

PYROLYSIS OF ETHYLENE EPISULFOXIDE

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Hartzell and Paige (1) observed by mass spectrometry and differential thermal analysis that ethylene episulfoxide decomposes into ethylene and sulfur monoxide near 100°C. Dodson and Sauers (2) carried out the controlled thermal decomposition of ethylene episulfoxide in the presence of dienes and obtained cyclic sulfoxides. They suggested that sulfur monoxide generated in the pyrolysis might be in the $^1\Sigma^+$ or in the $^1\Delta$ state. By observing and analyzing the microwave spectrum, Saito (3) determined the molecular structure which threw light on the property of the S-O and C-S bonds. The main purpose of the present work is to confirm the SO molecule in the pyrolysis of ethylene episulfoxide by microwave spectroscopy and to determine the electronic state in which the sulfur monoxide is generated, in order to understand the mechanism of the thermal decomposition.

The pyrolysis was done in a quartz tube of 15 mm in diameter and 300 mm in length, whose temperature was regulated up to 780°C. The vapor pressure was kept at 0.01 to 0.1 mmHg. The pyrolyzed gas was led for analysis to the Stark absorption cell of a conventional microwave spectrograph with 110, kHz Stark modulation (3).

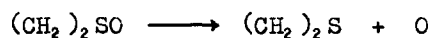
When the temperature of the reaction vessel was raised to about 185°C, the transition $J,K = 1,0 \leftarrow 0,1$ of SO in the ground $^3\Sigma^-$ state (4), was detected by the use of a strip-chart recorder. With raising temperature, the line became stronger and finally it was observable even on a CRO. Above 560°C the intensity of the line remained stationary. The sample pyrolyzed at 580°C and 0.02 mmHg was analyzed semi-quantitatively by the microwave spectra. The results are summarized in Table I.

TABLE I. Composition of the pyrolyzed ethylene episulfoxide

molecule	percentage	method
$(\text{CH}_2)_2\text{SO}$	2	CRO
SO	~ 3	CRO
SO ₂	20	CRO
S ₂ O	~24	CRO
H ₂ CO	0.8	CRO
$(\text{CH}_2)_2\text{S}$	≤ 0.3	recorder
$(\text{CH}_2)_2\text{O}$	≤ 0.04	recorder

The IR spectra of the final products of the pyrolysis indicated that their main components were ethylene and SO₂.

The results in Table I give us important informations on the mechanism of the thermal decomposition. First, ethylene sulfide and ethylene oxide were not found appreciably. It denotes that the abscission of the S-O bond,



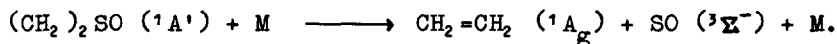
is not the main reaction in the thermal decomposition.

Thus it is certain that the compound first decomposes into ethylene and SO. The point to be considered is that ethylene is in a singlet state at the ordinary condition, whereas the SO molecule was found to be in a triplet state (4). Therefore, there must be some mechanisms which release the violation of spin conservation (5). Fig. 1 shows the relative energies of the lower electronic states of ethylene and SO. This obviously explains that the heat of decomposition of ethylene episulfoxide, which is estimated to be about 39 kcal/mol, is not enough to take the electronically excited states of ethylene into the reaction path. It should be noted that the singlet states of SO, especially the ¹Δ state, cannot be excluded, because it is only about 23 kcal/mol high above the ground state.

On the other hand, Uehara has searched an electron paramagnetic resonance line of the SO in the ¹Δ state in the pyrolyzed gas under the similar condition, but he has not succeeded to detect it (6). The sensitivity of the spectrograph he used was about 1×10^{-11} spins/gauss, which was sufficient enough to detect a signal of the ¹Δ SO in the reaction of atomic oxygen and OCS (7).

The lifetime of the SO in the ${}^1\Delta$ state should be rather long because the transition between the ${}^1\Delta$ and ${}^3\Sigma^-$ states is forbidden. Really, the radiative lifetime of the O_2 in the ${}^1\Delta_g$ state is about 45 minutes (8). Hence, it is very likely that the SO is directly brought to the ${}^3\Sigma^-$ state.

It is therefore concluded that the main reaction of the thermal decomposition will be the following mechanism that the molecule decomposes on a hot surface of the reaction tube to yield both ethylene and SO in the ground states;



But the possibility of the reaction which proceeds via the SO in the ${}^1\Delta$ state should not be excluded completely, because many unestablished assumptions have been used in the above consideration.

The SO molecule generated above decomposed into SO_2 , S_2O and sulfur. The reaction of SO was discussed in detail by Schenk and Steudel, and Hoyermann, Wagner and Wolfrum (9).

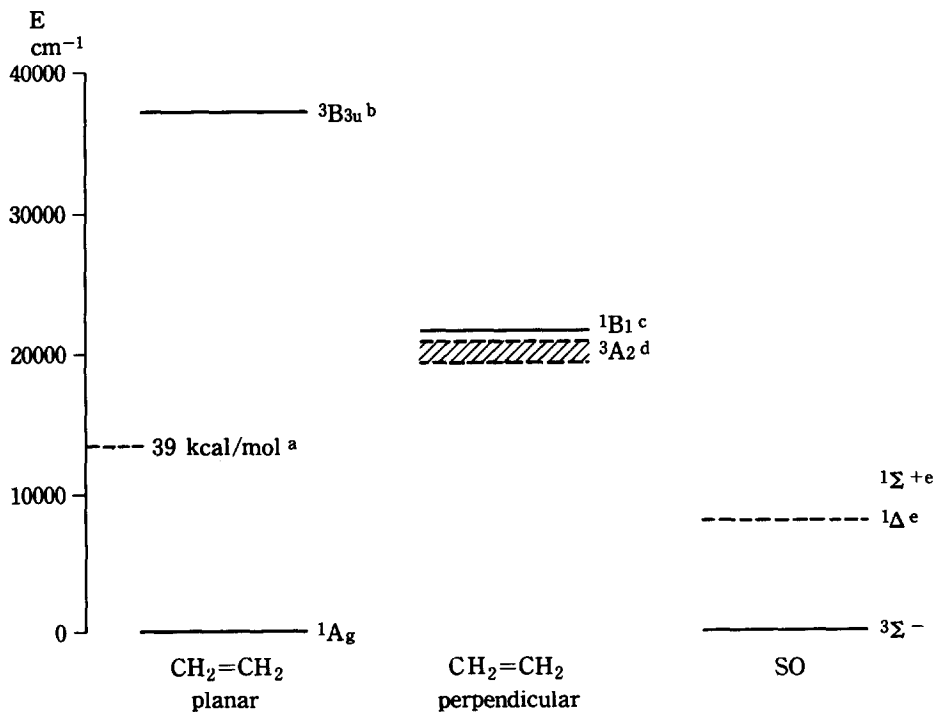
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Fig. 1. Energy levels of ethylene and SO



- a. The calculated value of the heat of decomposition of ethylene episulfoxide in the vapor phase; $(\text{CH}_2)_2\text{SO} \longrightarrow \text{CH}_2 = \text{CH}_2 + \text{SO}$.
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