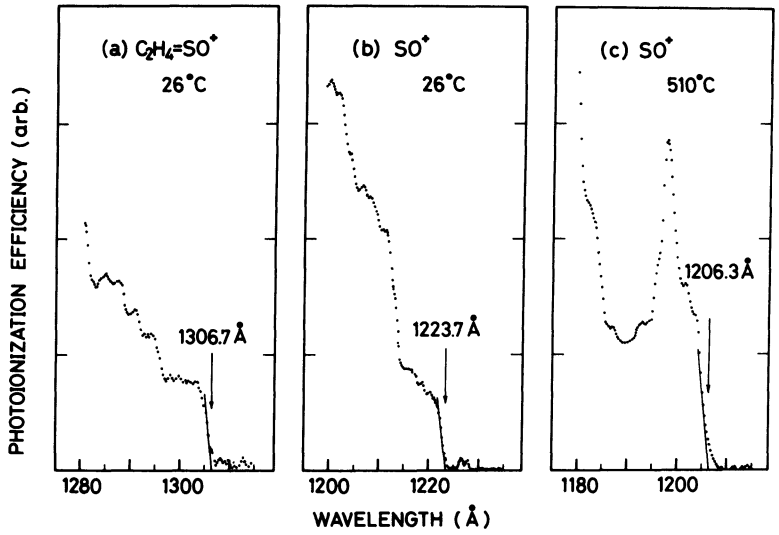

Fig. 4. The relative photoionization cross sections in the neighborhood of the threshold energies.
(a) The ion counts of C_2H_4=SO^+ at the room temperature, (b) The ion counts of SO^+ fragment ion from C_2H_4=SO at room temperature, (c) The ion counts of the SO radical at 510 °C.

Table 1. Summary of photoionization data for the system of ethylene sulfoxide

Ion	Threshold eV[a)]	Process	Temperature °C
SO^+	10.28±0.01	$SO(X^3\Sigma^-)+h\nu \rightarrow SO^+(X^2\Pi)+e$	510
SO^+	10.13±0.01	$C_2H_4{=}SO+h\nu \rightarrow C_2H_4(X^1A_{1g})+SO^+(X^2\Pi)+e$	26
$C_2H_4{=}SO^+$	9.49±0.02	$C_2H_4{=}SO+h\nu \rightarrow C_2H_4{=}SO^+{+}e$	26

a) Estimated uncertainties.

relating to C_2H_4=SO, the threshold energies were measured. Figure 4 shows the relative photoionization cross section of (a) C_2H_4=SO at room temperature, (b) SO^+ fragment ion from C_2H_4=SO at room temperature, (c) SO^+ ionized directly from the SO radical at 510 °C. $C_2H_4^+$ fragment ions at room temperature were not observed. These threshold energies are summarized in Table 1.

The IP of SO in the present work is in excellent agreement with the value of 10.29±0.02 eV obtained from photoelectron spectra by Jonathan *et al.*[7] and that of 10.21 eV obtained from the photofragmentation method by Dibeler and Liston.[11] Though, it was assumed that SO^+ ions might appear from $SO(a^1\Delta)$

produced by pyrolysis of C_2H_4=SO in the region longer than 1206.3 Å (=10.28 eV) by means of an allowed $SO^+(X^2\Pi)\leftarrow SO(a^1\Delta)$ ionization transition, in fact, SO^+ ions were not observed in this region as can be seen in Fig. 4(c). This results from the fact that the excited $SO(a^1\Delta)$ was almost completely deactivated to the ground state before it reached to the ionization chamber.

The AP of SO^+ fragment ion from C_2H_4=SO and the IP of C_2H_4=SO were determined. It is worth noting that the IP of the SO radical is about 0.15 eV higher than the AP of SO^+ from C_2H_4=SO. In the pyrolysis of C_2H_4=SO described in process (1), C_2H_4=SO must correlate to $SO(a^1\Delta)$ from spin conservation, thus decomposition to $C_2H_4+SO(a^1\Delta)$ is an endothermic reaction. The values of ΔH_f in the following reactions are derived by using the transition energy of $SO(a^1\Delta\leftarrow X^3\Sigma^-)$ from chemiluminescence studies of Barnes *et al.*[12]

$$C_2H_4{=}SO \begin{cases} \rightarrow C_2H_4+SO(a^1\Delta) \\ \qquad \Delta H_f = 13.3\pm0.1 \text{ kcal/mol}^\dagger \\ \rightarrow C_2H_4+SO(X^3\Sigma^-) \\ \qquad \Delta H_f = -3.5\pm0.1 \text{ kcal/mol} \end{cases}$$

The transitions to $SO^+(X^2\Pi)$ from both $SO(a^1\Delta)$ and $SO(X^3\Sigma^-)$ are allowed. It seems that the exothermicity of the reaction in pyrolysis contributes to the ionization of SO from parent molecule. Therefore, it stands to reason that the AP of SO^+ from C_2H_4=SO is lower than the IP of the SO radical. From these results and the IP of C_2H_4=SO, the following bond energies of $D_0(C_2H_4{=}SO)$ and $D_0(C_2H_4{=}SO^+)$ were obtained;

$$D_0(C_2H_4{=}SO) = 4640\pm30 \text{ cm}^{-1}$$

$$D_0(C_2H_4{=}SO^+) = 5160\pm30 \text{ cm}^{-1}$$

Furthermore, from a consideration of the temperature dependence of C_2H_4=SO, the activation energy in the system of C_2H_4=SO has been estimated.

This reaction is regarded as a first-order irreversible unimolecular decomposition reaction of the plug type, and, so, the following equation in logarithmic form is obtained;

$$\ln(C_0/C) = (k/v)l, \tag{4}$$

where C_0 and C are sample concentrations of the entrance and exit regions of the pyrolysis tube, respectively, and k is the rate constant, v is the flow rate, and l is the length of the pyrolysis tube. From the expressions for the rate constant, k expressed in terms of the frequency factor A, and the activation energy E, we obtain the following equation;

$$\ln(\ln(C_0/C)) = -E/RT + \ln Al/v. \tag{5}$$

†1 cal_{th}=4.184 J.

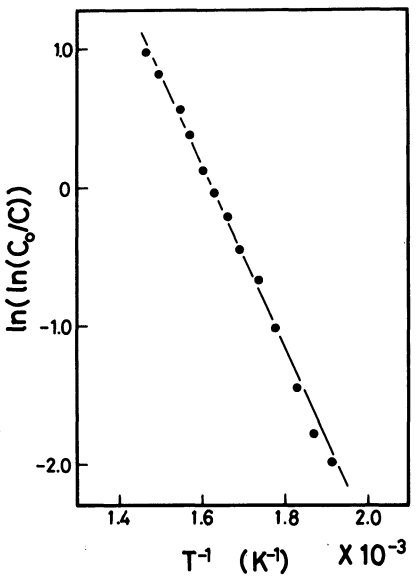

Fig. 5. Arrhenius plot of $\ln(\ln(C_0/C))$ versus T^{-1} obtained from the ion counts of C_2H_4=SO^+ in Fig. 2.

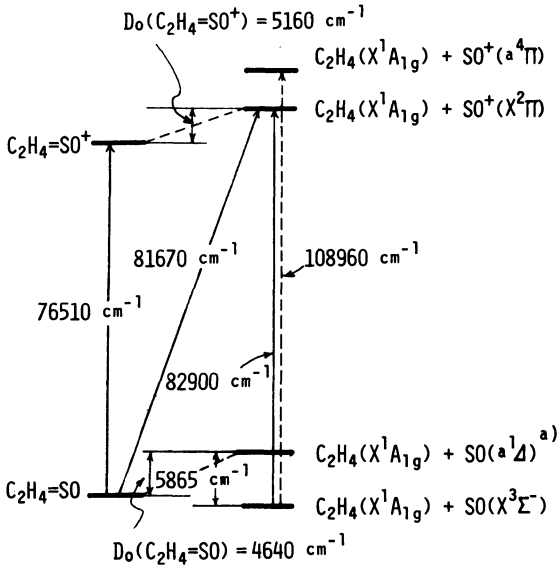

Fig. 6. The energy diagram of C_2H_4=SO and SO.
a) The energy difference between $a^1\Delta$ and $X^3\Sigma^-$ from Ref. 12.

Then the plot of $\ln(\ln(C_0/C))$ versus T^{-1} will yield the activation energy E from slope of the curve.

The plot of $\ln(\ln(C_0/C))$ versus T^{-1} which was obtained from the ion counts of C_2H_4=SO^+ in Fig. 2 is shown in Fig. 5. The activation energy was estimated to be 13.6 kcal/mol and was in excellent agreement with the value of $D_0(C_2H_4{=}SO)$ obtained from the above discussion.

The energy diagram of C_2H_4=SO and SO is summarized in Fig. 6.

Although the electronic state of C_2H_4=SO has not yet been studied, it is presumed that the electron in the highest occupied molecular orbital is an antibonding electron because the bond energy of the neutral state is

less than that of the ionic state.

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