

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

**Cyclic Sulfides. I. Ultraviolet Spectra of Ethylene Sulfides**ROBERT EARL DAVIS<sup>1</sup>*Received June 26, 1957*

The ultraviolet spectra of several ethylene sulfides have been measured in solution and in the gas phase. The spectra have been compared with those of the corresponding oxygen compounds. Several possible explanations of the origin of the absorption are discussed.

The first ethylene sulfide<sup>2</sup> was synthesized by Delépine<sup>3</sup> and was characterized by marked reactivity, ease of polymerization, and ease of ring opening. The chemical properties of this ring system have been reviewed by Schönberg.<sup>4</sup> In many respects the chemistry resembles that of the ethylene oxides.

The physical properties of ethylene sulfide have been subject to the investigation of several groups of workers. The infrared spectrum, vapor pressure, and some thermodynamic properties were measured as part of the American Institute Research Project 48A on sulfur compounds.<sup>5</sup> The dipole moment<sup>6</sup> has been reported and the structures of the sulfide and ethylene oxide have been compared on the basis of their microwave spectra.<sup>7</sup> The heats of combustion<sup>8</sup> of ethylenimine, ethylene oxide, ethylene sulfide, and cyclopropane have been compared in consideration of the strain energies of various three-membered rings. The present study has centered upon the ultraviolet spectra of several ethylene sulfides having various degrees of alkyl substitution.

aqueous potassium thiocyanate.<sup>11</sup> The material was dried over sodium sulfate and then over calcium sulfate and fractionally distilled through a seventeen plate column, b.p. 54.6–54.8° at 756 mm., into glass bulbs. The bulbs were then opened in a vacuum line and purified by repeated bulb-to-bulb distillations.

Propylene sulfide, b.p. 74.5–74.6°, was prepared from propylene oxide and aqueous thiourea<sup>12</sup> and purified in the same manner as ethylene sulfide. Cyclohexene sulfide was prepared from cyclohexene oxide and potassium thiocyanate<sup>13</sup> and purified by fractionation *in vacuo*, b.p. 73–74.5° at 22 mm. The sulfide was then purified by repeated bulb-to-bulb distillations on a vacuum line.

*Solvent.* ASTM iso-octane (Phillips) was repeatedly shaken with dilute sulfuric acid and then washed with water and dried over potassium carbonate. The iso-octane was fractionally distilled from phosphorus pentoxide. Further samples were purified by passage through active silica gel.

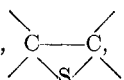
*Spectra.* The spectra were measured on a Beckman DU spectrophotometer and on a Model 11 Cary. The gas spectra were recorded using 5.00-cm. silica cells while the solution spectra were measured using 1.00-cm. cells. The spectrophotometers were calibrated against the benzene vapor spectrum. The extinction coefficients were expressed as  $\epsilon_m = A/cl$  for the solution spectra and  $e = A/pl$  for the gas spectra where  $A$  is the optical density,  $c$  the concentration in moles/liter,  $l$  is the optical path in centimeters, and  $p$  is the pressure in millimeters of mercury.

## EXPERIMENTAL

*Materials.* Ethylene oxide<sup>9</sup> was dried over calcium sulfate and fractionally distilled through a twenty-plate helix column. Propylene oxide<sup>9</sup> was purified in the same manner. Cyclohexene oxide was synthesized from 2-chlorocyclohexanol<sup>10</sup> and purified by careful fractionation.

Ethylene oxide was prepared from ethylene oxide and

(1) National Science Foundation predoctoral fellow, 1955–1957.

(2) The system, , has been called: ethylene

sulfide, thiacyclopropane, and thirane.

(3) M. Delépine, *Compt. rend.*, **171**, 36 (1920).

(4) A. Schönberg, *Houben-Weyl, Methoden der Organischen Chemie*, Vol. 9, Verlag, Stuttgart, 1955, pp. 148–169.

(5) G. B. Guthrie, D. W. Scott, and G. Waddington, *J. Am. Chem. Soc.*, **74**, 2795 (1952).

(6) H. H. Gunthard and T. Gaumann, *Helv. Chim. Acta*, **33**, 1985 (1950).

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

(8) R. A. Nelson, and R. S. Jessup, *J. Research Nat. Bur. Standards*, **48**, 206 (1952).

(9) Eastman Organic Chemicals.

(10) A. E. Osterburg, *Org. Syntheses*, Coll. Vol. I, 185 (1932).

## DISCUSSION

The ultraviolet absorption of the ethylene sulfide ring system is characterized by one band in the region of 2600 Å (38460 cm.<sup>-1</sup>) which is present in both the solution and gas phase spectra. The solution spectra have inflections in the region of 2450 Å (40820 cm.<sup>-1</sup>) while the gas phase spectra reveal a distinct second transition. Table I and Figures 1 and 2 present the data. The corresponding oxides are transparent in the ultraviolet and can be used as solvents in the range above 2100 Å. However, spectra are observed in the vacuum ultraviolet below 2000 Å. Liu and Duncan<sup>14</sup> measured the spectrum of ethylene oxide in the gas phase. Two electronic transitions at 1713.4 Å (58362 cm.<sup>-1</sup>) and at 1572.4 Å (63597 cm.<sup>-1</sup>) were observed and each was coupled to a vibrational mode such that transitions were observed at 1690.4 Å (59157 cm.<sup>-1</sup>) and 1545.0 Å

(11) Ref. 4, p. 154.

(12) W. Davies and W. E. Savige, *J. Chem. Soc.*, 317 (1950).

(13) E. E. van Tamelen, *Org. Syn.*, **32**, 39 (1952).

(14) T. Liu and A. B. F. Duncan, *J. Chem. Phys.*, **17**, 241 (1949).

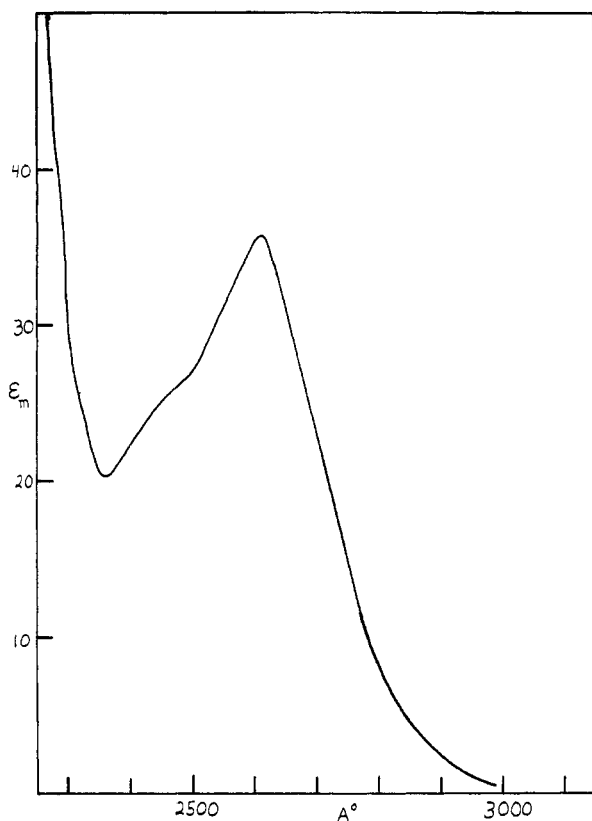
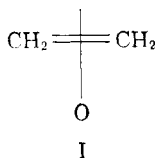


FIG. 1. ETHYLENE SULFIDE IN ISOCTANE.

(64722  $\text{cm}^{-1}$ ). Below 1435 Å the Rydberg transitions were observed.

The nature of the electronic transitions in the ethylene oxide system and in the sulfide is not completely understood. The bonding in the oxide has been disputed.<sup>15-18</sup> The molecule of ethylene oxide has been considered by Walsh<sup>18</sup> to be represented as a  $\pi$ -bond of ethylene binding the three nuclei (I).



Formula I is meant to imply that each carbon atom is trigonal forming three planar hybridized  $sp^2$  bonds and the remaining carbon valency is a pure  $2p_z$  orbital overlapping the  $2p_z$  of the other carbon and the  $2p_z$  of oxygen. The construction of a semi-localized bonding molecular orbital in LACO form has been given<sup>14</sup> and the observed transitions of ethylene oxide in the region of 1700–1500 Å have been considered as due to excitations to the anti-bonding forms of the orbital. This could be used as an explanation of

(15) A. D. Walsh, *Nature*, **159**, 165 (1947).

(16) R. Robinson, *Nature*, **159**, 400 (1947).

(17) C. A. McDowell, *Nature*, **159**, 508 (1947).

(18) A. D. Walsh, *Nature*, **159**, 712 (1947).

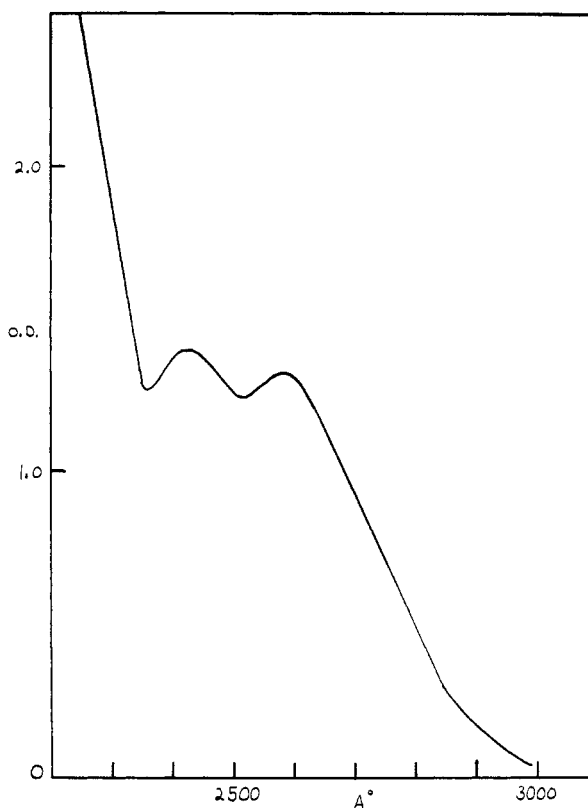


FIG. 2. OPTICAL DENSITY OF ETHYLENE SULFIDE ABSORPTION IN THE GAS PHASE AT 250 MM. PRESSURE.

the present data. Using the  $C_{2v}$  symmetry of the ethylene sulfide ring and taking the  $z$ -axis normal to the plane of the ring, the orbital would be described (without subscripts or normalization) as

$$\psi_{CCS} = z_1 + z_2 + 3p(S)$$

where  $(z_1 + z_2)$  represents the ethylenic contribution overlapping with the  $3p_z$  orbital on the sulfur atom. The excited states would then be transitions from  $[z_1 + z_2 + 3p(S)]^2$  to forms of  $[z_1 \pm z_2 \pm 3p(S)]^2$ . The sulfur atom having 3s and 3p electrons in contrast to oxygen's 2s and 2p electrons has its excited states at lower levels than those of oxygen. This is observed in the oxygen atom spectrum<sup>19</sup> compared to that of the sulfur atom spectrum. Thus it is expected and observed that sulfur compounds absorb at higher wavelengths. This explanation based upon the treatment of ethylene oxide by Walsh<sup>15,18</sup> and used for the ultraviolet discussion by Liu and Duncan<sup>14</sup> may be satisfactory for these systems and by analogy to the ethylene sulfides. However, doubts exist.

The absorption bands have weak intensities (20–40) which means that the oscillator strengths<sup>20</sup> are low. Low strengths or weak bands are generally "forbidden" transitions which are observed because

(19) *Atomic Energy Levels*, Nat. Bur. of Standards, Cir. No. 467, Vol. I, 1949.

(20) W. Kauzmann, *Quantum Chemistry*, Academic Press, New York, 1957, pp. 573, 644–666.

TABLE I  
ULTRAVIOLET SPECTRA IN ISOCTANE SOLUTIONS AT 25°

Compound	Maxima Å	$\epsilon_m$	Minima Å	$\epsilon_m$
Ethylene sulfide	2610 (2450) <sup>a</sup>	34.3 <sup>b</sup> 24.6	2370	20.4
Propylene sulfide	2624 (2450) <sup>a</sup>	35.0 25.0	2373	19.7
Cyclohexenesulfide	2625	39.3	2370	19.7

ULTRAVIOLET SPECTRA IN THE GAS PHASE

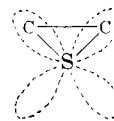
Compound	Maxima Å	$e \times 10^3$	Minima Å	$e \times 10^3$
Ethylene sulfide	2592 2430	1.13 <sup>c</sup> 1.16	2521 2364	1.06 1.09
Propylene sulfide	2611 2450	1.72 1.47	2500 2360	1.41 1.07

<sup>a</sup> Inflection. <sup>b</sup> Units: A liter mole<sup>-1</sup> cm.<sup>-1</sup> <sup>c</sup> Units: A mm.<sup>-1</sup> cm.<sup>-1</sup>

of perturbation effects. Thus the benzene bands in the region of 2600 Å are forbidden by selection rules based on the C<sub>2</sub> symmetry of benzene but vibrations of the atoms cause the absorption bands to appear with  $\epsilon_m$  in the range of 100. These bands are called "partially forbidden".

Another explanation for the origin of the spectra can be built using the C<sub>2v</sub> symmetry of the three membered ring compounds and some of the geometric requirements of some *d* orbitals. In this case the spectra would be considered as excitation

from an unbonded pair on the sulfur (*p* orbital) to a *d* orbital. The excited state would then appear as



Unfortunately it is difficult to describe the complete electronic states of these polyatomic sulfur compounds. Even hydrogen sulfide has not been analyzed with respect to the electronic spectrum. At least there are suggestive reasons why the ethylene sulfide system should exhibit some type of ultraviolet absorption above 2000 Å though the spectra might not be predicted before hand.

There is evidence in the literature of ultraviolet spectra of sulfur compounds that the degree of electronic charge on the sulfur atom in divalent sulfur compounds is related to the position of the absorption band. This will be considered in the following paper in this series on the effect of ring size upon the spectra of cyclic sulfides.

The author wishes to express his appreciation to Prof. W. E. Lyons for helpful discussions during the course of this investigation and to Prof. P. D. Bartlett for permission to publish this report.

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## Skeletal Rearrangement of $\beta,\beta,\beta$ -Triphenylpropionic Acid in the Hunsdiecker Reaction<sup>1,2</sup>

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Received June 17, 1957

The reaction of silver  $\beta,\beta,\beta$ -triphenylpropionate with bromine under conditions normally employed for the Hunsdiecker degradation proceeds anomalously to give the phenyl esters of  $\beta,\beta$ -diphenylacrylic and  $\alpha$ -bromo- $\beta,\beta$ -diphenylacrylic acids in moderate yield, with little bromodecarboxylation. Evidence is presented that this skeletal transformation proceeds by an ionic process probably involving 1,4-phenyl migration *via* a five-membered ring intermediate.

**Introduction.** Curtin and Hurwitz<sup>3</sup> in their preparation of a number of related radicals by decarbonylation of the appropriate aldehyde found evidence that the  $\beta,\beta,\beta$ -triphenylethyl radical (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CCH<sub>2</sub>• gives 100% rearrangement under these conditions to the  $\alpha,\alpha,\beta$ -triphenylethyl radical (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> by migration of a phenyl group. This rearrangement is appreciably faster than the

identically engendered transformation of the neophyl radical C<sub>6</sub>H<sub>5</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>• to the  $\beta$ -phenyl-*t*-butyl radical •C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>,<sup>4</sup> and presumably might occur even in the presence of an active substrate such as bromine.<sup>5</sup>

(4) W. H. Urry and M. S. Kharasch, *J. Am. Chem. Soc.*, **66**, 1438 (1944); S. Winstein and F. Seubold, *J. Am. Chem. Soc.*, **69**, 2916 (1947); F. Seubold, *J. Am. Chem. Soc.*, **75**, 2532 (1953). In the last reference, the neophyl rearrangement is deduced to possess an activation energy of about 8 kcal./mole.

(5) The neophyl rearrangement is apparently absent or at best present to the extent of 5–10% in such a reactive medium. Cf. (a) C. E. Berr, Ph.D. thesis, University of California at Los Angeles (1952); (b) J. W. Wilt, *J. Am. Chem. Soc.*, **77**, 6397 (1955); (c) W. T. Smith, Jr., and J. T. Sellas, *Trans. Kentucky Acad. Sci.*, **16**, 72 (1955).

(1) Abstracted in part from the thesis of Donald D. Oathoudt presented to the faculty of the Graduate School of Loyola University in partial fulfillment of the requirements for the degree of Master of Science, February, 1957.

(2) A preliminary report of this work appeared in *J. Org. Chem.*, **21**, 1550 (1956).

(3) D. Y. Curtin and M. J. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952).