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Detection of Sulfur Monoxide in the Pyrolysis of Ethylene Episulfoxide by Microwave Spectroscopy

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Microwave spectroscopy has been applied to the study of the pyrolysis of ethylene episulfoxide in the vapor phase. The rotational lines of SO in the electronic ground state, $^3\Sigma^-$, were observed with a good signal-to-noise ratio. The pyrolyzed sample of ethylene episulfoxide was analyzed semi-quantitatively by the use of the microwave spectra. It turned out that ethylene episulfoxide really decomposed into ethylene and sulfur monoxide. The mechanism of the thermal decomposition is discussed in detail.

Alkyl sulfoxides are interesting and important molecules, but only a few examples have been reported, for they are unstable.[1–7] Hartzell and Paige[3] and Negishi, Sato, Saito, and Fukuyama[7] synthesized ethylene episulfoxide by the direct oxidation of ethylene sulfide. Hartzell and Paige[3] observed, by means of mass spectrometry and differential thermal analysis, that it decomposed into ethylene and sulfur monoxide near 100°C. Dodson and Sauers[4] carried out the controlled thermal decomposition of ethylene episulfoxide in the presence of dienes and thus obtained cyclic sulfoxides. They suggested that the sulfur monoxide generated in the pyrolysis might be in the $^1\Sigma^+$ state or even in the $^1\Delta$ state. By observing and analyzing the rotational spectra of ethylene episulfoxide, Saito[8] determined the molecular structure and discussed the S–O and C–S bonds.

The microwave spectroscopy of free radicals has made considerable progress in recent years following a long pause after Dousmanis, Sanders, and Townes reported the OH radical.[9] Powell and Lide,[10] and Winnewisser, Sastry, Cook and Gordy[11] observed SO. Amano, Hirota and Morino[12] determined the r_e structure of SO. ClO[13] and SN[14] have also recently been studied by means of microwave spectroscopy.

The present work is concerned with the study of the pyrolysis of ethylene episulfoxide. The main purpose is to confirm the existence of SO in the pyrolyzed sample by means of microwave spectroscopy and, moreover, to ascertain the state in which the sulfur monoxide is generated in order to understand the mechanism of the thermal decomposition.

Experimental

The reaction vessel and the Stark absorption cell used are shown in Fig. 1. The reaction vessel was made of a quarz tube 15 mm in diameter and 300 mm long; the temperature of the vessel was controlled by varying the voltage applied to the heater. The temperature of the vessel was measured at the outer surface of the tube by a chromel-alumel thermometer. The vessel was connected by a Teflon coupler 8 mm in inner diameter with the Stark absorption cell of the microwave spectrograph. The absorption cell was made of an X-band waveguide 800 mm long; this waveguide was split in two in the centers of the narrow sides. The two pieces of the split waveguide were separated and fixed by Teflon spacers of the **H** form so as to serve as Stark electrodes. The inner dimensions of the electrodes were made equal to those of the X-band waveguide.

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1) S. B. Soloway, U. S. Pat. 2694073, *Chem. Abstr.*, **49**, 3465 (1955).

2) D. C. Dittmer and G. C. Levy, *J. Org. Chem.*, **30**, 636 (1965).

3) G. E. Hartzell and J. N. Paige, *J. Am. Chem. Soc.*, **88**, 2616 (1966).

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5) G. E. Hartzell and J. N. Paige, *J. Org. Chem.*, **32**, 459 (1967).

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7) A. Negishi, K. Sato, S. Saito and M. Fukuyama, Preprints for the 21st Annual Meeting of the Chemical Society of Japan, Suita (April, 1968).

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10) F. X. Powell and D. R. Lide, Jr., *J. Chem. Phys.*, **41**, 1413 (1964).

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12) T. Amano, E. Hirota and Y. Morino, *J. Phys. Soc. Japan*, **22**, 399 (1967).

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14) T. Amano, private communication.

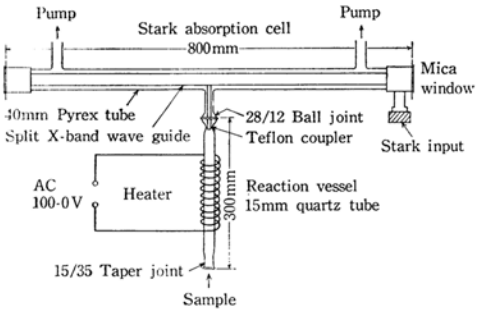

Fig. 1. Schematic diagram of reaction vessel and Stark absorption cell.

To prevent the decomposition and reaction of unstable molecules and radicals on the surface of the electrodes, the inner sides of the electrodes were coated with *"corning K"* coat.[10] The whole electrodes were then fixed in a Pyrex tube 40 mm in diameter by means of Teflon holders. The microweave spectrograph used was a conventional one with 110 kHz sinusoidal Stark modulation.[8] After passing through the absorption cell, the sample gas was led to a trap cooled to the temperature of liquid nitrogen, and then pumped by a rotary pump at the rate of 150 *l*/min.

The sample of ethylene episulfoxide, prepared by the oxidation of ethylene episulfide using perbenzoic acid, was kindly provided by Fukuyama, Sato and Makino.

Pyrolysis

The pyrolysis was done in the range from room temperature to 780°C and at pressures of from 0.01 to 0.1 mmHg. When the temperature of the reaction tube was raised gradually, at about 185°C the rotational line of sulfur monoxide in the electronic ground state, $^3\Sigma^-$, $J,K=1,0\leftarrow0,1$ at 30001.58 MHz,[10] was observed by the use of a strip-chart recorder, as is shown in Fig. 2. With a further rise in the temperature, the absorption line of the SO became stronger, until above 250°C it was observable on a CRO. Above 560°C, the intensity of the line remained stationary. The variation in the intensity with the temperature is presented in Fig. 3. Under similar conditions of pyrolysis, the intensity of the transition of ethylene episulfoxide, $3_{03}\leftarrow2_{02}$, at 31540.36 MHz[8] was followed. The temperature variation in the intensity is also shown in Fig. 3. It is clear that, above 560°C, ethylene episulfoxide decomposed by about 100%. The maximum signal-to-noise ratio of the absorption line of SO was about 5000, at 580°C and at 0.05 mmHg; this value was about twice as large as that of the SO generated in the reaction of atomic oxygen and OCS.[10,11]

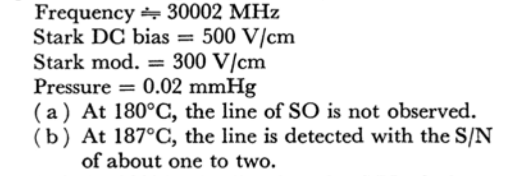

Fig. 2. Recorder tracings of the $J,K=1,0\leftarrow0,1$ transition of the SO molecule in the $^3\Sigma^-$ state, generated in the pyrolysis of ethylene episulfoxide.
Frequency ≒ 30002 MHz
Stark DC bias = 500 V/cm
Stark mod. = 300 V/cm
Pressure = 0.02 mmHg
(a) At 180°C, the line of SO is not observed.
(b) At 187°C, the line is detected with the S/N of about one to two.
(c) At 200°C, the line has the S/N of about seven.

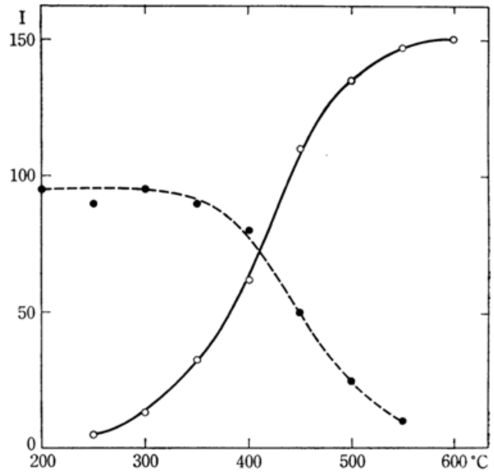

Fig. 3. Temperature variation of the absorption intensities of the lines for SO ($^3\Sigma^-$) and ethylene episulfoxide.
○ denotes the intensity of the $J,K=1,0\leftarrow0,1$ transition of SO at 30002 MHz.
● denotes the intensity of the $3_{03}\leftarrow2_{02}$ transition of ethylene episulfoxide at 31540 MHz.

Experimental Results

The sample pyrolyzed at 580°C and 0.02 mmHg was analyzed semi-quantitatively by the use of the microwave spectra. The absorption lines of $(CH_2)_2SO$, SO, SO_2, and H_2CO were measured on a CRO, and those of $(CH_2)_2S$ and $(CH_2)_2O$, on a strip-chart recorder. The concentrations of the stable molecules, such as $(CH_2)_2SO$, SO_2, H_2CO, $(CH_2)_2S$, and $(CH_2)_2O$, were determined by comparison with the corresponding standard samples.[15] The concentrations of the unstable

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[15] Y. Morino and E. Hirota, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **85**, 535 (1964).

TABLE 1. THE COMPOSITION OF THE PYROLYZED SAMPLE OF ETHYLENE EPISULFOXIDE

Molecule	Percentage	Method	Ref. to Mw spectra
$(CH_2)_2SO$	2	CRO	a)
SO	~ 3	CRO	b)
SO_2	20	CRO	c)
S_2O	~ 24	CRO	d)
H_2CO	0.8	CRO	e)
$(CH_2)_2S$	≤ 0.3	Reorder	f)
$(CH_2)_2O$	≤ 0.04	Reorder	f)

a) Ref. 8. b) Ref. 10.

c) Y. Morino, Y. Kikuchi, S. Saito and E. Hirota, *J. Mol. Spectry.*, **13**, 95 (1964). d) Ref. 16.

e) T. Oka, K. Takagi and Y. Morino, *J. Mol. Spectry.* **14**, 27 (1964).

f) G. L. Cunningham, Jr., A. *W.* Boyd, R. J. Myers and W. D. Gwinn, *J. Chem. Phys.*, **19**, 676 (1951).

molecules, SO[10] and S_2O,[16] were estimated by calculating the absorption intensity using the reported values of the microwave spectra. The results are listed in Table 1.

The final products of the pyrolysis were collected with a trap cooled at the temperature of liquid nitrogen; after vaporization, they were analyzed by the use of their infrared and microwave spectra. The main components of the products were ethylene and SO_2. The mole ratio between ethylene and SO_2 turned out to be about two.

Mechanism of Thermal Decomposition

It is interesting to consider the mechanism of the thermal decomposition of ethylene episulfoxide. The concentrations of ethylene sulfide and ethylene oxide were found to be less than 0.3% and 0.04% respectively, as is shown in Table 1. Thus, the abscission reaction of the S–O bond, which gives theatomicoxygen:

$$(CH_2)_2SO \longrightarrow (CH_2)_2S + O \tag{1}$$

is probably not the main one in the thermal decomposition.

Prior to discussing the other mechanisms in detail, it is necessary to know the energy levels of ethylene and SO, and the heat of the decomposition. According to Evans,[17] Mulliken,[18] and Kuppermann and Raff,[19] the lowest triplet state of planar ethylene, $^3B_{3u}$, is about 4.6 eV ($\fallingdotseq$37100 cm^{-1}) above the ground state, ^1A_g. Rabinovitch, Douglas, and Looney[20] obtained the energy value of the lowest singlet state of perpendicular ethylene as the activation energy of the *cis-trans* isomerization of 1,2-di-deutero-ethylene. The $^1B_1$ state is located 2.66 eV ($\fallingdotseq$21500 cm^{-1}) above the ground state of the planar ethylene. There has been no observation of the lowest triplet state of the perpendicular ethylene, but the calculations for the electronic states of ethylene by various MO methods[21] suggest that the lowest triplet state, $^3A_2$, is below the singlet state, $^1B_1$, by from 0.1 to 0.3 eV. Hence, it is reasonable to assume that the $^3A_2$ state is located somewhere between 2.36 and 2.56 eV ($\fallingdotseq$19100 and 20700 cm^{-1}) above the ^1A_g state.

Unfortunately, there is no reliable data on the electronic states of SO. On the basis of the discussions made by Carrington *et al.*,[22] and on the basis of the energy levels of the oxygen molecule,[23–25] it is plausible to estimate that the $^1\Delta$ state of SO is located near, or less than 8000 cm^{-1} above, the ground state, $^3\Sigma^-$.

On the other hand, the heat of the decomposition of ethylene episulfoxide to ethylene and SO in the vapor phase can be calculated by the use of the heat of the formation of dimethyl sulfoxide on the assumption that the heat of the formation of ethylene episulfoxide from dimethyl sulfoxide by dehydrogenation is equal to that of ethylene sulfide from dimethyl sulfide.[26] The decomposition, $(CH_2)_2SO \rightarrow CH_2 = CH_2 + SO$, was found to be an exothermic reaction of about 39±10 kcal/mol. (The uncertainty is mainly due to the assumption made above.)

The relative energies considered are shown schematically in Fig. 4. It is evident that the heat of decomposition is not enough to take the electronically-excited states of ethylene into the reaction path. The two possible reactions which yield both ethylene and sulfur monoxide in the ground states are as follows:

$$(CH_2)_2SO(^1A') + M \longrightarrow CH_2{=}CH_2(^1A_g) + SO(^3\Sigma^-) + M \tag{2}$$

$$(CH_2)_2SO(^1A') \longrightarrow CH_2{=}CH_2(^1A_g) + SO(^1\Delta,\ ^1\Sigma^+)$$

$$SO(^1\Delta,\ ^1\Sigma^+) + X \longrightarrow SO(^3\Sigma^-) + X \tag{3}$$

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16) D. J. Meschi and R. J. Myers, *J. Mol. Spectry.*, **3**, 405 (1959).

17) D. F. Evans, *J. Chem. Soc.*, **1096**, 1735.

18) R. S. Mulliken, *J. Chem. Phys.*, **33**, 1596 (1960).

19) A. Kuppermann and L. M. Raff, *ibid.*, **37**, 2497 (1962); *Discussions Faraday Soc.*, **35**, 30 (1963); *J. Chem. Phys.*, **39**, 1607 (1963).

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21) U. Kaldor and I. Schavitt, *ibid.*, **48**, 191 (1968).

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24) L. Herzberg and G. Herzberg, *ibid.*, **105**, 353 (1947).

25) R. M. Badger, A. C. Wright and R. F. Whitlock, *J. Chem. Phys.*, **43**, 4345 (1965).

26) "Landolt-Börnstein, Zahlenwerte und Funktionen," Vol. II, Part 4, ed. by K. Schäfer and E. Lax, Springer-Verlag, Berlin (1961).

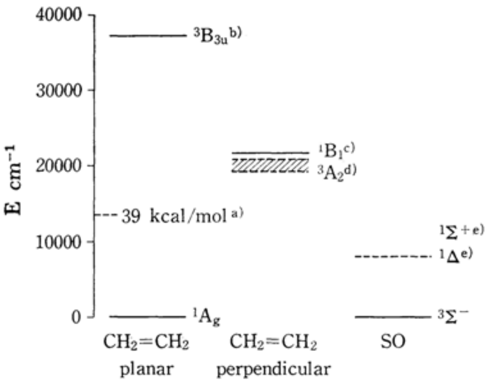

Fig. 4. Energy levels of ethylene and SO.
- a) The caluclated values of the heat of decomposition in the vapor phase, $(CH_2)_2SO \rightarrow CH_2{=}CH_2 + SO$
- b) Refs. 17—19.
- c) Ref. 20.
- d) Assumed from the calculated values by the various MO methods.[21]
- e) Assumed with inference for the oxygen molecule.[22-24]

The process (2) means the direct decomposition of ethylene episulfoxide into ethylene and sulfur monoxide by a collision with a third body, such as the hot surface of the reaction tube. Spin conservation[27] may be violated by such a collision. The reaction (3), however, is a reaction path which initially sets free the ethylene in the ground state and the sulfur monoxide in the excited singlet states. Then, the SO in the singlet states passes into the ground state under the influence of a third body.

According to Uehara,[28] no electron paramagnetic resonance lines of the SO in the $^1\varDelta$ state[29] were detected in the pyrolysis of ethylene episulfoxide under conditions similar to those described above. The sensitivity of the spectrograph he used was about 1×10^{-11} spins/gauss. The lifetime of $^1\varDelta$ SO should be rather long because the transition between the $^1\varDelta$ and $^3\Sigma^-$ states is forbidden. Really, in the case of oxygen, the radiative lifetime of the O_2 in the $^1\varDelta_g$ state is about 45 min.[25] Hence, the reaction (3) can not be the main process.

As a result, the main reaction of the thermal decomposition of ethylene episulfoxide must be (2): ethylene episulfoxide decomposes on the hot surface of the reaction tube to yield both the ethylene and SO molecules in the ground states.

In the above consideration, many unestablished assumptions have been used, such as those concerning the term energies of ethylene and SO, the heat of the decomposition of $(CH_2)_2SO$, and the sensitivity of the EPR spectrometer. The possibility of the reaction (3) should not, therefore, be excluded completely. To understand the mechanism further, it will be helpful to determine the heat of the decomposition of ethylene episulfoxide and to locate the $^1\varDelta$ and $^1\Sigma^+$ states of SO.

The SO molecule thus generated is unstable. The decomposition of the SO molecule has been studied by many investigators. Schenk and Steudel have reviewed the research into this problem up to 1964.[30] The reaction of SO has not been specifically investigated in this study, but it is meaningful to refer to the decomposition of SO, especially since the present system of reaction is almost free from the oxygen atom and the oxygen molecule. As Table 1 shows, the rotational lines of SO_2 and S_2O were observed immediately after the pyrolysis. It was also noticed that solid sulfur adhered to the inner walls of the reaction tube and the trap. These facts can be explained by the following reactions, which have already been discussed[30,31];

$$SO + SO \longrightarrow SO_2 + S$$
$$SO + S \longrightarrow S_2O$$

Schenk and Steudel[30] pointed out that the S_2O molecule was stable in the vapor phase, but that it polymerized in the cold trap and the polysulfur oxide decomposed into solid sulfur and SO_2 at room temperature. Thus, all of the oxygen atoms initially contained in the ethylene episulfoxide molecules passed into the SO_2 molecules. This mechanism explains why the ratio between ethylene and SO_2 in the final products of the pyrolysis was about two, by means of the following overall reaction:

$$6(CH_2)_2SO \longrightarrow 6CH_2{=}CH_2 + 3SO_2 + 3S$$

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27) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J. (1966), p. 276.

28) H. Uehara, private communication.

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