BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 663—666 (1969)

The Microwave Spectrum, Structure, and Dipole Moment of Ethylene Episulfoxide

Shuji SAITO

Sagami Chemical Research Center, Sagamihara, Kanagawa

(Received August 1, 1968)

The microwave spectra of the normal species as well as the ^{13}C and ^{34}S isotopic molecules of ethylene episulfoxide have been observed. The rotational constants thus obtained lead to the following structural parameters: S–O=1.483±0.003 Å, C–S=1.822±0.003Å, ∠OSC=111°1′±10′, ∠CSC=48°46′±10′, on the assumption that the C–H distance and the ∠HCH and ∠H_2CC angles are the same as those of ethylene sulfide. From the Stark shifts, the dipole moment has been determined to be μ_a=3.61±0.04 D, μ_c=0.89±0.01 D and μ_{total}=3.72±0.04 D. The bond nature of S–O and C–S has then been discussed on the basis of these data.

Ethylene episulfoxide, a three-membered ring compound, was initially prepared by Hartzell and Paige[1] by the direct oxidation of ethylene sulfide with sodium metaperiodate. They reported that ethylene episulfoxide undergoes dethionylation to yield ethylene and sulfur monoxide at a temperature near 100°C.[1] Dodson and Sauers carried out the thermal decomposition of ethylene episulfoxide in the presence of dienes and obtained cyclic sulfoxides.[2] Among the several sulfoxides reported,[1-5] dimethyl sulfoxide is well-known as a useful reactant for the oxidation of various functional groups to carbonyl compounds,[6] and as an excellent solvent for various organic and inorganic compounds. Compared with dimethyl sulfoxide, ethylene episulfoxide is far too unstable and more reactive even under mild conditions.

As ethylene episulfoxide is one of the simplest alkyl sulfoxides, it would be interesting to determine its molecular structure. The accumulated data on the structures of alkyl sulfoxides give a way of understanding the stability and reactivity of these compounds. Accurate r_e structures of the SO[7] and SO_2[8] molecules were obtained from the microwave spectra in the vibrationally-excited states. Pierce and Hayashi[9a] and Dreizler and Rudolph[9b] determined the r_s structure of dimethyl sulfide by analyzing the rotational spectra of various isotopic species. The r_0 structures of dimethyl sulfoxide[10] and ethylene sulfide[11] were obtained

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

2) R. M. Dodson and R. F. Sauers, *Chem. Commun.*, **1967**, 1189.

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

4) G. E. Hartzell and J. N. Paige, *ibid.*, **32**, 459 (1967).

5) R. C. Krug and D. E. Bosewell, *J. Heterocyclic Chem.*, **4**, 309 (1967).

6) a) N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H. O. Larson, O. Levand and W. M. Weaver, *J. Am. Chem. Soc.*, **79**, 6562 (1957). b) F. W. Sweat and W. W. Epstein, *J. Org. Chem.*, **32**, 835 (1967).

7) a) T. Amano, E. Hirota and Y. Morino, *J. Phys. Soc. Japan*, **22**, 399 (1967). b) F. X. Powell and D. R. Lide, Jr., *J. Chem. Phys.*, **41**, 1413 (1964). c) M. Winnewisser, K. V. L. N. Sastry, R. L. Cook and W. Gordy, *ibid.*, **41**, 1687 (1964).

8) a) S. Saito, *J. Mol. Spectry.*, to be published. b) Y. Morino, Y. Kikuchi, S. Saito and E. Hirota, *J. Mol. Spectry.*, **13**, 95 (1964).

9 a) L. Pierce and M. Hayashi, *J. Chem. Phys.*, **35**, 479 (1961). b) H. Dreizler and H. D. Rudolph, *Z. Naturforsch.*, **17a**, 712 (1962).

10) H. Dreizler and G. Dendl, *Z. Naturforsch.*, **19a**, 512 (1964).

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

by microwave spectroscopy. The purpose of this research is to determine the structure and the dipole moment of ethylene episulfoxide from its microwave spectrum.

Experimental

The sample of ethylene episulfoxide, prepared by the oxidation of ethylene sulfide using perbenzoic acid, was kindly provided by Fukuyama and Sato.[12] The microwave spectrum of ethylene episulfoxide was studied in the region from 8000 MHz to 36000 MHz with a conventional sinusoidal Stark-modulated spectrograph. Most of the measurements were carried out with a 3-m absorption cell at room temperature.

Microwave Spectrum

A tentative molecular model was first drawn by inference from analogous compounds, such as dimethyl sulfoxide[10] and ethylene sulfide.[11] The model was found to be a nearly prolate symmetric top with a dipole moment whose a and c components are about four and one Debyes respectively. Thus, strong a-type R branch transitions would be observed near every 11000 MHz, and weak c-type Q branch transitions would cover the whole region. The Stark effects should be rather large.

Table 1. Observed microwave transition frequencies of ethylene episulfoxide (C_2H_4SO) in the ground state (MHz)

Transition	f_{obs}	Δf[a]
a-type		
$1_{01} \leftarrow 0_{00}$	10519.30[b]	0.00
$2_{11} \leftarrow 1_{10}$	21258.84[b]	0.00
$2_{02} \leftarrow 1_{01}$	21033.96[b]	−0.16
$2_{12} \leftarrow 1_{11}$	20817.60[b]	0.00
$3_{12} \leftarrow 2_{11}$	31885.13[b]	0.36
$3_{21} \leftarrow 2_{20}$	31573.30[b]	0.46
$3_{22} \leftarrow 2_{21}$	31556.76[b]	0.42
$3_{03} \leftarrow 2_{02}$	31540.36[b]	0.38
$3_{13} \leftarrow 2_{12}$	31223.13[b]	0.17
c-type		
$1_{10} \leftarrow 0_{00}$	19477.78[c]	0.00
$2_{11} \leftarrow 1_{01}$	30216.64[c]	−0.68
$2_{02} \leftarrow 1_{10}$	12075.41[b]	−0.23
$3_{03} \leftarrow 2_{11}$	22357.24[c]	0.47
$1_{11} \leftarrow 1_{01}$	8737.19[b]	−0.69
$2_{12} \leftarrow 2_{02}$	8521.67[b]	0.32
$2_{21} \leftarrow 2_{11}$	26212.58[d]	−0.93
$2_{20} \leftarrow 2_{12}$	26879.98[d]	0.48

a) $\Delta f = f_{obs} - f_{calc}$. b) Accuracy ± 0.1 MHz.
c) Accuracy ± 0.2 MHz. d) Accuracy ± 0.4 MHz.

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

A search was made, using an oscilloscope, in the 10—12 GHz region, where the $1_{01} \leftarrow 0_{00}$ transitions were expected to occur on the basis of the molecular model described above. A good absorption candidate was located at 10519 MHz; this absorption showed a typical $J=1 \leftarrow 0$ Stark effect. The assignment of this line to the $1_{01} \leftarrow 0_{00}$ transition was confirmed by the observation at about 21 GHz of three $J=2 \leftarrow 1$ transitions which showed Stark patterns characteristic of the $J=2 \leftarrow 1$ transitions. From the a-type transitions thus assigned, the c-type transitions were predicted and searched for by means of a strip-chart recorder. The observed frequencies are given in Table 1. Subsequent measurements were made on the a-type transitions of the S-34 and C-13 species in natural abundance; the results are shown in Table 2.

Table 2. Observed microwave transition frequencies of $C_2H_4{}^{34}SO$ and $^{13}CCH_4SO$ (MHz)

Transition	f_{obs}	Δf[a]
$C_2H_4{}^{34}SO$		
$2_{11} \leftarrow 1_{10}$	21135.38[b]	0.00
$2_{02} \leftarrow 1_{01}$	20936.94[b]	0.00
$2_{12} \leftarrow 1_{11}$	20745.20[b]	0.00
$^{13}CCH_4SO$		
$2_{02} \leftarrow 1_{01}$	20675.92[b]	0.00
$2_{12} \leftarrow 1_{11}$	20440.96[b]	0.00
$1_{01} \leftarrow 0_{00}$	10340.52[b]	0.00

a) $\Delta f = f_{obs} - f_{calc}$. b) Accuracy ± 0.1 MHz.

Table 3. Rotational constants and centrifugal distortion constants of ethylene episulfoxide (MHz)

C_2H_4SO
$A = 14107.86 \pm 0.30$
$B = 5369.99 \pm 0.10$
$C = 5149.37 \pm 0.10$
$D_J = 0.015 \pm 0.010$
$D_{JK} = 0.006 \pm 0.015$
$C_2H_4{}^{34}SO$
$B = 5332.74 \pm 0.10$
$C = 5137.66 \pm 0.10$
$^{13}CCH_4SO$
$B = 5290.14 \pm 0.10$
$C = 5050.44 \pm 0.10$

The rotational constants for the normal species were obtained by using three low-J transitions. In the analysis of the spectra, the centrifugal distortion effect was calculated by the following symmetric-top expression:

$$W(J,K_1,K_1) = E(J,K_{-1},K_1) - D_J J^2(J+1)^2 - D_{JK} J(J+1) K_{-1}^2 - D_K K_{-1}^4$$

where $W(J,K_{-1},K_1)$ denoted the rotational energy including centrifugal effects; $E(J,K_{-1},K_1)$ the rigid rotor rotational energy, and the other terms the usual centrifugal terms. This treatment is possible because the ethylene episulfoxide molecule is very close to a prolate symmetric top: $b_p=-0.01247$. The rotational spectra for the S-34 and C-13 species were analyzed in a similar way, using the centrifugal distortion corrections determined from the analysis of the normal species. The rotational constants and the centrifugal distortion constants are listed in Table 3.

Dipole Moment

Stark effect coefficients were measured for the $M=0$, $1_{01}\leftarrow 0_{00}$ transition and for the $M=1$ and 0 components of the $2_{02}\leftarrow 1_{01}$ transition. The Stark displacements were compared with those of the OCS molecule, for which the dipole moment was taken to be 0.7124 D.[13] The observed Stark coefficients and the comparison with the calculated values are shown in Table 4. μ_a was determined

Table 4. Stark coefficients and dipole moment of ethylene episulfoxide

Transition		$\Delta\nu/E^2$(MHz)/(V/cm)$^2\times 10^4$ obs	obs-calc
$1_{01}\leftarrow 0_{00}$	$M=0$	1.696	0.000
$2_{02}\leftarrow 1_{01}$	$M=0$	−0.463	0.000
	$M=1$	0.437	0.001
$\mu_a=3.61\pm0.04$ D		$\mu_c=0.89\pm0.01$ D	
$\mu_{total}=3.72\pm0.04$ D			

to be 3.61±0.04 D and μ_c, to be 0.89±0.01 D. They yield a value of 3.72±0.04 D for the total dipole moment, which makes an angle of 13°51′ with *a* principal axis. The orientation of the dipole moment relative to the molecular framework was not uniquely determined. The structural calculation described in the next section indicates that the S–O bond axis makes an angle of 42°2′ with the *a* axis, and the plane containing the C_2S ring, an angle of 24°46′ with the *a* axis, so that there are two possibilities, 28°11′ and 55°53′, for the angle between the S–O bond and the total dipole moment. In view of the fact that the dipole moment of ethylene episulfoxide is composed mainly of one S–O and two C–S bond moments, the former possibility, 28°11′, seems preferable to the latter. Figure 1 thus shows only the former configuration.

Molecular Structure

Seven structural parameters are necessary for specifying the molecular structure of ethylene episulfoxide. Fortunately, seven rotational constants have been obtained: three for the normal, two for the S-34, and two for the C-13 species. It seems inadequate to use the rotational constants, *B* and *C*, of the S-34 species for the determination of the structure, because the sulfur atom is so near the center of gravity that the structure derived from the rotational constants of the S-34 species is apt to be affected by zero-point vibrations.

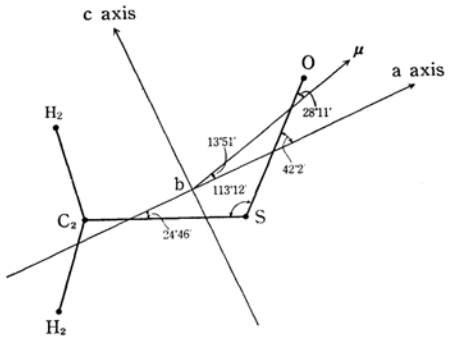

Fig. 1. Structure of ethylene episulfoxide.

Among the seven structural parameters, the most interesting ones are those which describe the episulfoxide part of the molecule. It can be expected that the ethylene part of ethylene episulfoxide is almost the same as that of ethylene sulfide. This prediction is understandable in view of the structures of dimethyl sulfide[9] and dimethyl sulfoxide[10] studied by microwave spectroscopy. Moreover, as a result of the small mass of the hydrogen atom, the moments of inertia depend only slightly on any assumption concerning the configuration of the ethylene part. Hence, we assume that the ethylene part of ethylene episulfoxide is the same as that of ethylene sulfide, that is, that C–H=1.078 Å, ∠HCH=116°0′, and $\angle H_2CC=151°43'$.[11] The four remaining parameters, the S–O and C–S distances, and the ∠OSC and ∠CSC angles are determined to give the five observed rotational constants for the normal

Table 5. r_0 structure of ethylene episulfoxide

r(S–O)	1.483 ± 0.003 Å
r(C–S)	1.822 ± 0.003 Å
∠OSC	110° 1′ ± 10′
∠CSC	48°46′ ± 10′
r(C–C)[a]	1.504 ± 0.003 Å
assumed parameters	
r(C–H)	1.078 Å
∠HCH	116° 0′
$\angle H_2CC$	151°43′

a) r(C–C) distance is not independent of the other parameters listed above.

13) S. A. Marshall and J. Weber, *Phys. Rev.*, **105**, 1502 (1957).

and C-13 species. The structure thus obtained is given in Table 5.

Discussion

The molecular structure of ethylene episulfoxide determined above gives some clue for understanding the properties of alkyl sulfoxides, which have rarely been discussed. The S–O and C–S bond distances of the related compounds previously reported are compared in Table 6 with those of ethylene episulfoxide obtained in this work. The S–O and C–S bond moments of ethylene episulfoxide can be evaluated from the values of the total dipole moment given in Table 4 if the C–H bond moments are disregarded. These results are also listed in Table 6, along with the bond moments

Table 6. S–O and C–S bond distances and bond moments in various compounds

Molecule		r(S–O)	μ(S–O)	r(C–S)	μ(C–S)
$(CH_2)_2SO$[a]	r_0	1.483 Å	2.53 D	1.822 Å	1.06 D
$(CH_3)_2SO$[b]	r_0	1.47_7 Å	2.70 D	1.81_0 Å	1.47 D
$(CH_2)_2S$[c]	r_0	.....	.....	1.819 Å	1.01 D
$(CH_3)_2S$[d]	r_s	.....	.....	1.802 Å	1.15 D
$(CH_3)_2S_2$[e]	r_0	.....	.....	1.81_0 Å	1.38 D
SO[f]	r_e	1.48108 Å	1.55 D	.....	.....
SO_2[g]	r_e	1.4308 Å	1.58 D[i]	.....	.....
S_2O[h]	r_0	1.465 Å	1.58 D	.....	.....

a) This work. b) Ref. 10.
c) Ref. 11. d) Ref. 9.
e) D. Sutter, H. Dreizler and H. D. Rudolph, *Z. Naturforsch.*, **20a**, 1676 (1965).
f) Ref. 7. g) Ref. 8.
h) D. J. Meschi and R. J. Myers, *J. Mol. Spectry.*, **3**, 405 (1959). i) G. F. Grable and W. V. Smith, *J. Chem. Phys.*, **19**, 502 (1951).

of related compounds, which were calculated in a similar way. It may be seen that the S–O bond length of ethylene episulfoxide is longer than those of SO_2 and S_2O, and almost equal to that of SO. As was expected prior to the measurements, ethylene episulfoxide has nearly the same S–O bond distance as dimethyl sulfoxide. The C–S bond length of ethylene episulfoxide is a little longer than those of dimethyl sulfide, dimethyl disulfide, and dimethyl sulfoxide, and is almost equal to that of ethylene sulfide. This comparison indicates that the S–O bond of ethylene episulfoxide is almost a double bond, while the C–S bond is almost a single bond.

On the other hand, the C–S bond moment of ethylene episulfoxide is quite normal and is nearly the same as that of ethylene sulfide within the limits of experimental error, whereas the S–O bond moment is considerably larger than those of SO, SO_2, and S_2O. The unusual polarity of the S–O bond can be understood by means of the molecular orbital calculations made by Moffitt.[14] Using the self-consistent LCAO method, he calculated the bond order and the formal charge distribution in the SO, SO_2, SO_3, R_2SO, and R_2SO_2 molecules. He predicted that the dipole moments for alkyl sulfoxides would be about 3.5 D; according to the difference between the electronegativities of the alkyl groups and the sulfur atom, the positive charge moves considerably farther from the negatively-charged oxygen atom, and the C–S bonds of alkyl sulfoxides are weaker than those in alkyl sulfones and alkyl sulfides because the former has hardly any 3*s* electrons of the sulfur atom.

The weakness of the C–S bond has been demonstrated by the experimental finding that ethylene episulfoxide decomposes near 100°C.[1] This has also been confirmed by microwave spectroscopy detecting the rotational lines of sulfur monoxide in the ground state. The thermal decomposition of ethylene episulfoxide will be reported in a separate paper.

The author would like to express his hearty thanks to Professor Yonezo Morino for his encouragement and for the valuable advice given throughout this work. He also wishes to thank Dr. M. Fukuyama and Mr. K. Sato for providing a sample of ethylene episulfoxide.

14) W. Moffitt, *Proc. Roy. Soc.* (*London*), **A200**, 409 (1950).