

larography. Whereas the cobalt of  $B_{12a}$  is easily reduced to the bivalent state,  $E_{1/2} = -0.04$  v., and at a more negative potential reduced to the univalent state,  $E_{1/2} = -1.02$  v.,  $B_{12}$  undergoes only a single two-electron reduction,  $E_{1/2} = -1.12$  v. *vs.* S.C.E. We have observed also that  $B_{12a}$  can be hydrogenated to  $B_{12r}$  without a catalyst.

There appear, then, to be four classes of cobaltic amines with respect to their polarography:

Class	Material	Half-wave potential $E'$	$E''$	$n$	Valence change
I	Most amines, <sup>11</sup> <i>e.g.</i> , $\text{Co}(\text{NH}_3)_6^{3+}$	-0.00 to	-1.3 to	1	3 to 2

(11) J. B. Willis, J. A. Friend and D. P. Mellor, *THIS JOURNAL*, **67**, 1680 (1945).

Cl <sub>2</sub>		-0.04	-1.4	2	2 to 0
II	$B_{12a}$	-0.04		1	3 to 2
	$B_{12a}, B_{12r}$		-1.02	1	2 to 1
III	$B_{12}^{7+}$	-1.12		2	3 to 1
	$B_{12}(\text{CN})^{-8}$	-1.35		2	3 to 1
	$\text{K}_4\text{Co}(\text{CN})_6\text{H}_2\text{O}^{12}$	-1.3		1	2 to 1
IV	$\text{K}_3\text{Co}(\text{CN})_6\text{H}_2\text{O}^{12}$	-1.45		2	3 to 1

**Acknowledgment.**—The authors wish to express their appreciation of the aid they have received from The Squibb Institute for Medical Research.

(12) D. N. Hume and I. M. Kolthoff, *ibid.*, **71**, 867 (1949).

AMES, IOWA

[CONTRIBUTION FROM THE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

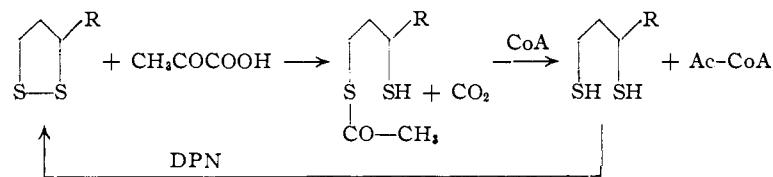
## The Chemistry of 1,2-Dithiolane (Trimethylene Disulfide) as a Model for the Primary Quantum Conversion Act in Photosynthesis<sup>1a</sup>

BY J. A. BARLTROP,<sup>1b</sup> P. M. HAYES AND M. CALVIN

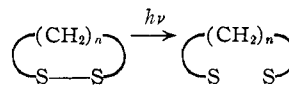
RECEIVED MARCH 24, 1954

Some chemical and photochemical observations on 1,2-dithiolane and its derivatives with particular reference to the possible mode of function of the naturally occurring system, 6-thioctic acid, are discussed. Experimental evidence is presented to demonstrate that the strain energy in this 5-membered ring is not less than 6.5 kcal. and probably larger. Reagents which both oxidize and reduce this ring are described together with the conditions required for its reformation from the corresponding dithiol. Evidence is adduced to indicate that the primary product of photolysis of this ring in acidic media is very likely a thiol and sulfenic acid or derivative thereof.

Although plants which are allowed to photosynthesize in  $\text{C}^{14}\text{O}_2$  rapidly assimilate labeled carbon into a series of compounds, very little of the  $\text{C}^{14}$  finds its way into the intermediates of the Krebs tricarboxylic acid cycle during illumination. If, after a period of photosynthesis, the light is turned off, the compounds of the Krebs cycle rapidly become labeled.<sup>2</sup> Thus there is a reaction path linking the photosynthesis and Krebs cycles which becomes blocked during illumination. With the discovery<sup>3-6</sup> that 6-thioctic acid is a coenzyme for the oxidative decarboxylation of pyruvate to active acetyl groups, which through CoA feed carbon into the Krebs cycle,<sup>7,8</sup> Calvin and Massini<sup>9</sup> suggested that the process could be formulated as



Moreover, since the coenzyme must be present in its oxidized form in order that the oxidation of pyruvic acid may proceed, these authors suggested that the reducing power formed in the presence of light shifted the steady-state conditions of the coenzyme toward its reduced (dithiol) form and thus reduced the rate at which intermediates of the photosynthetic cycle entered the TCA system. At this point, specimens of the isomeric 4-, 5- and 6-thioctic acids became available to us through the courtesy of Dr. T. H. Jukes of Lederle Laboratories. The ultraviolet absorption spectra of these compounds (Fig. 1) showed a displacement of the absorption peak to progressively longer wave lengths as the size of the disulfide ring diminished, a phenomenon which might well be due to ring-strain. If one supposes that the absorption band is due to a transition



then assuming to a first approximation that the excited states of all the disulfides have the same energy

(1) (a) The work described in this paper was sponsored by the U. S. Atomic Energy Commission; (b) Rockefeller Fellow, 1952-1953, while on leave of absence from Brasenose College and the Dyson Perrins Laboratory, Oxford University, England.

(2) A. A. Benson and M. Calvin, *J. Exptl. Bot.*, **1**, 63 (1950).

(3) (a) L. J. Reed, I. C. Gunsalus, *et al.*, *THIS JOURNAL*, **73**, 5920 (1951); (b) E. L. Patterson, *et al.*, *ibid.*, **73**, 5919 (1951).

(4) I. C. Gunsalus, I. Struglia and D. I. O'Kane, *J. Biol. Chem.*, **194**, 859 (1952).

(5) L. J. Reed and B. G. DeBusk, *THIS JOURNAL*, **74**, 3457 (1952).

(6) M. W. Bullock, *et al.*, *ibid.*, **74**, 3455 (1952).

(7) S. Ochoa, J. R. Stern and M. C. Schneider, *J. Biol. Chem.*, **193**, 691 (1951).

(8) S. Korkes, A. DelCamilo, I. C. Gunsalus and S. Ochoa, *ibid.*, **193**, 721 (1951).

(9) M. Calvin and P. Massini, *Experientia*, **8**, 445 (1952).

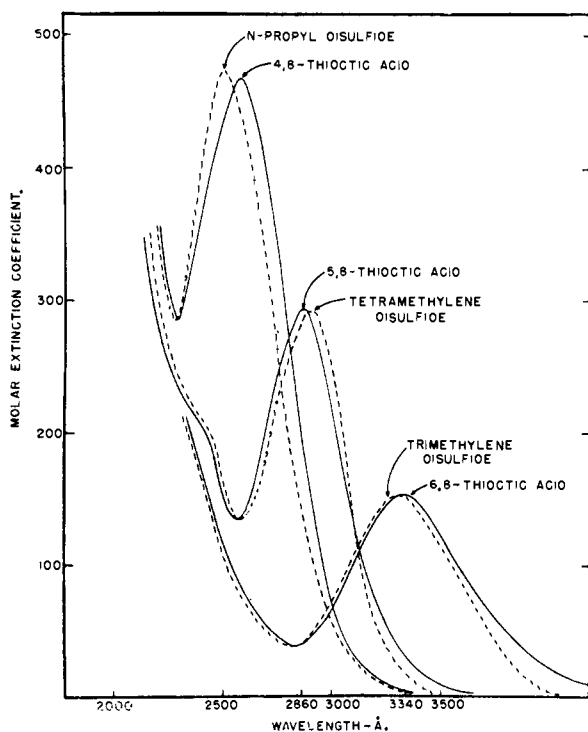


Fig. 1.—Absorption spectra of some disulfides in alcohol.

curves (Fig. 2) and that the transitions all reach the same point on the upper curve, the differences in  $\lambda_{\max}$  would correspond to differences in the energies of the ground states, *i.e.*, to ring strain. On this basis the shift from  $\lambda_{\max}$  2500 Å. for straight chain aliphatic disulfides to  $\lambda_{\max}$  *ca.* 3300 Å. for 6-thioctic acid implies that the latter experiences a strain of *ca.* 25–30 kcal. ( $\Delta = \Delta_G + \Delta_U$  in Fig. 2), and that hence the dissociation energy of the S–S bond ( $E_D$  in Fig. 2) will be reduced by a like amount. Any difference ( $\Delta_U$  in Fig. 2) in the energy of the excited state reached in the ring compound from that reached in an open chain compound will have to be subtracted from this value. The published values for  $D$  (R–S–S–R) vary from 50<sup>10</sup>–70<sup>11</sup> kcal.; thus the ring strain might reduce the dissociation energy of the ring S–S bond to *ca.* 30–40 kcal. There is another quite independent method of estimating the strain in this ring based upon purely structural considerations, together with some measured single bond rotational barriers. Of prime consideration is the apparent<sup>12,13</sup> requirement that the stable configuration about the S–S bond be the one having the dihedral angle equal to 90° and a rotational barrier of at least 10 kcal. This barrier is presumably in the 180° or *trans* position. The 0° or *cis* position which would be the one demanded in the trimethylene disulfide ring might be expected to have a somewhat higher barrier. A similar qualitative suggestion was made by Affleck

(10) A. H. Sehon, *THIS JOURNAL*, **74**, 4723 (1952); M. L. Huggins, *ibid.*, **75**, 4125 (1953).

(11) J. L. Franklin and H. E. Lumpkin, *ibid.*, **74**, 1024 (1952).

(12) D. W. Scott, H. L. Finke, M. E. Gross, G. B. Guthrie and H. M. Huffman, *ibid.*, **72**, 2424 (1950).

(13) D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, R. E. Pennington and Guy Waddington, *ibid.*, **74**, 2478 (1952).

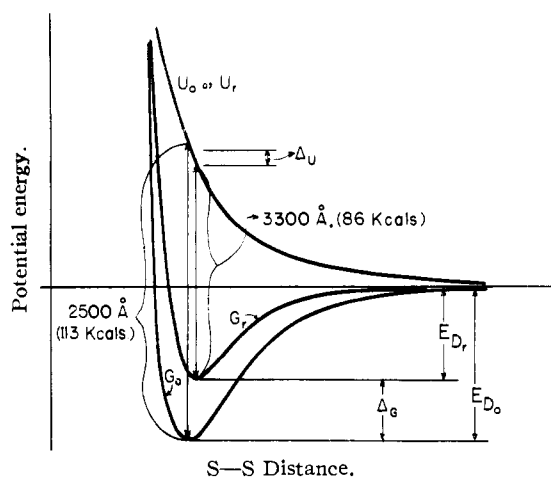


Fig. 2.—Schematic representation of the potential curves and transitions for the cyclic and open-chain disulfides.

and Dougherty<sup>14</sup> based upon observations of the relative stability of a series of polymethylene disulfides. We do not propose here to elaborate further on the origin of this barrier but simply to suggest that it is at least partly due to the repulsion between the two non-bonding pairs of primarily *p* electrons on the sulfur atoms.<sup>15–17</sup> Presumably it is the changing hybridization of these and the non-bonding *s* electrons as well, which is induced by the geometrical requirements of the ring which is responsible for the shift in ultraviolet absorption. An examination of the constitution of this ring shows that the largest dihedral angle that it is possible to achieve without major changes in the C–C bond is approximately 45°. Under this circumstance, the three pairs of methylene hydrogens lie opposed to each other in a position of maximum potential energy as judged from considerations of the rotational barriers in ethane and propane.<sup>17</sup> Pitzer has given the potential barrier for the rotation of a methyl group in propane as 3.4 kcal. If we take a minimum of 6 kcal. for the CH (six) repulsions and use a cosine law with a maximum of 10 kcal. to estimate the potential energy remaining in the S–S bond at a dihedral angle which approaches 45° (5 kcal.), we arrive at a minimum strain energy of approximately 11 kcal. In view of the great uncertainty in the normal S–S bond energy it does not seem fruitful to pursue these estimates any further.

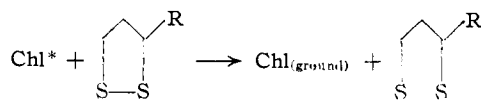
The evidence is that light absorbed by the chlorophyll and associated pigments in plants is passed on as quanta of less than 40 kcal. of energy, and this led directly to the notion that 6-thioctic acid was itself the substance involved in the conversion of the electromagnetic energy of the quantum into chemical bond energy and that the process of quantum conversion in photosynthesis was the fission of the disulfide bond of 6-thioctic acid to give the di-thiyl radical, *i.e.*

(14) J. G. Affleck and G. Dougherty, *J. Org. Chem.*, **15**, 805 (1950).

(15) L. Pauling, *Proc. Nat. Acad. Sci.*, **35**, 495 (1949).

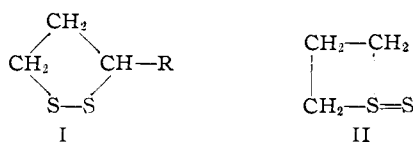
(16) E. N. Lassetre and L. B. Dean, *J. Chem. Phys.*, **17**, 317 (1949).

(17) K. S. Pitzer, *Faraday Soc. Disc.*, 1951, "Hydrocarbons."



Suggestions as to the subsequent transformations of the diradical have already been outlined in a preliminary communication.<sup>13</sup> The purpose of the present paper is to describe in detail some of the experiments mentioned there as well as new ones, and to amend and amplify the suggestions.

In order to assess the probability of the preceding ideas, it became necessary to learn something of the fundamental properties of dithiolane ring systems. Since 6-thioctic acid is difficult to prepare, trimethylene disulfide (dithiolane) (I, R = H) was selected as a model substance. It had been prepared by Affleck and Dougherty<sup>14</sup> from the bis-Bunte salt



derived from trimethylene dibromide, but we were not aware of this at the time. The only previous work on this substance was recorded by Hagelberg<sup>19</sup> and Autenrieth and Wolff<sup>20</sup> who describe it as a colorless crystalline substance m.p. ca. 71–75°, and which the latter authors believed to be a dimer. When trimethylene dibromide was condensed with sodium disulfide in aqueous ethanol and the ethanol evaporated, the distillate had a bright yellow color like 6-thioctic acid and an ultraviolet absorption spectrum which showed a peak at  $\lambda_{\text{max}}$  3300 Å. and had a general form almost identical with 6-thioctic acid. This observation led to the method of isolation and purification described in the Experimental section. A substance, almost certainly thiacyclobutane was formed as a by-product. The trimethylene disulfide was obtained in only 9% yield; the main reaction product appears to be the "dimer" of Autenrieth and Wolff<sup>20</sup> since it can be crystallized to a colorless solid m.p. ca. 75°. It can be depolymerized slowly to trimethylene disulfide by steam distilling with Na<sub>2</sub>S<sub>2</sub> and NaOH.<sup>21</sup> This, rather than monomeric trimethylene disulfide, appears to have been the product obtained by Yur'ev and Levi<sup>22</sup> by pyrolysis of thiacyclobutane.

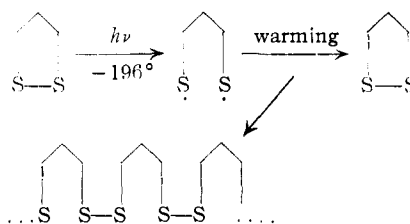
Tetramethylene disulfide, similarly prepared and described by Affleck and Dougherty<sup>14</sup> as an oil, was found to be a crystalline solid m.p. 32–33°. Trimethylene disulfide could only be obtained in solution. All attempts to isolate it in a pure state were terminated by polymerization. It was recognized by the close similarity between its ultraviolet spectrum and that of 6-thioctic acid, the constitution of which has been established, and also by an independent molecular weight estimation. The fact that trimethylene disulfide is yellow seems to have escaped previous notice, although this seems to be a characteristic property of the dithiolane system

- (18) M. Calvin and J. A. Bartrop, *THIS JOURNAL*, **74**, 6153 (1952).  
 (19) L. Hagelberg, *Ber.*, **23**, 1086 (1890).  
 (20) W. Autenrieth and K. Wolff, *ibid.*, **32**, 1368 (1899).  
 (21) F. O. Davis and E. M. Fetters, *THIS JOURNAL*, **70**, 2611 (1948).  
 (22) Y. K. Yur'ev and I. S. Levi, *Dokl. Akad. Nauk, S.S.S.R.*, **73**, 953 (1950).

since 6-thioctic acid, 4,4-dimethyldithiolane<sup>23</sup> and 4,4-spirocyclohexyldithiolane<sup>24</sup> are also yellow.

Trimethylene disulfide is stable to reduction by sodium borohydride but is reduced very rapidly by zinc and dilute acid to trimethylene dithiol, from which trimethylene disulfide can be recovered quantitatively by oxidation with iodine. This observation also provides proof of structure since it excludes the alternative formulation II (*cf.* Backer and Evenhuis<sup>23</sup>). Trimethylene disulfide also was obtained in excellent yield from trimethylene dithiol by oxidizing with air in the presence of alkali or of hydriodic acid, the latter reaction presumably depending on the formation of iodine as an intermediate.

The suggestion as formulated earlier as to the possible function of 6-thioctic acid in photosynthesis included the photochemical fission of the S–S bond into thiyl radicals. The polymerization of trimethylene disulfide in light is consistent with the suggestion—but in order to obtain more definitive evidence, trimethylene disulfide was photolyzed in an ether–pentane–alcohol glass<sup>25</sup> at –196°. Under these conditions, one could expect that the thiyl radicals produced by photolysis would be preserved from further reaction (a) because the rigid solvent would prevent their approaching each other and thus recombining and (b) because at the low temperature employed the insufficiency of thermal activation energy would prevent their attacking the solvent. Hence it should be possible to build up a considerable concentration of thiyl radicals. When trimethylene disulfide was photolyzed under these conditions, a clear, pale salmon-colored glass resulted which appeared to be stable in liquid N<sub>2</sub>, but which on warming a few degrees to the point at which the glass lost its rigidity, rapidly became turbid with polymer. The clarified solution now contained more than 50% of the original trimethylene disulfide (Fig. 5). These results are consistent with the interpretation



Confirmation of the production of free radicals<sup>26</sup> by photolyzing trimethylene disulfide was sought by using diphenylpicrylhydrazyl which is itself a free radical, stable to air, and which has been used before in the detection of radicals.<sup>27</sup> Diphenylpicrylhydrazyl, with and without trimethylene disulfide solution, was both illuminated and kept in the dark. The color of the hydrazyl faded only when mixed

- (23) H. J. Backer and N. Evenhuis, *Rec. trav. chim.*, **56**, 129 (1937).  
 (24) H. J. Backer and A. F. Tamsma, *ibid.*, **57**, 1183 (1938).  
 (25) G. N. Lewis, D. Lipkin and T. T. Magel, *THIS JOURNAL*, **63**, 3005 (1941).  
 (26) Since the initial preparation of this manuscript there appeared some confirmatory evidence for the photo-dissociation of aromatic disulfides into free radicals; M. S. Kharasch, W. Nudenberg and T. Meltzer, *J. Org. Chem.*, **18**, 1233 (1953).  
 (27) C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1217 (1951).

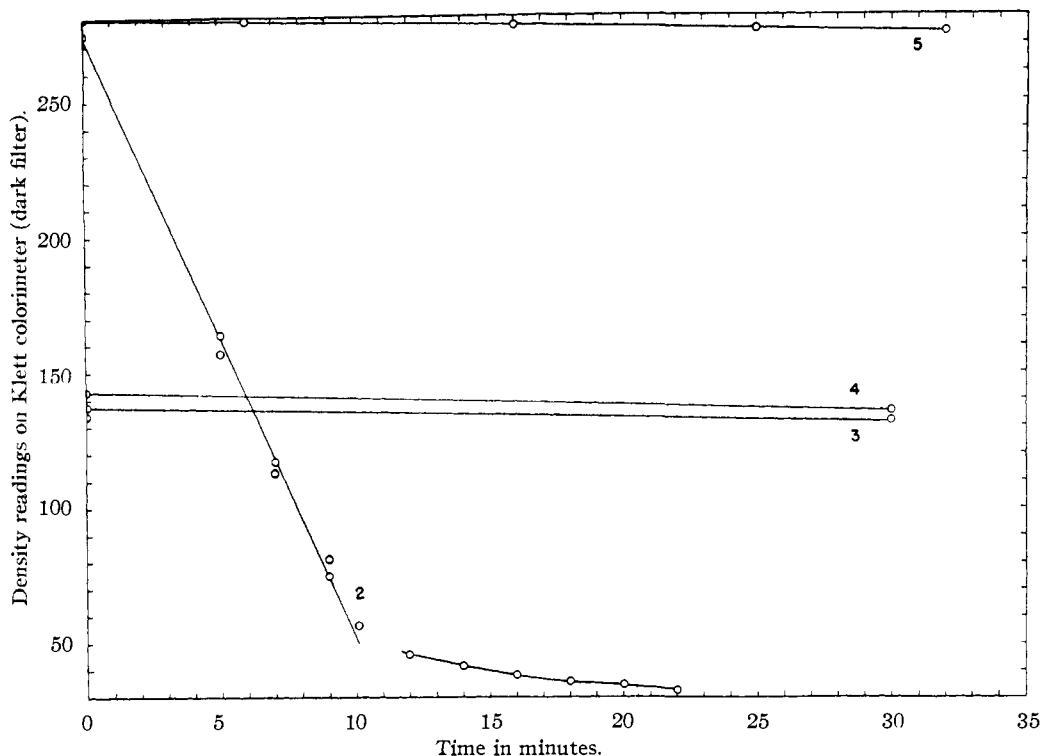


Fig. 3.—Photolysis of diphenylpicrylhydrazyl in the presence of trimethylene disulfide; readings taken against a dark red

filter No. 66: 1, in dark after illumination; 2, picrylhydrazyl + C1CC1 in light; 3, picrylhydrazyl in dark; 4, picrylhydrazyl in light; 5, picrylhydrazyl + C1CC1 in dark.

with trimethylene disulfide and exposed to light (see Fig. 3). This result was also consistent with the notion that trimethylene disulfide on photolysis gave radicals, these then reacting with the hydrazyl. However, we realize now that this experiment no longer affords proof of the formation of radicals for subsequent work has shown that the picrylhydrazyl color fades on adding thiols and as is shown below, thiols are generated when the disulfide is illuminated in ethanol solution.

The theory of quantum conversion as it was out-

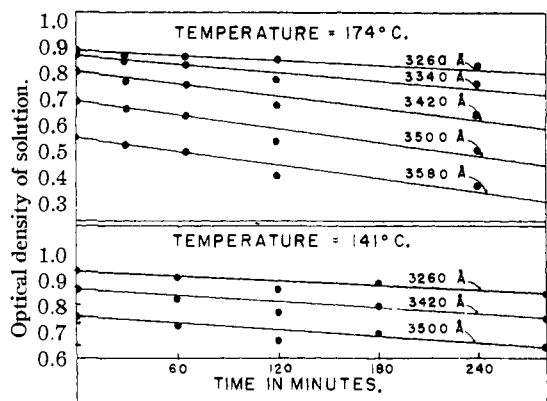
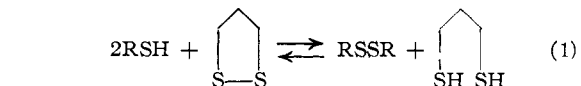
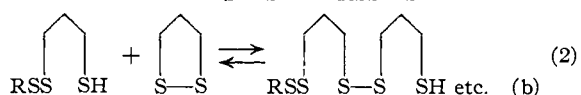
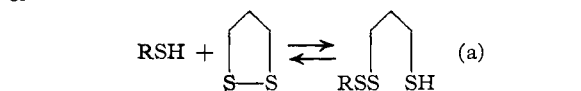


Fig. 4.—Kinetics of pyrolysis of C1CC1 in *n*-octane.

lined previously also required that the S-S bond be in a condition to be ruptured by a quantum of less than 40 kcal. The estimate of ring strain given earlier derived from spectral data is based on several assumptions of uncertain validity. That based on purely structural considerations is somewhat better. In order to arrive at a more accurate value for the difference in the S-S dissociation energy between an aliphatic disulfide and trimethylene disulfide (*i.e.*, ring strain) we exploited the observation that aliphatic thiols reacted in a reversible manner with trimethylene disulfide. After adding a thiol, the trimethylene disulfide was partly destroyed, the amount of destruction being correlated with the amount of thiol added, and dilution of the solution causing a regeneration of trimethylene disulfide. The equilibrium being observed could be either



or



The equilibrium constant calculated for reaction

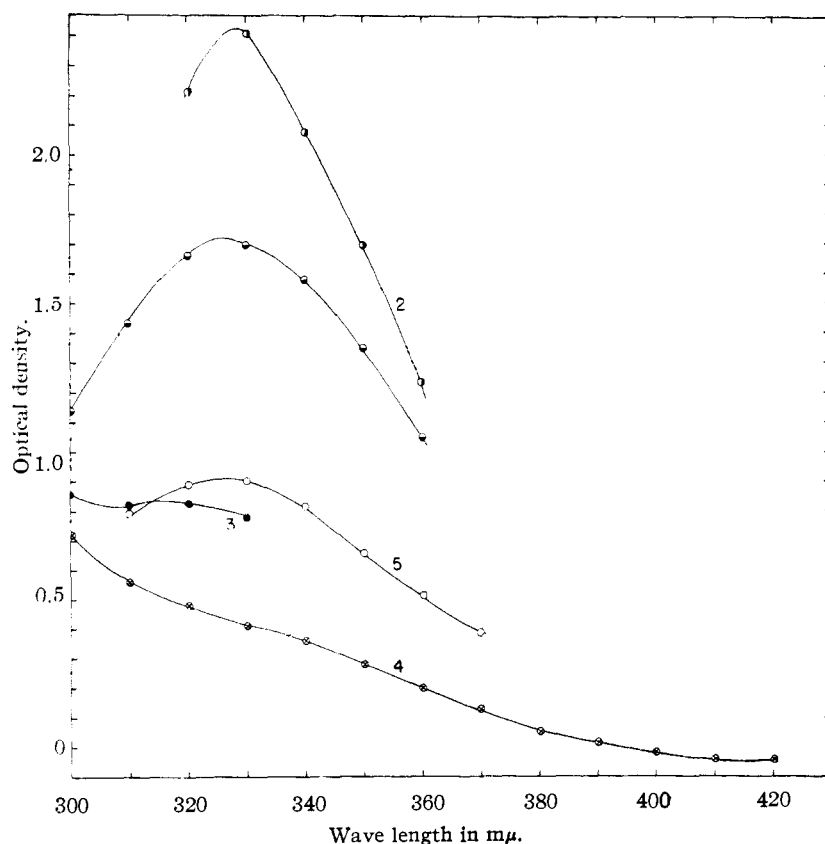


Fig. 5.—Low temperature photolysis of trimethylene disulfide and its reversal:

1, S—S in E.P.A. before photolysis (room temp.); 2, 1 at  $-196^{\circ}$ ; 3, 1 after 10 min. photolysis; 4, 1 after 20 min. photolysis; 5, 4 after warming slowly to room temp. and centrifuging.

1 does not fit the data obtained. The complex of reactions 2 can be given a simple mathematical formulation by noting that for each added thiol group reacting with trimethylene disulfide a new thiol group is generated. If it is assumed that all the thiols in reaction (a) have the same equilibrium constant for the reaction with trimethylene disulfide, then, since in the experiments herein reported there is always a large excess ( $>10$  fold) of added thiol, a good approximation to the over-all equilibrium constant can be represented by

$$K = \frac{[\text{aliphatic disulfide}]}{[\text{cyclic disulfide}] \times [\text{thiol}]}$$

Values of  $K$  calculated from the data by this equation are reasonably constant for the reactions of trimethylene disulfide with both benzyl mercaptan and  $\beta$ -mercaptoethanol.

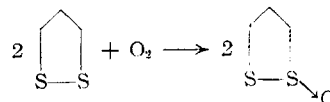
For the reaction with benzyl mercaptan conducted at  $24.1$  and  $35.85^{\circ}$ , the free energies of reaction are  $\Delta F_{24.1} = -1.67$  kcal. and  $\Delta F_{35.8} = -1.75$  kcal., respectively; hence  $\Delta H = -6.3$  kcal.  $\Delta H$ , which is a measure of the differences in bond energy between the cyclic disulfide and an aliphatic disulfide is thus a measure also of the ring strain in trimethylene disulfide. It should be noted that although there is *ca.* 6 kcal. of heat energy available to drive the reaction to the right, this is opposed by

an entropy term  $T\Delta S$  of *ca.* 4.5–5 kcal. so that only *ca.* 1.5–2 kcal. of free energy is left.

As an alternative method of deriving information concerning the stability of the S—S bond in trimethylene disulfide, the kinetics of the polymerization of the substance in *n*-octane were investigated. The activation energy of such a reaction would be the same as the dissociation energy of the S—S bond, if the reaction were unimolecular in the disulfide and if the rate-determining step required the homolytic fission of the bond. However, it was found that the reaction was abnormal in that the activation energy was extremely low (*ca.* 8.7 kcal.) and the apparent  $PZ$  factor fantastically small. Whatever may be the interpretation of these results it is clear that the reaction is not a simple one, and the values obtained have little relevance to the problem under investigation.

As an approach to an inquiry into the intermediate oxidation levels of the disulfide, the oxidation of trimethylene disulfide by air, by hydrogen peroxide and by ammonium persulfate was investigated. Preliminary tests showed that trimethylene disulfide was not oxidized readily by air, but was rapidly photo-oxi-

dized in the presence of a suitable photosensitizer. Figure 6 shows that while trimethylene disulfide and zinc tetraphenylporphin individually were almost stable to oxygen both in visible light and in the dark, a mixture of the two rapidly absorbed oxygen upon illumination. When the reaction was followed quantitatively (Fig. 7) it emerged that the oxygen was absorbed in the ratio of one atom of oxygen per mole of trimethylene disulfide suggesting that the over-all reaction was



This formulation of the oxidation product as a disulfide monoxide was supported by the close similarity between its ultraviolet absorption spectrum and the spectrum of the monoxide of 6-thioctic<sup>28</sup> acid (Fig. 9). At this point we should, perhaps, mention that further experiments have shown that photochemical destruction of the disulfide sensitized for red light by zinc tetraphenylporphin which was mentioned in the earlier communication<sup>18</sup> was probably caused by traces of oxygen. The ammonium persulfate oxidation of trimethylene

(28) We are indebted to Dr. T. H. Jukes of Lederle Laboratories for a specimen of this substance.

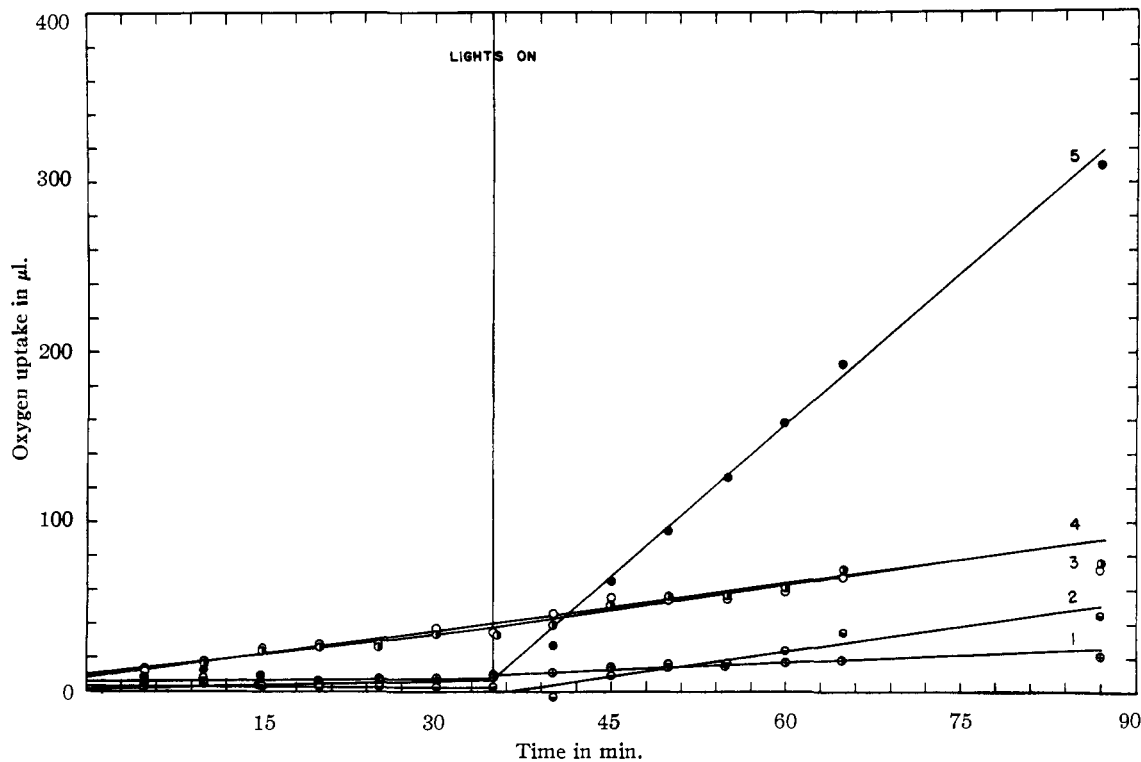


Fig. 6.—Photo-oxidation of S—S catalyzed by zinc tetraphenyl porphin: 1, S—S + P.E.; 2, porphin + P.E.; 3, porphin + Bz; 4, S—S + Bz; 5, porphin + S—S + Bz + P.E.

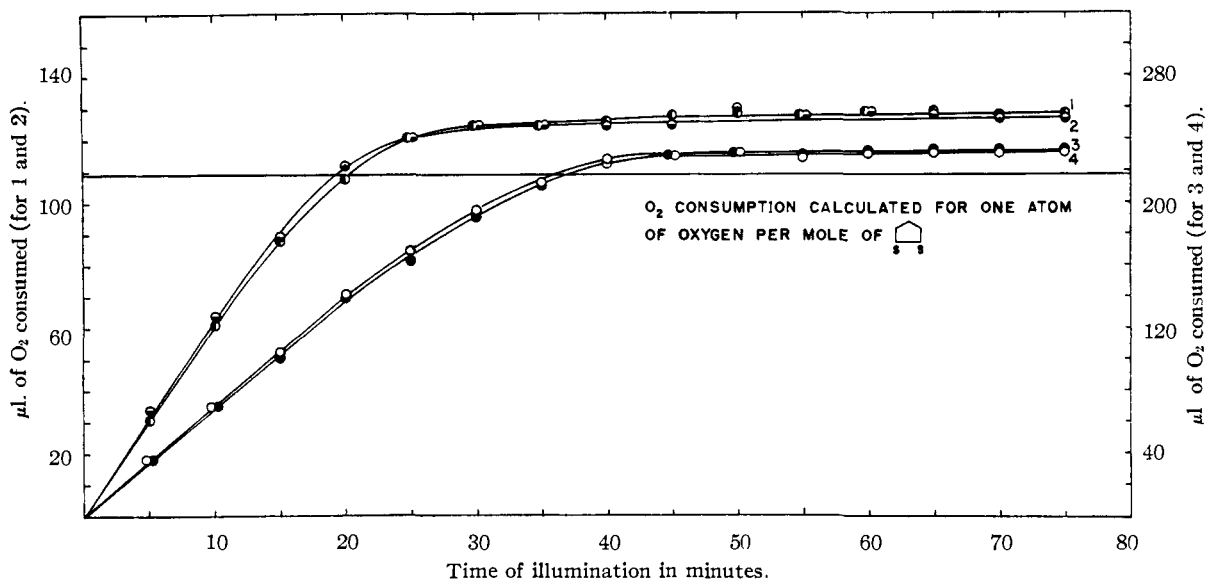


Fig. 7.—Stoichiometry of the photo-oxidation of S—S catalyzed by zinc tetraphenylporphin at 11°.

disulfide gave comparable results. Figure 10 shows the rapid course of the reaction and the isosbestic point indicates that the oxidation followed one course only. The diluted reaction mixture had an ultraviolet spectrum virtually identical (allowing

for the end absorption of the ammonium bisulfate formed) with those of 6-thioctic acid monoxide and the photo-oxidation product of trimethylene disulfide described previously. Furthermore, only one mole of ammonium persulfate can probably have

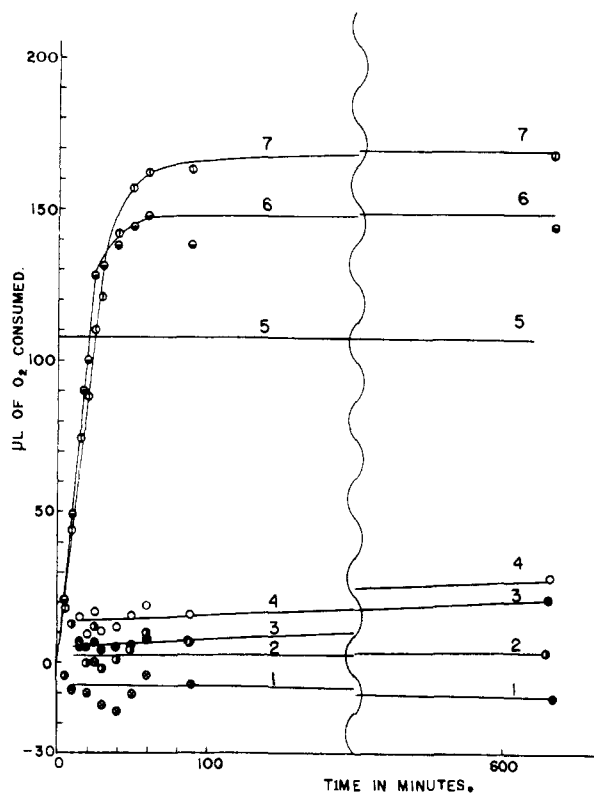


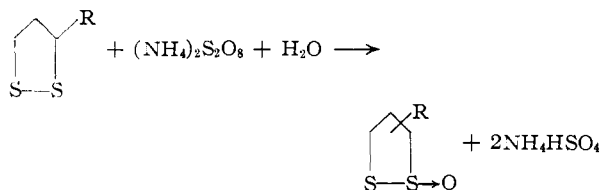
Fig. 8.—Stoichiometry of photooxidation of S—S catalyzed by zinc tetraphenylporphin at 24°: 1 and 2, zinc

tetraphenylporphin alone; 3 and 4, S—S alone; 5, calcu-

lated O<sub>2</sub> absorption for one atom of O<sub>2</sub> per mole of S—S; 6

and 7, porphin + S—S.

been used per mole of trimethylene disulfide since the same product was obtained even with an excess of trimethylene disulfide. Also 6-thioctic acid, oxidized with one mole of ammonium persulfate, gave a product the spectrum of which resembled closely the spectrum of authentic 6-thioctic acid monoxide, and the extinction coefficient of the 2440 Å. peak of the oxidation product assuming 100% yield (which is justified by the isobestic point) is within the limits of experimental error identical with that of 6-thioctic monoxide. This accumulation of data proves that the course of the reaction is



In this context it is interesting to note that di-*n*-propyl disulfide is stable to oxidation under these conditions. Trimethylene disulfide monoxide was

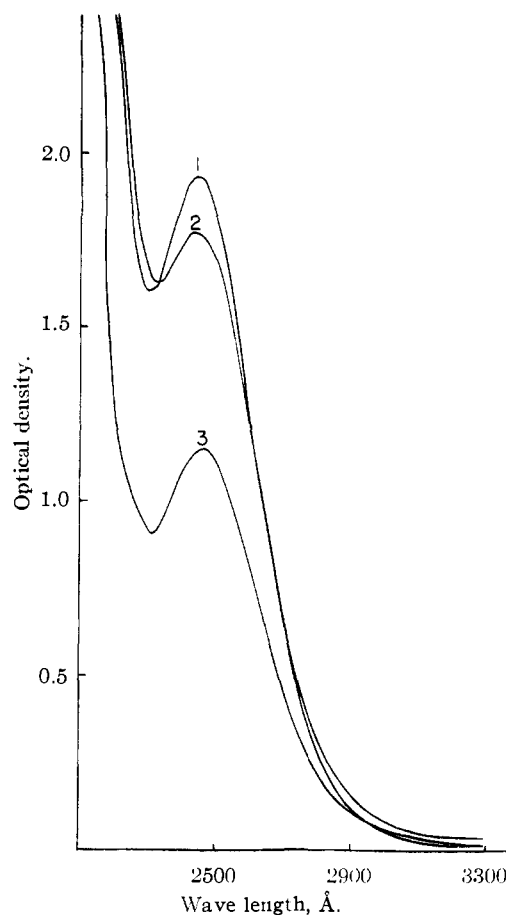


Fig. 9.—Absorption spectra of disulfide monoxides in alcohol: 1, 6-thioctic acid monoxide (Lederle) in 95% EtOH,  $1.89 \times 10^{-3} M$ ,  $\lambda_{\text{max}} 2440 \text{ \AA}$ ,  $\epsilon_{\text{max}} 1025$ ; 2, product of ammonium persulfate oxidation of 6-thioctic acid,  $1.72 \times 10^{-3} M$ ; 3, product of ammonium persulfate oxidation of trimethylene disulfide,  $1.135 \times 10^{-3} M$ .

found to be stable to acid in the cold but it was destroyed instantaneously by alkali. Disulfide monoxides are a little-investigated group of compounds of which the best known are allicin<sup>29</sup> and 6-thioctic acid monoxide.<sup>30</sup> They have been prepared previously by oxidizing disulfides with *t*-butyl hydroperoxide<sup>30</sup> and with peracids.<sup>31</sup> The course of the reaction between trimethylene disulfide and hydrogen peroxide was too complicated to be elucidated spectroscopically, but little, if any, monoxide appeared to be formed directly.

The fact that 6-thioctic acid seems to be the coenzyme directly responsible for the oxidative decarboxylation of  $\alpha$ -keto acids led us to investigate the non-enzymic reactions between  $\alpha$ -keto acids and trimethylene disulfide. When pyruvic acid or  $\alpha$ -ketoglutaric acid was heated in alcoholic solution with trimethylene disulfide very little change occurred. Next,  $\alpha$ -ketoglutaric acid and trimethylene disulfide were exposed to ultraviolet irradiation in a nitrogen atmosphere. It was found that whereas

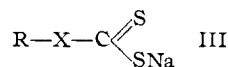
(29) C. J. Cavallito, J. S. Buck and C. M. Suter, *THIS JOURNAL*, **66**, 1950 (1944).

(30) M. W. Bullock, S. A. Brockman, E. L. Patterson, J. V. Pierce and E. I. R. Stokstad, *ibid.*, **74**, 3455 (1952).

(31) C. J. Cavallito, *et al.*, *ibid.*, **69**, 1710 (1947).

control tubes containing trimethylene disulfide only rapidly became turbid due to polymerization, the tubes containing trimethylene disulfide and  $\alpha$ -ketoglutaric acid remained clear, although spectroscopic examination showed the complete destruction of the trimethylene disulfide. A series of similar experiments was performed with pyruvic, oxalic and acetic acids. The following facts emerged. (1) With pyruvic and oxalic, as with  $\alpha$ -ketoglutaric acid, the solution remained clear upon photolysis, but with acetic acid polymerization of the trimethylene disulfide was inhibited only partly. (2) No detectable quantity of  $\text{CO}_2$  was formed during the pyruvic and oxalic acid experiments. (3) The  $\text{H}^+$  concentration was unchanged by photolysis. (4) Amperometric titration for thiols with  $\text{Ag}^+$  showed that rather less than one thiol group was formed per molecule of trimethylene disulfide. (5) Iodine titration revealed the presence of reducing substances in the solution in addition to the thiols. Since the added acids were apparently unchanged by the photolysis and since acetic acid which is a weaker acid than pyruvic and oxalic acids was less effective as a polymerization inhibitor than the others, it appeared likely that these substances were inhibiting polymerization merely by virtue of their acidity and that mineral acids would exercise a similar effect. This was found to be the case. Photolysis of trimethylene disulfide in the presence of hydrochloric acid, again caused no change in the acid titer. Also *ca.* one thiol group was liberated per molecule of trimethylene disulfide and excess reducing power was revealed by iodine oxidation as with the organic acids. A small quantity of hydrogen sulfide was detected by a lead acetate paper.

The difference between the iodine and silver titrations posed the question as to which should be accepted as the index of thiol concentration. It was found in model titrations with other thiols that with freshly prepared solutions the  $\text{I}_2$  and  $\text{Ag}^+$  titers agreed, but that with aged solutions, partially oxidized by air, the iodine titer was much higher than the silver titer. This suggested that while both silver and iodine were equally effective for estimating pure thiols, iodine was also reduced by some of the oxidation products of thiols, and therefore the silver was probably the more specific reagent. We attempted to confirm this value (from  $\text{Ag}^+$  titration) for the  $-\text{SH}$  concentration by developing a new analytical method. It is known that both alcohols and thiols react with carbon disulfide under alkaline conditions to form xanthates (III,  $\text{X} = \text{O}$ ) and trithiocarbonates (III,  $\text{X} = \text{S}$ ), respectively



Model experiments revealed that thiols react instantaneously while alcohols form xanthates only slowly. Furthermore, the spectra of trithiocarbonates are readily distinguishable from those of xanthates (see Fig. 12). By adding approximately the calculated amount of carbon disulfide and sodium hydroxide to the solution, and observing the instantaneous formation of the characteristic peaks at *ca.* 3000 and 3350  $\text{\AA}$ . the presence of microscopic

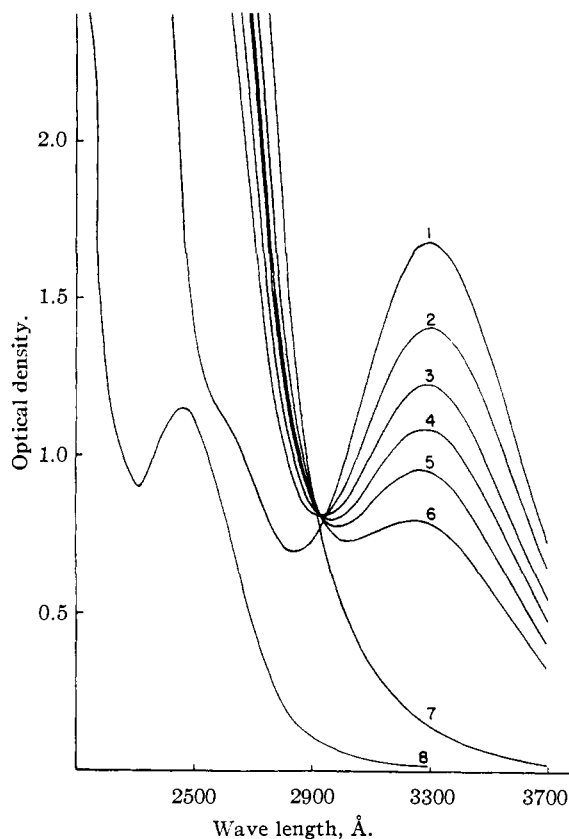


Fig. 10.—Oxidation of trimethylene disulfide by ammonium persulfate: 1, initial disulfide; 2, 1 +  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ; 3, 4, 5, 6, 7 = 2 at  $T = 0, 4, 9, 15, 25$  min. and 16 hr.; 8 = 7 diluted 10 times with 95% EtOH.

amounts of thiols in alcoholic solution may readily be detected. Unfortunately, the formation of trithiocarbonate appears to be reversible and the uncertainty as to the extent of reaction means that the method, while useful for qualitative detection, is of little value for quantitative estimation. Nevertheless, comparison between the heights of the 3000 and 3350  $\text{\AA}$ . peaks obtained from the reaction between the photolysis solution and carbon disulfide on the one hand and those of the trithiocarbonates derived from benzyl mercaptan and  $\beta$ -mercaptoethanol on the other indicated the formation of about one and less than two thiol groups from one molecule of trimethylene disulfide.

The finding that approximately one thiol group was formed from each molecule of trimethylene disulfide on photolysis raised the question of whether one group was attached to each 3-carbon fragment derived from the trimethylene disulfide or whether the photolysis produced a mixture containing some trimethylene dithiol and some 3-carbon units without thiol groups, the average being one thiol for each  $\text{C}_3$  unit.

Separate experiments had shown that trimethylene dithiol could readily be oxidized and in excellent yield to trimethylene disulfide by iodine under acid conditions or by hydroxylamine and alkali. In spite of repeated experiments no trimethylene disulfide could be found in any of the photolysis solutions after these treatments, thus demonstrating



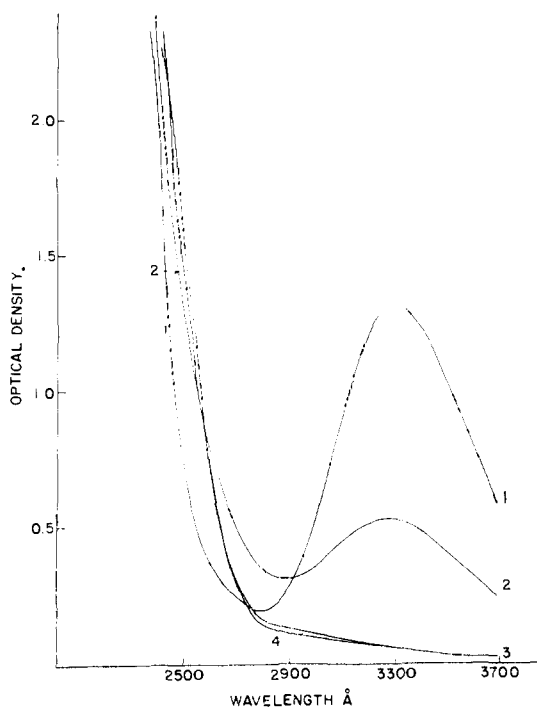
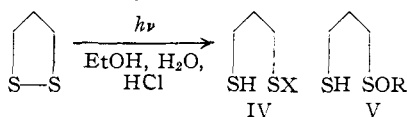


Fig. 11a.—Photolytic behavior of acidic alcoholic solution of trimethylene disulfide at room temperature: 1, original TMDS peak; 2, TMDS after 15 min. photolysis; 3, TMDS after 60 min. photolysis; 4, TMDS after 105 min. photolysis.

that the course of the photolysis could be represented schematically as



Having now established that one of the sulfur atoms of trimethylene disulfide was transformed on photolysis into a thiol, it became pertinent to inquire into the nature of the other, *i.e.*, what is “—S—X” in IV? Since one of the original sulfur atoms has been reduced, it follows that one or more of the components of the initial solution must have been oxidized. This could be accomplished in two ways: the components could either be directly dehydrogenated to some oxidation product which then became attached to the other sulfur atom or direct addition of one of the components to the S—S bond might take place.

The only substances present in the solution before photolysis are trimethylene disulfide, hydrochloric acid, water and ethanol. The simple oxidation of any of these to *e.g.*, chlorine, acetaldehyde, acetic acid, hydrogen peroxide, etc., is excluded since, for reasons of stoichiometry, trimethylene dithiol would also have to be formed. Their formation can only be reconciled with the absence of trimethylene dithiol if they subsequently react with one of the thiol groups of the dithiol giving VI, VII and VIII.

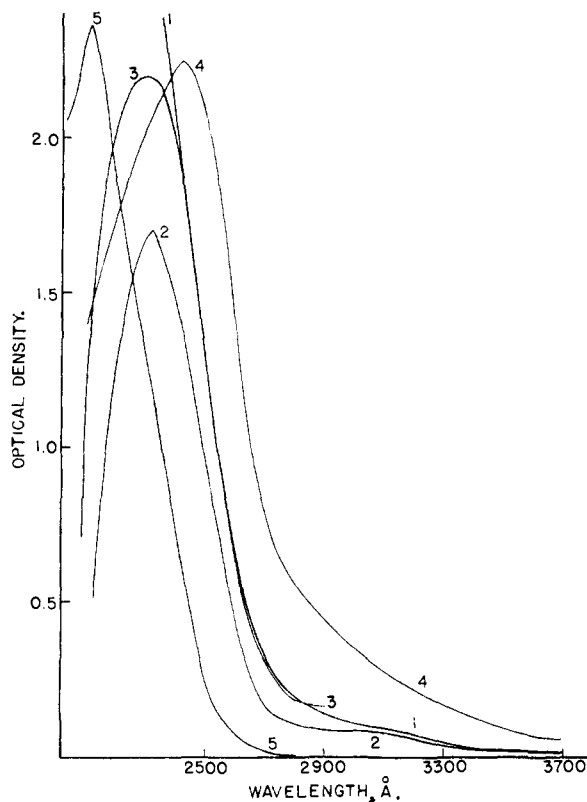
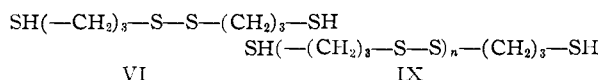
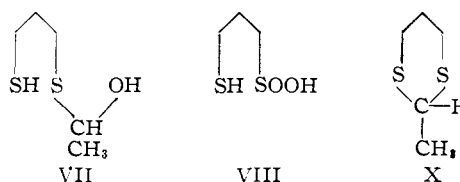


Fig. 11b.—Trimethylene disulfide acid photolysis solution after standing and with thiol compensation: 1, photolysis soln. (*vs.* EtOH); 2, photolysis soln.  $1 \times 10^{-2} M$ ; *vs.*  $\text{HSCH}_2\text{CH}_2\text{OH } 1.0 \times 10^{-2} M$ ; 3, photolysis soln.  $1 \times 10^{-2} M$ ; *vs.*  $\text{HSCH}_2\text{CH}_2\text{OH } 0.5 \times 10^{-2} M$ ; 4, photolysis soln.  $1 \times 10^{-2} M$ ; *vs.*  $\text{HSCH}_2\text{CH}_2\text{OH } 1 \times 10^{-2} M$  after standing overnight. 5,  $\text{HSCH}_2\text{CH}_2\text{OH } 1.0 \times 10^{-2} M$  *vs.* EtOH.



All these are improbable. It is difficult to see why interaction between chlorine (or hydrogen peroxide) and trimethylene dithiol should stop at VI—one would expect polymers of the type IX to be formed simultaneously. Also aliphatic disulfides have a peak  $\lambda_{\text{max}} \cong 2500$ ,  $\epsilon_{\text{max}} \cong 500$  (see Fig. 1) no evidence for which can be found in the ultraviolet spectrum of the photolysis solution (Fig. 12). The structure VII, a thio semiacetal, would certainly dehydrate into the cyclic thioacetal X and thus eliminate all thiol groups. Having considered direct oxidation of one of the components, the only other possibility for the primary photochemical act is addition of one of the solution components to the S—S bond of trimethylene disulfide. This leads to structures (V, R = H), (V, R =  $\text{C}_2\text{H}_5$ ), (IV, X = Cl) and to XI.

The structure (V, R = H) would be a sulfenic acid. With the exception of a sulfenic acid derived from anthroquinone<sup>32</sup> none are known to exist.

(32) K. Fries, *Ber.*, **45**, 2965 (1912).

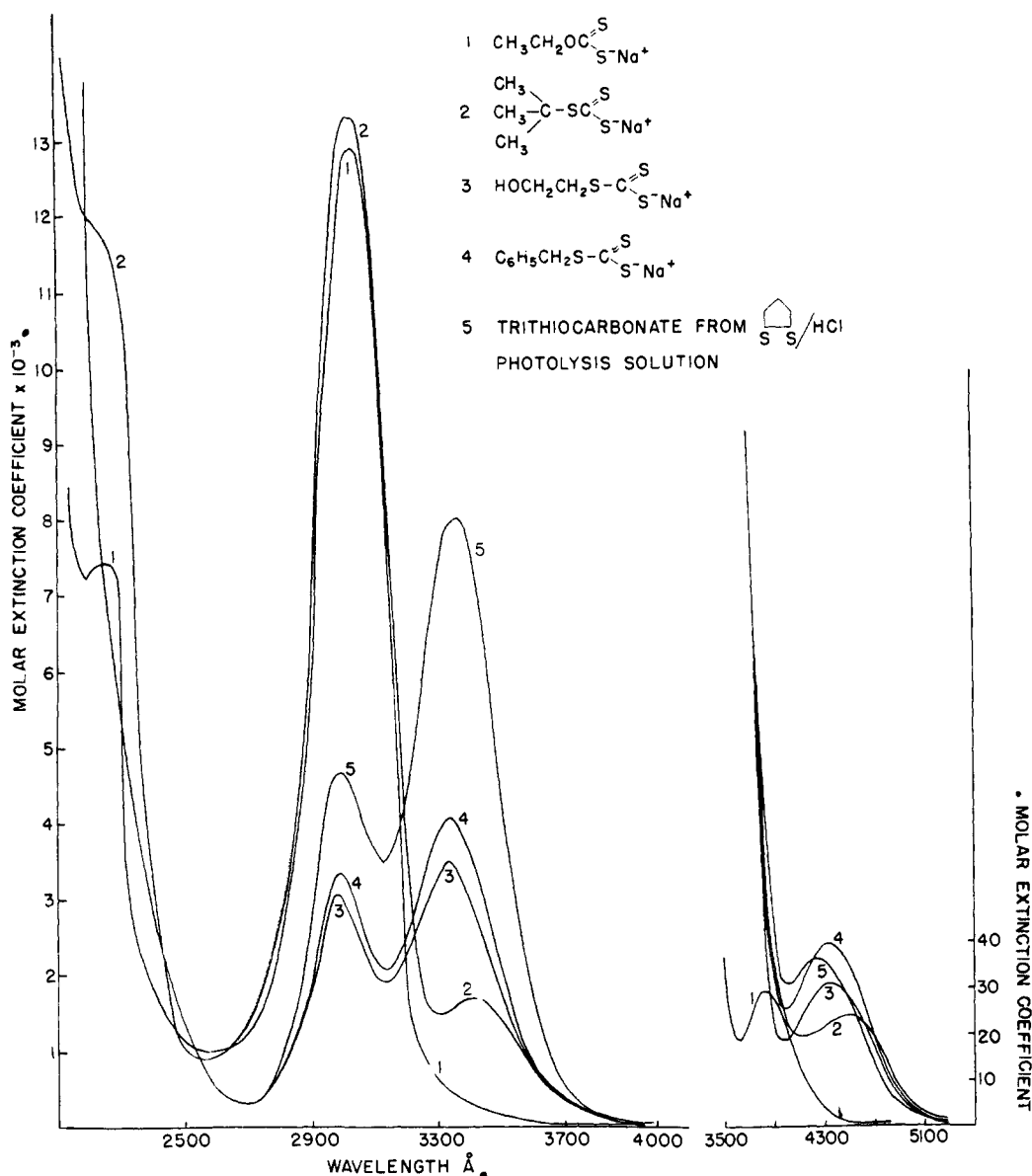
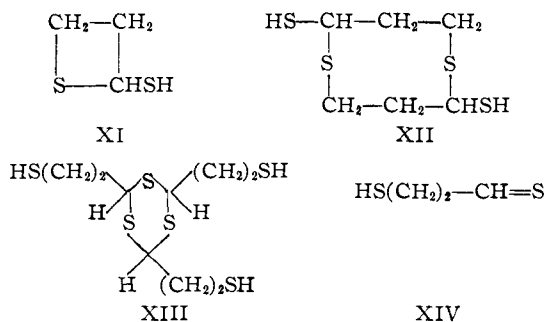


Fig. 12.—Trithiocarbonate formed by photolysis solution.

All attempts to prepare them have resulted in mixtures of dismutation products such as sulfenic acids, disulfides, thiosulfonic esters and thio ketones.<sup>33</sup>



The substance (V, R = C<sub>2</sub>H<sub>5</sub>) is a sulfenic ester.

(33) N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.*, **39**, 269 (1946).

Little is known of these substances.<sup>33</sup> The sulfonyl chloride (IV, R = Cl) would certainly not preserve its identity in the photolysis solution but might be expected to yield mixtures of substances such as sulfenic anhydride<sup>34</sup> and the usual dismutation products of sulfenic acids. So far as we have been able to ascertain, no semithioacetals are known. This does not exclude the possible formation of XI as the primary photochemical product, but on structural grounds we would expect it to be transformed into XII or more likely XIII through equilibration with the isomeric thiol thioaldehyde XIV. Thus general considerations suggest the conclusion that the primary photochemical transformation occurring when trimethylene disulfide is photolyzed should lead to XI or to (IV, X = OH, OEt or Cl) and that the actual solution obtained at the end of photolysis should consist either of one or more of

(34) Th. Zinke, *Ann.*, **406**, 106 (1914); **391**, 57 (1912).

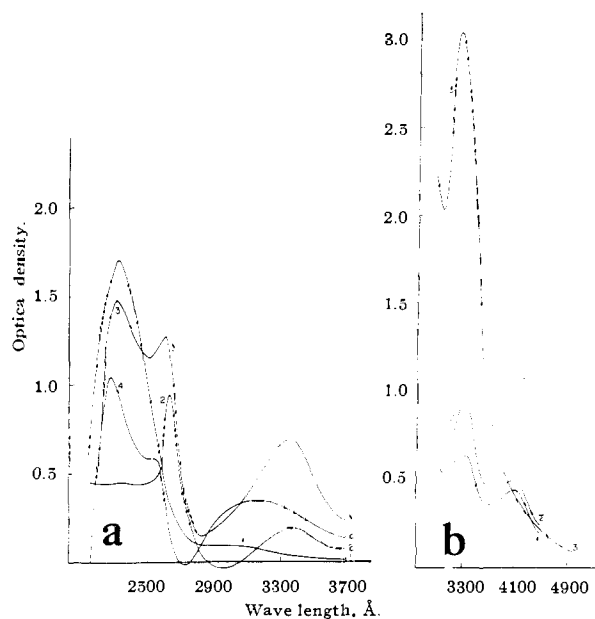


Fig. 13.—Effect of alkali on photolysis solution: (a) effect of  $\text{OH}^-$  on photolysis solution: 1, photolysis solution  $1.02 \times 10^{-2} M$ ; 2, photolysis solution +  $\text{NaOH}$ ; 3, =2 after 15 hours; 4, =3 after reacidifying, filtering and diluting slightly; all vs.  $\text{HSCH}_2\text{CH}_2\text{OH}$   $1.02 \times 10^{-2} M$ . (b) Effect of  $\text{OH}^-$  on TMDS photolysis solution: 1, photolysis soln. after adding  $\text{OH}^-$ ; 2, =1 after 25 min.; 3, =1 after 3 days.

these entities or of some transformation product or products derived therefrom.

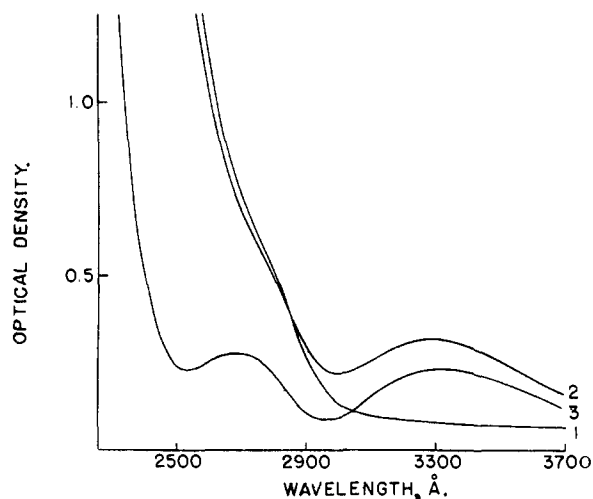


Fig. 14.—Stability of trimethylene disulfide to both acid and alkaline photolysis solution: 1, initial photolyzed trimethylene disulfide solution (1 equiv.  $\text{HCl}$ ); 2, photolysis solution 1 + 1 cc. of trimethylene disulfide solution; 3, distillate from alkaline 2.

At this point it became necessary to investigate the photolysis solution chemically in order to attempt to discriminate among these possibilities, but first in order to orientate the investigations we decided to experiment with model sulfenic esters. The only aliphatic sulfenic esters described in the lit-

erature are ethyl and methyl *t*-butyl sulfenate (XV) prepared by Rheinholdt and Motzkus.<sup>35</sup>



The ultraviolet absorption spectrum of the ethyl ester was found to have a characteristic peak at 2655 Å.,  $\epsilon_{\text{max}}$  70.5 (see Fig. 15). Spectroscopic investiga-

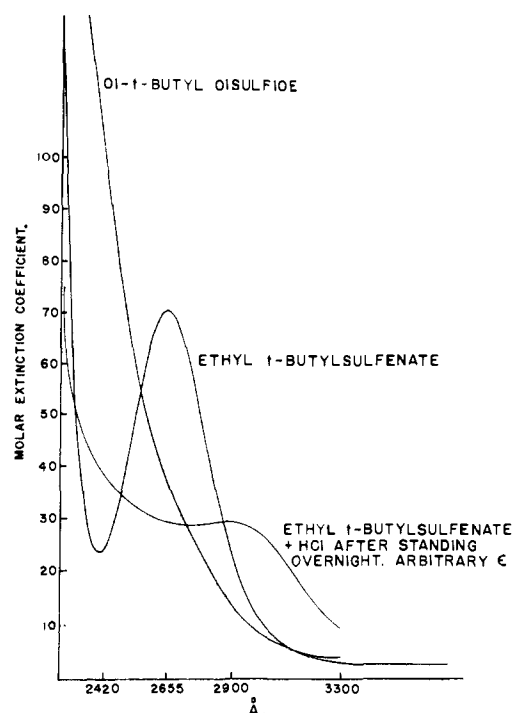


Fig. 15.—Absorption spectra in alcohol and sensitivity of ethyl *t*-butylsulfenate to acid.

tion then showed that the substance was stable to *ca.*  $M/40$  sodium hydroxide in aqueous alcohol for many hours. Hydroxylamine also had no detectable effect. Dilute acid, on the other hand, rapidly destroyed the ester in the cold to give a solution with an ultraviolet peak at *ca.* 2880 Å. Thus the sulfenic ester seems chemically to be related more closely to ethers than to esters. Because of the possible simultaneous occurrence in the photolysis solution of thiols and sulfenic esters, the reaction between (XV,  $\text{R} = \text{C}_2\text{H}_5$ ) and thiols was investigated. Under neutral conditions, thiols were without effect upon the *t*-butyl sulfenic ester in the cold. On making alkaline, however, a rapid reaction occurred (Fig. 16). With trimethylene dithiol, ethyl *t*-butyl sulfenate rapidly gave a moderate yield of trimethylene disulfide identified by its characteristic ultraviolet absorption peak at 3300 Å. Thus the ester oxidizes thiols to disulfides under alkaline conditions. It can function also as an oxidizing agent under acid conditions as shown by the rapid liberation of iodine from dilute hydriodic acid solutions.

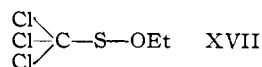
The known tendency of sulfenic derivatives to

(35) H. Rheinholdt and E. Motzkus, *Ber.*, **74**, 657 (1939); *C. A.*, **32**, 484 (1938).

dismute<sup>36</sup> into disulfides and other products suggested that the 2880 Å. peak mentioned earlier which develops on treating ethyl *t*-butyl sulfenate with acids might be due to di-*t*-butyl disulfide. In order to elucidate this point, some of the disulfide was synthesized by oxidizing *t*-butyl mercaptan with iodine in aqueous alcohol. It was observed during the preparation that although the iodine was rapidly destroyed, no definite end-point could be discerned; the solution became gradually yellow and then brown and the unforgettable and unmistakable smell of sulfenyl iodides developed, suggesting that the disulfide was fissioned by the slight excess of iodine into *t*-butyl sulfenyl iodide (XVI). The formation of sulfenyl iodides from aliphatic disulfides under these conditions is unique in our experience, although Fuson, *et al.*,<sup>37</sup> have shown that it is possible to fission di- $\beta$ -chloroethyl disulfide with chlorine in  $\text{CCl}_4$  solution into the sulfenyl chloride. This anomaly associated with the *t*-butyl disulfide was reflected also in its ultraviolet spectrum (Fig. 15). The substance is yellow, in contrast with all other known aliphatic disulfides, and instead of showing the characteristic 2500 Å. peak of aliphatic disulfides only end absorption was manifested. Thus the 2880 Å. peak mentioned above cannot be due to di-*t*-butyl disulfide. At this point it may be pertinent to point out that the spectrum of sodium *t*-butyl trithiocarbonate (Fig. 12) is also markedly different from those of the other trithiocarbonates.

These interesting observations on *t*-butyl disulfide suggested a more extended investigation in which it was discovered that the substance was an oxidizing agent capable of both liberating iodine from dilute hydriodic acid and oxidizing trimethylene dithiol to trimethylene disulfide, though much less effectively than ethyl *t*-butylsulfenate.

In view of the spectral anomalies associated with *t*-butyl compounds, we decided to make another sulfenic ester for comparison purposes. Trichloromethyl sulfenyl chloride was commercially available. It was treated with sodium ethoxide under conditions similar to those described for the synthesis of the *t*-butyl analog by Rheinholdt and Motzkus<sup>35</sup> to give ethyl trichloromethylsulfenate (XVII). We experienced difficulty in obtaining good analytical data for this substance—a difficulty



mentioned by Rheinholdt and Motzkus<sup>35</sup> in connection with the *t*-butyl analog. The substance had an absorption maximum in the same region as the *t*-butyl sulfenate (Fig. 18), but inverse chemical properties. Thus in contrast to ethyl *t*-butylsulfenate, the trichloromethyl sulfenic ester was stable to acid and sensitive to alkali. We are thus placed in the embarrassing position of having to decide which, if either, of these two model sulfenic esters is in fact a model for the supposed substance (V, R =  $\text{C}_2\text{H}_5$ ). In view of the profound change in chemical properties caused by introducing a tri-

(36) There appears to be no verb in the English language dictionary corresponding to the noun dismutation. In this paper, we propose to rectify this regrettable omission by introducing a new verb, "to dismute."

(37) R. C. Fuson, C. C. Price, *et al.*, *J. Org. Chem.*, **11**, 469 (1946).

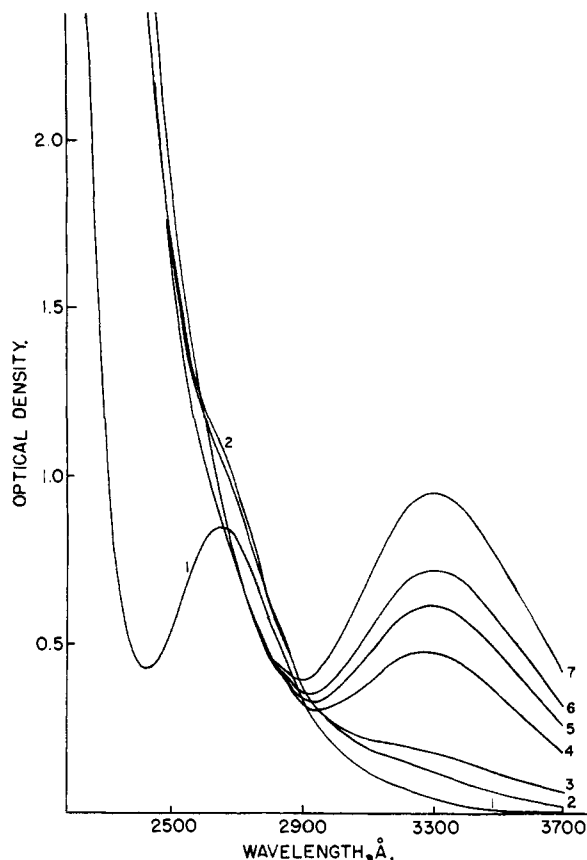


Fig. 16.—Oxidizing power and kinetics for ethyl *t*-butylsulfenate on trimethylene dithiol in alkaline solution: 1, ethyl *t*-butylsulfenate; 2, 1 + trimethylene dithiol; 3, 2 after ~10 min.; 4, 3 diluted ~1 volume with EtOH and added  $\text{K}_2\text{HPO}_4$ ; 5, 4 after 5 min.; 6, 4 after 15 min.; 7, 4 after 180 min.

chloromethyl group in a compound (*cf.* chloral and acetaldehyde) we inclined to the belief that the *t*-butylsulfenic ester was the better chemical analog, although it might not be good as a spectroscopic model.

A large number of experiments were performed on the solution obtained by photolyzing trimethylene disulfide in the presence of acid in the attempt to determine its precise constitution. The facts which emerged are these: On photolysis the 3300 Å. band of trimethylene disulfide gradually disappeared and a more intense absorption built up at wave length <2500 Å., but even when all the trimethylene disulfide had been destroyed, there was a residual absorption in the region just short of 3300 Å. (Fig. 11). No absorption maximum could be detected in the spectrum of the solution photolyzed at room temperature. However, thiols which have already been shown to be present in the solution show a similar absorption (see Fig. 11b) and it seemed possible that the thiol absorption was masking the bands of the groups present in the photolyzed solution. In order to neutralize as far as possible this masking thiol absorption, a solution of  $\beta$ -mercaptoethanol of concentration equal to the concentration of the initial trimethylene disulfide (silver titrations described earlier demonstrated the

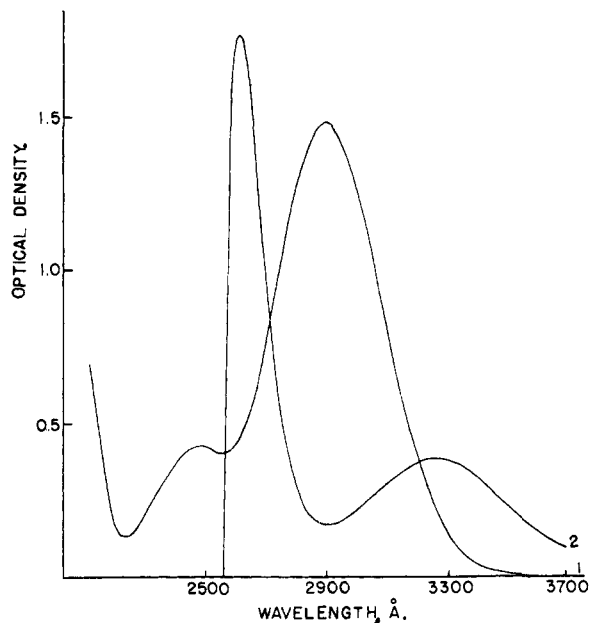


Fig. 17.—Absorption spectra of trichloromethylsulfenyl chloride: 1, trichloromethylsulfenyl chloride in EtOH; 2, trichloromethylsulfenyl chloride in  $\text{CCl}_4$ .

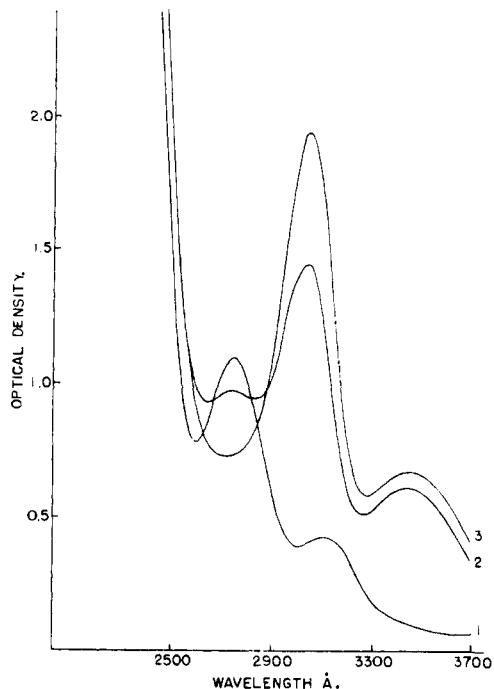


Fig. 18.—Sensitivity of ethyl trichloromethylsulfenate to alkali: 1, ethyl trichloromethylsulfenate before adding NaOH; 2, 50 min. after adding NaOH; 3, ethyl trichloromethylsulfenate 4 hours after adding NaOH (concn. different from 1).

formation of *ca.* one thiol group per initial trimethylene disulfide molecule present at the commencement of photolysis) was introduced into the compensating cell of the spectrophotometer. In this way, the instrument will subtract automatically the absorption due to the thiol and the resultant spectrum should then represent the absorption of other

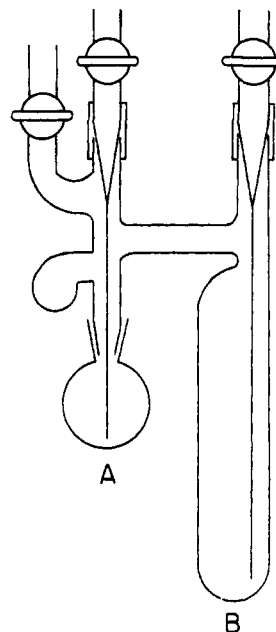


Fig. 19.—Equipment for demonstrating spectroscopically the chemical behavior of photolysis solution: A, Cary absorption cell; B, photolysis cell.

groups present in the photolyzed solution. When this was done (Fig. 11b) a maximum appeared at 2320 Å. That this band probably is not an artifact is indicated by the fact that it remains in essentially the same position ( $\lambda_{\text{max}}$  2290 Å.) when only one-half of the previous concentration of thiol is introduced into the compensating cell. That the photolysis solution contains entities sensitive to acid is

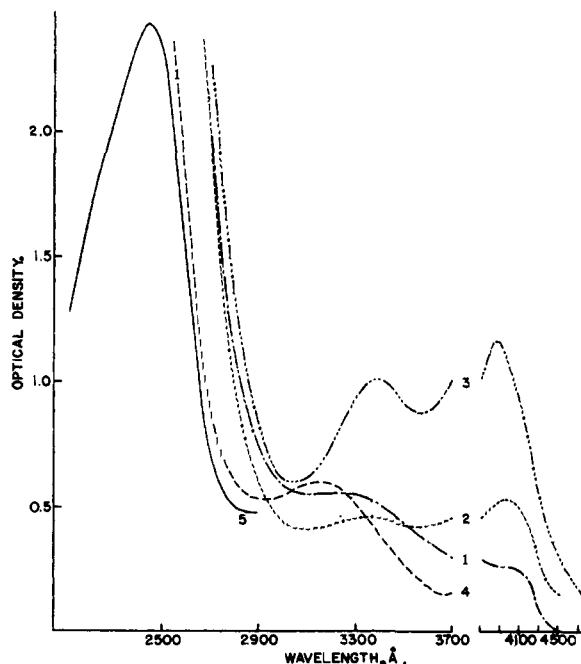


Fig. 20.—Photolysis of trimethylene disulfide in alkaline medium: 1, trimethylene disulfide + NaOH after 10 min. photolysis; 2, after 25 min. photolysis; 3, after 105 min. photolysis; 4, 3 after acidification; 5, 4 with thiol compensation.

demonstrated by the fact that while no change occurs in the spectrum if the solution is kept at  $-20^\circ$  for 24 hours, keeping it at room temperature causes the 2320 Å. peak to move 2420 Å. (Fig. 11b).

The photolysis solution is very sensitive to alkali which causes instantaneous elimination of the 2320 Å. peak and the development of maxima at 2629 Å. and more slowly at 3340 Å. and 4100 Å. and still more slowly at 2310 Å. On reacidifying, the bands at 3340 and 4100 Å. are destroyed immediately and replaced by bands at 2820 and 2350 Å. Making alkaline again causes reappearance of the 3340 and 4100 Å. maxima. With variations in degree, reference to Figs. 13 and 20 shows that similar phenomena were encountered both with solutions of trimethylene disulfide photolyzed at low temperatures and in solutions photolyzed in the presence of sodium hydroxide. Especially notable is what appears to be a definite maximum of low intensity at  $\approx 3100$  Å. in the low temperature photolysate.

In the time at our disposal, it has proved impossible to unravel completely the complexities in these transformations occurring in photolyzed solutions of trimethylene disulfide. But certain conclusions are inescapable.

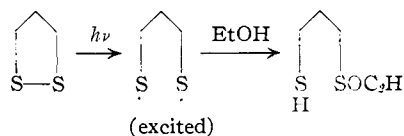
Firstly, the photolyzed solution is markedly unstable, particularly to alkali. Secondly, the solution possessed oxidizing power. This is demonstrated by the oxidation of trimethylene dithiol to trimethylene disulfide. Also the bands which appear at 3340 and  $\sim 4200$  Å. when the solution is made alkaline and their disappearance when it is reacidified are strongly reminiscent of dithiocarboxylic acids. Hantzsch and Bucerius<sup>38</sup> give for dithioacetic acid,  $\lambda_{\max}$  2950 Å. and for the ammonium salt,  $\lambda_{\max}$  3330 Å. The formation of dithio acids from a substance which before photolysis was at the oxidation level of a disulfide must involve oxidation. Whether the tentative assignment of those bands to dithio acids is correct or not, the transformation of compounds of the photolysis solution into substances absorbing at such long wave lengths can only mean the development of multiple carbon or sulfur bonds (*i.e.*, oxidation) for these bonds can be developed in the absence of halogens. Furthermore, the formation of unequivocally acid substances such as those giving rise to these bands requires the presence of oxidizing agents in the original photolysis solution. Thirdly, the solution possesses reducing power in addition to that furnished by the liberated thiol groups, as shown by the value for the iodine titer.

The arguments advanced earlier in this paper limited the structure of the primary photolytic product to (V, R = OH, OEt, Cl) or to XI. The fact that similar products appear to be formed when trimethylene disulfide is photolyzed under both alkaline and acid conditions, as well as with a variety of acid anions, eliminates structures (V, R = Cl).

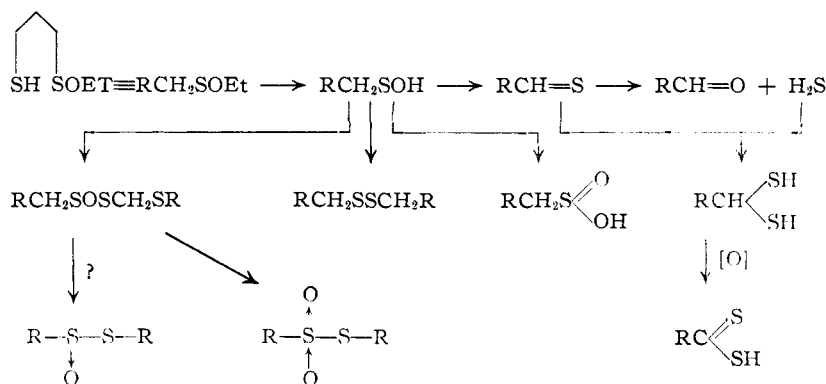
(38) A. Hantzsch and W. Bucerius, *Ber.*, **59**, 793 (1926).

We can find no rationale by which to explain the diversity of products derivable from the photolyzed solution in terms of the structure XI and we are left only with (V, R = OH or OEt).

We can thus postulate with reasonable confidence the idea that when trimethylene disulfide is photolyzed in ethanol solution the sulfenic ester (V, R = OEt) is the primary chemical product

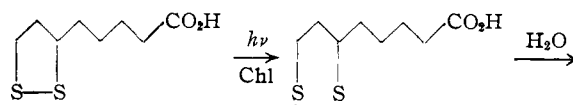


and that the solution at the end of the photolysis contains its transformation products. The well-established instability of sulfenic acid derivatives, their extreme tendency to dismute (shown also by sulfur monoxide, the inorganic analog), and their oxidizing power are completely in accord with the data obtained from photolyzed solutions of trimethylene disulfide. Furthermore, hydrogen sulfide which was detected in the photolyzed solutions is an expected decomposition product of certain sulfenic acids (*cf.* Schöberl<sup>39</sup>). The various decomposition products could be derived by such reactions as

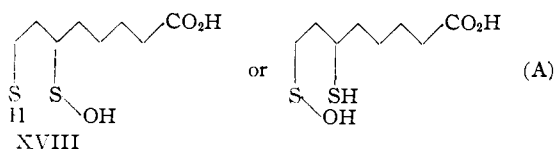


and what has been discovered of the properties of the photolyzed solution is entirely consistent with this formulation.

If the suggestion that photolysis of trimethylene disulfide in ethanol solution leads to a sulfenic ester be correct, the question immediately arises, as to what is its relevance to the process of photosynthesis. In an earlier communication, Calvin and Bartrop<sup>18</sup> advanced arguments in support of the idea that  $\beta$ -thioctic acid was directly involved in the quantum conversion step of photosynthesis but the steps by which water was oxidized to molecular oxygen was not specified. The above work with trimethylene disulfide leads us directly to the further suggestion that water itself or some very closely related hydroxylic substance is the primary hydrogen donor, *i.e.*, that the primary photochemical act of photosynthesis involves the splitting of the O-H bond as



(39) A. Schöberl, *ibid.*, **70B**, 1186 (1937).



It is difficult to assess the feasibility of this process from considerations of the energy changes involved since most of the critical data are lacking. However, assigning values of 120 and 85 kcal., respectively, to the bond energies of the O-H ( $E_{O-H}$ ) and S-H ( $E_{S-H}$ ) bonds, the change in energy of the system would be

$$\Delta E \text{ (kcal.)} = 35 + (E_{S-S} - E_{S-O})$$

No thermodynamic measurements involving the S-O link have been reported in the literature and there seems to be a considerable diversity of opinion on the S-S bond. However, we may estimate the difference ( $E_{S-S} - E_{S-O}$ ) by analogy with  $F_2$  (35),  $Cl_2$  (57) and  $FCl$  (60)<sup>40</sup> to be zero or somewhat negative. Since  $E_{S-S}$  for the dithiolane ring seems to be at least about 6 kcal. less than that for an open chain disulfide the net energy requirement for the reaction would be about 30 kcal. If the size of the quantum passed on by the chlorophyll is something less than 40 kcal., then this process would not only be possible but would represent a relatively efficient utilization of the quantum.

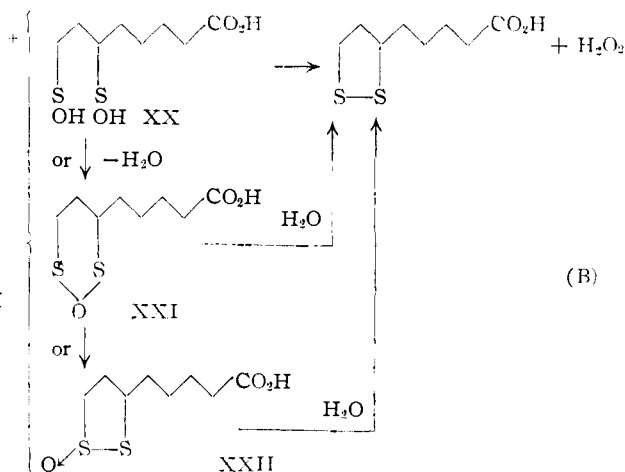
It should be noted that sulfenic acids are the sulfur analogs of alkyl hydroperoxides. Thus in one step, the oxygen of water (or its hydroxylic relative) has been brought to the oxidation level of peroxide while one of the hydrogen atoms has been raised to a reduction potential approaching that of molecular hydrogen.<sup>41</sup> In order to liberate oxygen from water the energy of several quanta is required, and how these may be accumulated has been the subject of prolonged discussion.<sup>42</sup> Assuming only a single type of quantum conversion process always producing the same chemical entity, we must have a dismutation between two such systems whereby one drops to a low energy state and the other is raised to a higher energy level; repetition of these dismutations, if necessary, would lead ultimately to a system with sufficient energy to effect the fission of water. Now, what emerges more clearly than anything else from a survey of the literature on sulfenic acids is their tendency to dismute.<sup>34</sup> The only known sulfenic acids are those of Fries<sup>32</sup>—all other attempts to prepare them have resulted merely in the isolation of their dismutation

(40) K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Inc., New York, N. Y., 1953.

(41) M. Calvin, "Mercaptans and Disulfides," presented at the Conference on Glutathione, Ridgefield, Conn., November 20-22, 1953. Academic Press, Inc., New York, N. Y., 1954.

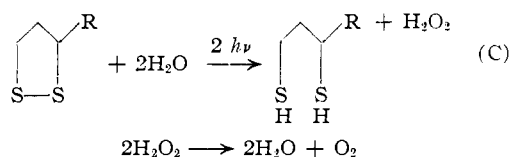
(42) E. I. Rabinowitch, "Photosynthesis. I," 1951; "Photosynthesis. II. Part 1," Interscience Publishers, Inc., New York, N. Y., 1945.

products. Similarly, all reactions in which sulfenic acids have been postulated as intermediates lead to the decomposition or dismutation products of sulfenic acids. We thus feel justified in suggesting that the thioctic sulfenic acid (XVIII) once formed, would dismute. In view of our limited understanding of the chemistry of sulfenic acids the nature of this dismutation is difficult to predict, but in order to crystallize the situation, we tentatively propose a dismutation into 6,8-dithioloctanoic acid (XIX) and a molecule at the energy level of hydrogen peroxide (possibly XX, XXI or XXII) which then decomposes into hydrogen peroxide and 6-thioctic

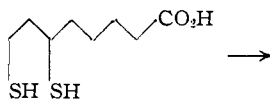
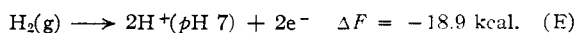
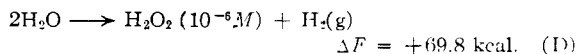


The dithiol XVIII can then provide the reducing power required to convert carbon dioxide into sugars—possibly through the reduction of TPN or DPN.<sup>43</sup> The hydrogen peroxide may lead through catalase to molecular oxygen.

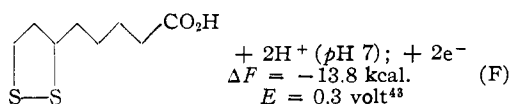
Adding equations A and B gives the over-all reaction



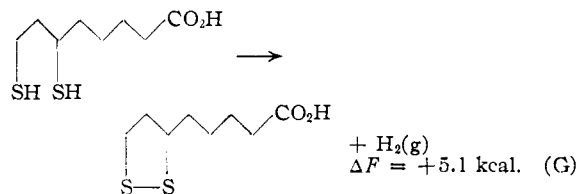
and this leads, on purely stoichiometric grounds, to the requirement that four quanta be utilized for each molecule of oxygen evolved, not considering losses or any other concomitant energy requirements that might exist. The question still remains to be answered—is quantum conversion by the mechanism of equation C thermodynamically possible? The literature contains the data



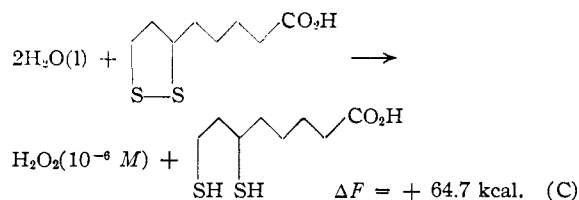
(43) I. C. Gunsalus, in McCollum-Pratt Institute Symposium on "Mechanism of Enzyme Action," Johns Hopkins University Press, Baltimore, Md., 1954.



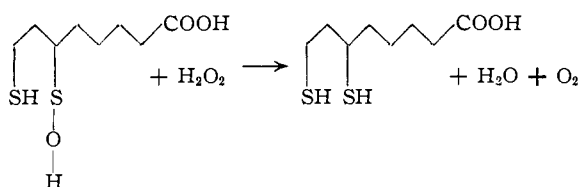
Subtracting E from F



From D and B by subtraction we get



Hence the increase in free energy involved in the proposed photosynthetic equation (C) is  $\cong 65$  kcal. Since this has to be provided by two quanta, the energy of the excitation passed on by chlorophyll should be not less than  $\cong 32$  kcal., a figure which is well within the bounds of possibility. The energy required for a photosynthesis process following the above mechanism might well be less than *ca.* the 65 kcal. per atom of oxygen liberated calculated above, for two reasons. Firstly, it is entirely possible that the plant might be able to evolve oxygen directly from the dismutation product B without necessarily using the energy-rich hydrogen peroxide as an intermediate.<sup>44</sup> Secondly, should hydrogen peroxide be an intermediate, then it is, in principle, possible usefully to recover the energy stored in the molecule by using it as a reducing agent, *e.g.*



thus providing a three quantum route to one molecule of oxygen. These considerations of the energy relationships lend support to the proposed scheme for the quantum conversion process in photosynthesis.

### Experimental Part

1. **Synthesis of Trimethylene Disulfide.**—Pulverized sodium sulfide nonahydrate (120 g.) was dissolved in boiling 95% ethanol (500 cc.) and heated under reflux with sulfur (17 g.). When the sulfur had dissolved, the brown two-phase solution was dispersed by shaking and added during 20 minutes to a boiling solution of trimethylene dibromide (49 cc., 0.48 mole) in 95% ethanol (250 cc.). The mixture was then distilled under reduced pressure: 750 cc. of a bright yellow distillate (A) was collected. More 95% ethanol was added to the residue which was again distilled under reduced pressure to give 600 cc. of a pale yellow distillate (B). The optical densities (at 3300 Å.) of solutions A and B were 6.7

(44) A. H. Mehler, *Arch. Biochem. Biophys.*, **33**, 65 (1951); **34**, 339 (1951).

and 1.98, respectively. Since trimethylene disulfide prepared this way sometimes contains a significant amount of thiacyclobutane, the molar extinction coefficient of the 3300 Å. band of trimethylene disulfide will have a contribution due to this impurity. This may be removed by fractionating the solution through a 15-plate column until no more distillate with an ultraviolet peak  $\lambda_{\text{max}}$  2720 Å. distills.<sup>45</sup> The bulk of the reaction product is a solid which may be obtained from benzene-chloroform as colorless crystals, m.p. *ca.* 73°. This is presumably the "dimer" obtained by Autenrieth and Wolff.<sup>20</sup> It may be depolymerized slowly to trimethylene disulfide by steam distilling with strong sodium hydroxide and sodium disulfide.

(a) **Molecular Weight of Trimethylene Disulfide.**<sup>46</sup>—Ten cc. of crude trimethylene disulfide in petroleum ether (*ca.* 1 M) was evaporated in a vacuum desiccator leaving 1.35 g. of crude trimethylene disulfide, a few mg. of polymer and possibly traces of petroleum ether. This was taken up in 10 ml. of benzene. The freezing point of 43.75 g. of benzene to which 1-ml. aliquots of this solution were added successively was determined with a Beckmann thermometer. The maximum depression ( $\Delta T_f$ ) was 0.703° (for 47.57 g. of benzene and 0.684 g. of trimethylene disulfide) with a maximum deviation from linearity (of the intermediate points) in the weight of trimethylene disulfide/weight of benzene *vs.*  $\Delta T_f$  plot of  $<0.005^\circ$ . Using 5.49° as the freezing point and 30.4 cal./g. as the heat of fusion of benzene, the found molecular weight is 104 for trimethylene disulfide (calcd. molecular weight 106).

2. **Synthesis of Tetramethylene Disulfide.**—This preparation is similar to that of trimethylene disulfide except that tetramethylene dibromide is used. The reaction mixture was extracted with light petroleum instead of being distilled. The extract was concentrated and distilled under reduced pressure. Tetramethylene disulfide was collected at 82° (150 mm.) and was purified by sublimation. It formed colorless needles (25% yield), m.p. 32–33°.

*Anal.* Calcd. for  $\text{C}_4\text{H}_8\text{S}_2$ : S, 53.34. Found: S, 53.30.

3. **Properties of Trimethylene Disulfide.**—The substance can be obtained in the form of an unstable, unpleasant smelling oil by cautiously evaporating a pentane solution under strongly reduced pressure in a stream of nitrogen. Attempts to distill it even under reduced pressure caused it to be transformed into a colorless rubbery polymer on the walls of the condenser. In solution it is destroyed by oxygen and is polymerized by light. Even in the dark in an atmosphere of nitrogen at sub-zero temperatures, solutions will sometimes become turbid if kept in certain flasks. However, pure solutions of the disulfide can readily be obtained from the partially polymerized solutions by distilling under reduced pressure. Iodoacetamide does not react with it in the cold and it is stable to reduction by sodium borohydride, as is the related 6-thioctic acid. It is, however, much more rapidly reduced by zinc dust in the presence of dilute hydrochloric acid than are other aliphatic disulfides. Also, in contrast to other aliphatic disulfides, trimethylene disulfide appears to be stable to the action of potassium cyanide solution.

4. **Extinction Coefficient of Trimethylene Disulfide.**—A freshly distilled aqueous ethanol solution of trimethylene disulfide was found spectroscopically to be free from dimer and polymers (optical density of 3300 Å. band 0.801). One hundred cc. of this solution was reduced in a stoppered measuring cylinder by shaking with zinc dust (200 mg.) and concentrated hydrochloric acid (1.5 cc.). Spectroscopic examination showed reduction to be almost complete in five minutes and quantitative in ten minutes. The small amount of unreacted zinc was spun down and the amount of dithiol solution was treated under nitrogen with 10 cc. of  $1.022 \times 10^{-2} N$  iodine ( $I_2$ ) and immediately back titrated under nitrogen with  $1.00 \times 10^{-2} N$  sodium thiosulfate solution; 4.83 cc. of thiosulfate was required as the average of several titrations. Hence, normality of trimethylene dithiol =  $(10.22 - 4.83)/5 \times 10^{-2}$ , *i.e.*, molarity =  $1/2 \times$

(45) Dr. G. Waddington, (private communication) gives  $\lambda_{\text{max}}$  (in iso-octane) *ca.* 2760 Å.

(46) We are indebted to Dr. D. F. Bradley, of our laboratory, for the freezing point determinations.



normality =  $0.539 \times 10^{-2} M$ . Therefore, molar extinction coefficient of trimethylene disulfide =  $0.801 / (0.539 \times 1.015) \times 10^2$  (where the factor 1.015 corrects for dilution of disulfide by added hydrochloric acid) = 147.

**5. Quantitative Reoxidation of Trimethylene Dithiol to Trimethylene Disulfide by Iodine.**—Three cc. of the solution of trimethylene dithiol obtained in the preceding experiment was treated with 2.8 cc. of  $1.022 \times 10^{-2} N$  aqueous iodine solution. (The data of the preceding experiment show that this corresponds to 88.5% oxidation of the dithiol.) The partially oxidized solution examined spectroscopically showed trimethylene disulfide (optical density of the 3300 Å. band is 0.37). The solution was quite clear, indicating absence of polymers. The original disulfide solution of the preceding experiment (optical density 0.801) was diluted during reduction by a factor of 1.015 and during the iodine reoxidation diluted further by a factor of 5.8/3. Thus, if the original disulfide had been reduced quantitatively and reoxidized without dilution, the calculated optical density of the 3300 Å. band would be

$$0.37 \times \frac{5.8}{3} \times \frac{100}{88.5} \times 1.015 = 0.82$$

Since the actual optical density of the initial disulfide is 0.801 the yield of trimethylene disulfide obtained by oxidizing trimethylene dithiol with iodine equals 102%.

**6. Catalyzed Aerial Oxidation of Trimethylene Dithiol.** (a).—Twenty cc. of a freshly distilled aqueous ethanol solution of trimethylene disulfide (3300 Å. band optical density 0.89) was reduced with zinc dust (50 mg.) and concentrated hydrochloric acid (0.2 cc.). To 2.5 cc. of this solution was added 0.5 cc. of an approximately  $10^{-2} N$  iodine in aqueous potassium iodide. Some trimethylene disulfide was formed (optical density of 3300 Å. band 0.23). After various intervals of time the spectrophotometer cell containing the reaction mixture was opened to the atmosphere, closed, shaken vigorously to aerate the mixture and then re-examined spectroscopically. By repetition of these operations the optical density of the 3300 Å. band increased gradually to a maximum value of 0.74. Had no dilution taken place during the addition of the iodine solution, the height of the band would have been  $0.74 \times (3/2.5) = 0.89$ . Since the optical density of the initial trimethylene disulfide is 0.89, this corresponds to a 100% yield in the reduction and aerial reoxidation of the disulfide.

(b).—A solution of trimethylene dithiol in 95% ethanol (approximately  $10^{-2} M$ ) was shaken with air. No trimethylene disulfide was found spectroscopically. Ten cc. of the solution was agitated for ten minutes with zinc dust (25 mg.) and concentrated hydrochloride (0.1 cc.) and centrifuged from unreacted zinc dust. The supernatant solution was shaken with air and examined spectroscopically. No detectable amount of trimethylene disulfide was formed. Potassium iodide (23 mg.) dissolved in water (0.2 cc.) was added to 3 cc. of the supernatant solution and the mixture then shaken with air. Trimethylene disulfide was formed rapidly. Trimethylene dithiol was also oxidized rapidly to trimethylene disulfide by shaking with air in the presence of sodium hydroxide.

**7. Photolysis of Diphenylpicrylhydrazyl and Trimethylene Disulfide.**—The following solutions were prepared: diphenylpicrylhydrazyl (8.3 mg.) in ethanol (100 cc.) and freshly distilled trimethylene disulfide in aqueous ethanol ( $1.19 \times 10^{-2} M$ ). The apparatus was a closed Klett tube fitted with a side arm and gas inlet and outlet through stopcocks. It was charged with the hydrazyl solution (10 cc.) and the disulfide solution (1 cc.). After deoxygenating the mixture in a stream of pure nitrogen saturated with ethanol for half an hour, the fading of the diphenylpicrylhydrazyl, both in the light and in the dark, was followed by density measurements in a Klett colorimeter using a red filter. Illumination was effected between opposed photospot lamps behind infrared absorbing filters, the apparatus being kept cool in an air blast. A control experiment was performed by introducing into the apparatus a mixture of the diphenylpicrylhydrazyl (10 cc.) and ethanol (1 cc.) and repeating the above sequence of operations. The data obtained are shown in Fig. 3. Previous experiments had shown that the colorimeter density measurements were proportional to the concentration of diphenylpicrylhydrazyl.

**8. Pyrolysis of Trimethylene Disulfide in *n*-Octane.**—A solution of trimethylene disulfide in light petroleum was

prepared by diluting a freshly distilled alcoholic solution of the substance with water and extracting with several small portions of light petroleum and washing and drying the extract. This extract was diluted with approximately 20 times its volume of *n*-octane to give a solution of approximately  $6.8 \times 10^{-3} M$ . Five-cc. portions of this mixture were pipetted into thick-walled tubes, deoxygenated, sealed and heated in the dark at 141° and 174°. After appropriate time intervals, the tubes were opened and the spectra of the contents recorded with a Cary recording spectrophotometer. The height of the 3300 Å. band was used to estimate the amount of the disulfide which had been destroyed. The graph (Fig. 4) shows the data obtained. From the linear plot of unreacted disulfide against time, the pyrolysis would seem to be first order with respect to the disulfide. Because the products of the reaction appeared to have an adsorption band at short wave lengths, the tail of which extended as far as 3300 Å., an attempt was made to correct for this by taking the height of the main absorption band of trimethylene disulfide at wave lengths longer than 3300 Å. The fact that the slope of the graphs for various wave lengths, changes little indicates that this effect is probably small. The most accurate kinetic data are probably derived from the results at 3300 Å.

174°: Velocity constant  $k_2 = (2.3/t) \log (X_0/X)$  where  $X_0$  and  $X$  concentrations of trimethylene disulfide at  $t = 0$  and  $t = t$  sec.

Substitute  $X_0 = 0.65$ ,  $X = 0.44$ ,  $t = 14,400$  sec.

$$k_2 = 2.70 \times 10^{-5} \text{ sec.}^{-1}$$

141°:  $X_0 = 0.74$ ,  $X = 0.60$ ,  $t = 16,800$  sec.

$$k = 1.24 \times 10^{-5} \text{ sec.}^{-1}$$

Substituting these values for  $k_1$  and  $k_2$  into the relation

$$\Delta H_2 = \frac{RT_1 T_2}{T_2 - T_1} \times 2.3 \log \frac{k_2}{k_1}$$

gives  $\Delta H = 8.7$  kcal.

**9. Photolysis of Trimethylene Disulfide at Low Temperatures in Ether-Pentane-Alcohol Glass** (Fig. 5).—A freshly distilled solution of trimethylene disulfide in aqueous ethanol was diluted with water and extracted into *n*-pentane. The extract was washed with water, dried over calcium sulfate and then diluted with ether and alcohol in the ratio: pentane extract 5 parts, ether 5 parts, alcohol 2 parts, and the spectrum recorded. The solution was introduced into a 1-cm. Corex spectrophotometer cell, deoxygenated in nitrogen and sealed. The cell was mounted in a quartz Dewar attached to a Beckman spectrometer and rapidly cooled in liquid nitrogen. When the solution had set to a transparent glass, the spectrum was taken after first pumping off the liquid nitrogen to a level below that of the light path. The cell was reimmersed in liquid nitrogen and ultraviolet radiation from a high pressure mercury arc filtered by a 2 mm. Corning filter No. 7740 was focused upon the disulfide with a quartz lens. The spectrum of the solution was taken again after 20 and 30 minutes, by which time very little, if any, of the disulfide was left. At this point the solution was of a delicate pale salmon pink color. Sudden crystallization of the glass prevented our examining the spectrum at wave lengths longer than 4200 Å. The bulk of the liquid nitrogen was now distilled off, but the cells were kept in the Dewar flask so that they might warm up very slowly in the dark. When they had attained room temperature, the cell originally containing the disulfide was found to be turbid. The solution was clarified by ultracentrifuging and its spectrum taken. The reappearance of the characteristic 3300 Å. and of the disulfide with an optical density of 0.95 indicates a >50% recovery of the disulfide.

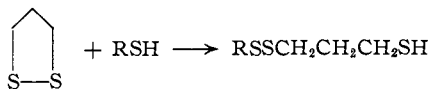
**10. Equilibrium between Trimethylene Disulfide and  $\beta$ -Mercaptoethanol.** (a).—A freshly distilled aqueous ethanol solution of trimethylene disulfide examined spectroscopically in a 1-cm. cell had an optical density of 1.42 at 3300 Å.  $\beta$ -Mercaptoethanol (23.5 mg. = ca. 20  $\mu$ ) was weighed into a spectrophotometer cell, trimethylene disulfide solution (3.0 cc.) added, and the optical density of the 3300 Å. band recorded on a Cary spectrophotometer as a function of time. The optical density dropped rapidly at first and then leveled off to a constant value of 1.06.

(b).—The sequence of operations described in (a) was repeated using  $\beta$ -mercaptoethanol (110 mg.  $\cong$  100  $\mu$ ) and tri-

methylene disulfide solution of initial optical density of 1.68; final optical density = 0.65.

(c).—The equilibrated solution of (b) was diluted with two volumes of ethanol. This caused the optical density to increase to a final value of 0.365.

Assume the equilibrium being measured is



if  $a$ ,  $b$  and 0 are the initial concentrations of these entities, respectively, then at equilibrium after  $x$  moles of reaction, their concentrations are  $(a - x)$ ,  $(b - x)$ <sup>47</sup> and  $x$  and the equilibrium constant will be

$$K = \frac{\text{aliphatic disulfide}}{\text{cyclic disulfide} \times \text{thiol}} = \frac{x}{b(a - x)}$$

For (a) above,  $a = (1.42/147) \times (3.0/3.02) = 0.960 \times 10^{-2}$  mole/liter where 147 = extinction coefficient of trimethylene disulfide and the factor 3.0/3.02 corrects for dilution of disulfide by the added  $\beta$ -mercaptoethanol

$$a - x = 1.06/147 = 0.721 \times 10^{-2} \text{ mole/liter}$$

$$x = 0.239 \times 10^{-2} \text{ mole/liter}$$

$$b = 23.5/3 \times 78 = 10.05 \times 10^{-2} \text{ mole/liter}$$

Hence  $K = 3.30$  and for (b) and (c),  $K = 3.31$  and 3.20, respectively.

11. **Equilibrium between Trimethylene Disulfide and Benzyl Mercaptan.** (A).—(1) The experiment described above for  $\beta$ -mercaptoethanol was repeated using benzyl mercaptan (20  $\lambda$ ) which was added to trimethylene disulfide, initial and final optical densities = 1.75, 0.97, respectively. Since the density of benzyl mercaptan is 1.058,  $K$  is 13.9. (2) More benzyl mercaptan (40  $\lambda$ ) was added to the equilibrated solution; new final optical density = 0.545; hence  $K = 12.8$ . (3) The equilibrated solution of 2 was diluted with two volumes of ethanol; the new equilibrium optical density is 0.33; hence  $K = 12.7$ .

(B).—(1) Benzyl mercaptan (5  $\lambda$ ) added to trimethylene disulfide, initial and final optical densities of 3300  $\text{\AA}$ . band were 1.44 and 1.20, respectively; hence  $K = 13.8$ . (2) More benzyl mercaptan (15  $\lambda$ ) added; new equilibrium optical density = 0.81; hence  $K = 13.4$ . (3) Equilibrated solution of 2 was diluted with 15 volumes of ethanol. Equilibrium optical density measured in 5 cm. cell = 0.43; hence  $K = 11.1$ .

**Strain Energy of Trimethylene Disulfide.**—Equilibrium determinations similar to those described above were performed in 1-cm. photometer cells surrounded by a jacket through which water at constant temperature circulated. At equilibrium the actual temperature in the reaction vessel was recorded. (a) 24.1°: Freshly distilled trimethylene disulfide solution (optical density 1.55) (3.0 cc.) was added to benzyl mercaptan (26.0 mg.). At equilibrium the optical density was 0.71; hence  $K_{24.1} = 16.9$ . (b) 35.8°: Trimethylene disulfide solution (optical density 1.51) (3.00 cc.) added to benzyl mercaptan (28.6 mg.). At equilibrium the optical density was 0.81; hence  $K_{35.8} = 11.23$ . Substitution of these data into the isochore

$$\log \frac{(K)_2}{(K)_1} = \frac{-\Delta H}{4.576} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

gives  $\Delta H = -6.34$  kcal.

12. **Catalyzed Photooxidation of Trimethylene Disulfide.** (a).—The photooxidation was followed in a Warburg apparatus at 18° using solutions of zinc tetraphenylporphyrin in benzene and trimethylene disulfide in ligroin. The following mixtures were introduced into Warburg vessels: (A) porphyrin solution-benzene, 0.5 cc.:2.5 cc.; (B) porphyrin solution-ligroin, 0.5 cc.:2.5 cc.; (C) porphyrin solution-ligroin-trimethylene disulfide, 0.5 cc.:2.3 cc.:0.2 cc.; (D) trimethylene disulfide-ligroin, 0.2 cc.; 2.8 cc.; (E) trimethylene disulfide-benzene, 0.2 cc.:2.8 cc. Oxygen consumption by these mixtures was followed both in the dark and in the light. Figure 6 exhibits the data obtained.

(b).—The solution of zinc tetraphenylporphyrin in ethanol ( $2.4 \times 10^{-4}$  M) and a freshly distilled aqueous ethanol

solution of trimethylene disulfide ( $0.972 \times 10^{-2}$  M) were made up. The following mixtures of these solutions were introduced into Warburg vessels: (A) Into two (no. 1 and 2) vessels 1 cc. of trimethylene disulfide, 0.2 cc. of porphyrin, 1.5 cc. of ethanol; (B) into two vessels (no. 3 and 4) 2 cc. of trimethylene disulfide, 0.3 cc. of porphyrin, 0.5 cc. of ethanol. After equilibrating at 11.2° in the dark, the vessels were illuminated and the oxygen consumption obtained as a function of time. The graph (Fig. 8) records the results obtained and shows that slightly more than one atom of oxygen was consumed per mole of trimethylene disulfide. In a similar experiment conducted at 24° rather more oxygen was consumed. When the oxidations were complete the solutions were combined, diluted with a little water, and fractionated under reduced pressure. The spectrum of the ethanol distillate which apparently contains the sulfoxide derived from trimethylene disulfide compared almost identically with the sulfoxide of 6-thioctic acid.

13. **Chemical Oxidation of Disulfide.**—Since  $\text{H}_2\text{O}_2$  did not give a simple oxidation of the disulfide other oxidizing agents were tried. Ammonium persulfate was found to be suitable. To 9.4 cc. of trimethylene disulfide in 90% ethanol (O.D. 1.67 =  $1.17 \times 10^{-2}$  M) was added 110  $\lambda$  of 1 M  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (aq. soln.). This was allowed to stand at room temperature for 16 hours. The disulfide band rapidly disappears and is replaced by the monoxide band at 2450  $\text{\AA}$ . Assuming the extinction coefficient of the sulfoxide equals 1025 the calculated height of the 2450  $\text{\AA}$ . band (diluted ten times) =  $1.67 \times 1025/147 \times 10 = 1.16$ ; found 1.15 (Fig. 10). A corresponding result was obtained with 6-thioctic acid.

**Photolysis of Trimethylene Disulfide in Presence of Acids.** A. **With  $\alpha$ -Ketoglutaric Acid.**—Into each of two Pyrex test-tubes was introduced 6 cc. of trimethylene disulfide (ca. M/100) in 80% EtOH + 1 cc. of M/2 solution  $\alpha$ -ketoglutaric acid in 80% EtOH. Two control tubes each containing 6 cc. of the trimethylene disulfide solution alone were also made up. The tubes were deoxygenated in a stream of  $\text{N}_2$ , sealed and exposed in pairs to the following conditions: (a) one pair was kept in the dark for 24 hours; (b) the other pair was illuminated for three hours under an 8 watt ultraviolet lamp. Spectroscopic investigation of the tube contents demonstrated that no change occurred with (a). With (b) the tube containing the  $\alpha$ -ketoglutaric acid remained clear, while the control rapidly became turbid then milky. Further, in the clear solution, all the trimethylene disulfide had been destroyed, but no new characteristic absorption peak appeared.

B. **With Acetic, Oxalic and Pyruvic Acids—Quantitative Data.**—In these experiments, the concentration of trimethylene disulfide in a freshly distilled ethanolic solution was estimated spectroscopically. The trimethylene disulfide mixed with the required amount of the organic acid was diluted with water to ca. 80% EtOH, deoxygenated in nitrogen, sealed in Pyrex glass tubes and photolyzed under a bank of six 4 watt tubular ultraviolet lamps for 1.75 hours. With acetic acid, a turbidity slowly developed but with the other acids, the solutions were clear after photolysis. Controls without added acid rapidly became turbid. The cell contents were examined spectroscopically in order to confirm the complete destruction of the trimethylene disulfide and were then titrated with microburets: (a) potentiometrically against NaOH, (b) against  $\text{KI}_3$ , (c) against  $\text{Ag}^+$  amperometrically to estimate thiol groups (following the procedure of Rosenberg, *et al.*<sup>48</sup>). The results of these titrations are exhibited in Table I.

**Estimation of Thiols by Titration against  $\text{I}_2$  and  $\text{Ag}^+$ .**—In view of the results of the preceding experiments it became desirable to learn something of the validity of these methods for estimating thiols. 0.01 N solutions of  $\beta$ -mercaptoethanol and trimethylene dithiol in aqueous EtOH (ca. 80%) which had been made up several months previously were titrated on the micro scale against 0.1 N  $\text{I}_2$  (using starch) and amperometrically against 0.1 N  $\text{AgNO}_3$  using the procedure of Rosenberg, *et al.*,<sup>48</sup> with the results shown in Table II. However, new solutions made up from freshly distilled thiols and from pure cysteine hydrochloride gave the results shown in Table III.

It thus appears that in the absence of certain unidentified interfering substances  $\text{I}_2$  and  $\text{Ag}^+$  titrations give, within the

(47) Note that the total thiol group concentration remained constant and equal to  $b$  for any amount of reaction  $x$ .

(48) S. Rosenberg, J. C. Perrone and P. L. Kirk, *Anal. Chem.*, **22**, 1186 (1950).

TABLE I

ANALYSIS OF SOLUTIONS OBTAINED BY PHOTOLYZING TRIMETHYLENE DISULFIDE IN THE PRESENCE OF ORGANIC ACIDS

Added acid	Acidity of soln. before photolysis, $\times 10^2 N$	Acidity of soln. after photolysis, $\times 10^2 N$	Concn. of -SH after photolysis, (Ag <sup>+</sup> titration), $\times 10^2 N$	Concn. of -SH after photolysis, (I <sub>2</sub> titration), $\times 10^2 N$	Concn. of trimethylene disulfide before photolysis, $\times 10^2 M$
Acetic	2.43	2.46	..	2.1	2.0
Pyruvic	2.3	2.22 <sup>a</sup>	1.2	2.3	2.0
Oxalic	4.38	4.44 <sup>a,b</sup>	1.5	2.4	2.0

<sup>a</sup> Solutions tested for presence of CO<sub>2</sub> by bubbling pure N<sub>2</sub> through portions of the photolyzed mixture into NaOH then adding BaCl<sub>2</sub>—no CO<sub>2</sub> was found. <sup>b</sup> Titer virtually unchanged after heating to 200° for ca. 10 minutes. Also, unchanged oxalic was found to be present by treating with alkaline CaCl<sub>2</sub>, collecting the precipitate, washing, precipitating the Ca<sup>++</sup> with 2 N H<sub>2</sub>SO<sub>4</sub> and testing the supernatant solution for oxalic acid by reduction to glycolic acid and treating with 2,7-dihydroxynaphthalene and concd. H<sub>2</sub>SO<sub>4</sub>.<sup>49</sup> Also, the presence of oxalic acid was demonstrated by paper chromatography.<sup>50</sup>

TABLE II

	-SH estimated by I <sub>2</sub> titrn., $\times 10^2 N$	Ag <sup>+</sup> titrn., $\times 10^2 N$
$\beta$ -Mercaptoethanol	5.1	3.55
Trimethylene dithiol	9.2	5.6

TABLE III

	-SH estimated by I <sub>2</sub> titrn., $\times 10 N$	Ag <sup>+</sup> titrn., $\times 10 N$
$\beta$ -Mercaptoethanol	1.1	1.08
Cysteine hydrochloride	1.2	1.15
Trimethylene dithiol	1.13	1.08 <sup>a</sup>

<sup>a</sup> Precipitate formed during titration.

limits of experimental error, the same value for thiol concentration and that the presence of ethanol does not interfere noticeably.

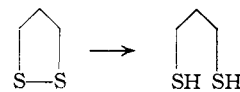
**Photolysis of Trimethylene Disulfide in Presence of Hydrochloric Acid. Quantitative Data.**—A freshly distilled aqueous ethanol solution of trimethylene disulfide had optical density for 3300 Å. peak as 2.05 corresponding to  $1.39 \times 10^{-2} M$ . Twenty-five cc. of this solution and 400  $\lambda$  of 0.95 N aqueous HCl (calcd. for 1 equiv. 366  $\lambda$ ) was introduced into a modified Pyrex "lollipop" (a vessel with flat sides furnished with an exit tube and a capillary reaching almost to the bottom of the vessel, both tubes being sealed to stopcocks). The solution was deoxygenated for 20 minutes in a stream of pure N<sub>2</sub> saturated in alcohol vapor introduced through the capillary and then isolated from the atmosphere by turning the stopcocks. Photolysis was conducted for 1.75 hours at a distance of ca. 2" from a bank of eight 4 watt tubular ultraviolet lamps, the apparatus being kept cool with an air blast. At the end of the photolysis, the solution was quite clear and spectroscopic examination (Fig. 11) revealed the complete disappearance of the trimethylene disulfide 3300 Å. band. Lead acetate papers showed the presence of a trace of H<sub>2</sub>S in the photolysis solution. The solution was then titrated.

(a) **Potentiometric:** Initial solution before photolysis, 300  $\lambda$  = 46.6  $\lambda$  of 0.1 N NaOH  $\therefore$  [H<sup>+</sup>] =  $1.56 \times 10^{-2} M$ ; solution after photolysis, 300  $\lambda$  = 47.95  $\lambda$  of 0.1 N NaOH  $\therefore$  [H<sup>+</sup>] =  $1.60 \times 10^{-2} N$ .

(b) **Iodometric:** Photolysis solution, 250  $\lambda$  = 58.8, 58.2  $\lambda$  of  $1.06 \times 10^{-1} N I_2$   $\therefore$  [-SH] =  $2.48 \times 10^{-2} M$ . The end-point, observed with the aid of starch, was not good—the blue color rapidly disappeared.

(c) **Amperometric:** 300  $\lambda$  of photolysis solution = 35.4, 36.2, 35.6, 35.8, 34.2, 33.6  $\lambda$  of  $1.02 \times 10^{-1} N AgNO_3$ ; 35.1  $\lambda$  average  $\therefore$  [SH] =  $1.2 \times 10^{-2} N$ .

The calcd. value of -SH assuming reaction



$$= 2 \times 1.39 \times 24/25.6 = 2.7 \times 10^{-2} N.$$

**Xanthates and Trithiocarbonates.**— $\beta$ -Mercaptoethanol, benzyl mercaptan and *t*-butyl mercaptan dissolved in ethanol were mixed in a Cary spectrophotometer cell with slightly more than the calculated amount of carbon disulfide, then treated with 1 N sodium hydroxide. The yellow color of trithiocarbonates, developed instantaneously. Figure 12 shows the spectra obtained. A similar experiment, conducted with a specimen of the solution obtained by photolyzing trimethylene disulfide in the presence of hydrochloric acid, gave the same characteristic peaks. When alkali was similarly added to a solution of carbon disulfide, alone, in ethanol, the paler color of the xanthate (see Fig. 12) developed much more slowly.

**Properties of Photolyzed Solution.**—(a) Spectrum of photolyzed solution is virtually unchanged by heating 5 cc. to 70° for 20 minutes with 50  $\lambda$  of concd. HCl. (b) On making just alkaline with NaOH, the photolysis solution slowly becomes yellow as a peak gradually develops at ca. 3400 Å. (Fig. 13) and later turbid. After standing overnight and centrifuging, the solution possesses a good peak at 3380 Å. This is not due to trimethylene disulfide since, on acidifying, the solution becomes turbid, and the peak largely disappears and distillation of the solution under reduced pressure gives a distillate with no absorption at 3300 Å.

(c) Making the solution strongly alkaline and distilling under reduced pressure gives no trimethylene disulfide. Apart from end absorption below ca. 2300 Å., the distillate shows only a minor peak at ca. 2700 Å. due to traces of thiacyclobutane in the original trimethylene disulfide.

(d) Reduced pressure distillation of the photolysis solution gives a spectrum similar to that in (c) except that the 2700 Å. peak is now an inflection on side of greater end absorption.

(e) Oxidizing the thiol groups in photolysis solution with I<sub>2</sub> and then distilling under reduced pressure gave a distillate with a peak at 3380 Å., which for some time was believed to be due to impure trimethylene disulfide ( $\lambda_{\max}$ . 3300 Å.) derived by oxidation of trimethylene dithiol present in the photolysis solution. However, this possibility was eliminated because reduced pressure distillation of the acidic photolysis solution gave no dithiol since oxidation of the distillate with I<sub>2</sub> gave a turbid solution which on redistillation gave no trimethylene disulfide. A control experiment in which a small amount of synthetic dithiol was first added to the photolysis solution before distillation, I<sub>2</sub> oxidation and redistillation gave the 3300 Å. peak of trimethylene disulfide, thus demonstrating that the photolysis solution did not destroy trimethylene dithiol and that hence there was no trimethylene dithiol present in the original photolysis solution. Another control experiment (Fig. 14) in which trimethylene disulfide was added to the photolysis solution which was then distilled showed trimethylene disulfide in the distillate, thus proving that trimethylene disulfide also was not destroyed by the photolysis solution.

(f) Further proof of the absence of trimethylene dithiol in the photolysis solution was obtained from the observation that trimethylene dithiol could be oxidized virtually quantitatively to trimethylene disulfide by hydroxylamine. A few  $\lambda$  of trimethylene dithiol in 3 cc. of ca. 80% aqueous ethanol was warmed to 50° in a Cary spectrophotometer cell with 3.5 N NaOH (600  $\lambda$ ) and 4 N NH<sub>2</sub>OH, HCl solution (300  $\lambda$ ). The rapid formation of trimethylene disulfide could be observed from the development of the characteristic 3300 Å. peak. In a similar experiment in which the photolysis solution was treated with alkali and hydroxylamine, no development of the 3300 Å. peak could be observed.

(g) No H<sub>2</sub>O<sub>2</sub> was present in the photolysis solution since (i) adjusting the pH to 7, diluting with water and adding catalase caused no liberation of O<sub>2</sub> although catalase added to alcoholic H<sub>2</sub>O<sub>2</sub> of equivalent ethanol concentration did give off oxygen; (ii) bleaching of PbS-impregnated paper failed to occur. Also a photolysis experiment conducted with a piece of PbS paper suspended in the solution failed to cause bleaching of the pigment.

(49) F. Feigl, "Qualitative Analysis by Spot Tests," Elsevier Publishing Co., New York, N. Y., 1946.

(50) A. A. Benson, private communication.

**Ethyl *t*-Butylsulfenate.**—This was prepared according to the directions of Rheinholdt and Motzkus.<sup>85</sup> It was a colorless mobile, pleasant smelling liquid, b.p. 65° (90 mm.). Kept in sealed glass ampoules at 5° it is quite stable, but exposed to the air it rapidly turns yellow and appears to change at least partly into di-*t*-butyl disulfide. The spectrum in ethanol showed  $\lambda_{\max}$  2655 Å.,  $\epsilon_{\max}$  70.5 (Fig. 15).

**Effect of Acid and Alkali on Ethyl *t*-Butylsulfenate.** (a).—The sulfenic ester (5  $\lambda$ ) was dissolved in ethanol (3 cc. of 80%) and the spectrum taken. Seventy  $\lambda$  of 1 *N* NaOH was added and the spectrum retaken. A slight increase in absorption throughout the spectrum was observed but no specific change. No further change occurred even after 12 hours.

(b).—The sulfenic ester (5  $\lambda$ ) in 3 cc. of 80% aqueous ethanol was treated in a spectrophotometer cell with 70  $\lambda$  of 1 *N* HCl and spectra recorded at appropriate intervals of time. A rapid change occurred in the spectrum leading to increased absorption throughout the spectrum. After standing overnight, all the sulfenic ester had been destroyed and a new as yet unidentified peak had appeared at ca. 2900 Å. (Fig. 15).

**Di-*t*-butyl Disulfide.**—This was prepared by oxidizing an alcoholic solution of *t*-butyl mercaptan with aqueous KI<sub>3</sub> solution. No definite end-point could be observed. As the iodine solution was added, the solution became browner and the characteristic smell of sulphenyl iodides gradually developed. The excess I<sub>2</sub> was destroyed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and the disulfide isolated with pentane and distilled. The disulfide was obtained as a yellow oil, b.p. 85° (25 mm.). *Anal.* Calcd. for C<sub>8</sub>H<sub>18</sub>S<sub>2</sub>: C, 53.4; H, 10.1; S, 36.0. Found: C, 54.25; H, 9.86; S, 36.1. Repeated fractionation failed to remove the yellow color. The ultraviolet spectrum (in EtOH) in contrast to other aliphatic disulfides showed no characteristic band at 2500 Å.; instead it revealed only an end absorption extending into the visible (Fig. 15).

**Oxidation by Ethyl *t*-Butylsulfenate and by Di-*t*-butyl Disulfide.**—A Cary spectrophotometer cell was fitted with an attachment provided with two side arms to hold reagents, with an inlet capillary and an exit tube, both tubes being furnished with stopcocks: (a) Into the Cary cell was introduced 90% ethanol (3 cc.) and 1 *N* aqueous KI (50  $\lambda$ ). Into the side arms of the attachment was introduced the sulfenic ester (5  $\lambda$ ) in ethanol (50  $\lambda$ ) and 1 *N* HCl (50  $\lambda$ ) in ethanol (50  $\lambda$ ). The attachment was assembled and the system deoxygenated in a stream of purified nitrogen for ten minutes beyond the time the effluent gases showed zero oxygen content in a Pauling oxygen analyzer. The taps were then closed. The HCl was then dumped into the Cary cell and the very slow development of the I<sub>2</sub> color induced by traces of O<sub>2</sub> was plotted as a function of time. The sulfenic ester was then tipped into the HI solution. I<sub>2</sub> was immediately liberated and continued to be formed at a considerable speed ca. 500 times greater than that due to traces of O<sub>2</sub>.

(b) A similar experiment was performed using di-*t*-butyl disulfide (5  $\lambda$ ) in EtOH (50  $\lambda$ ) in one side arm, HCl (50  $\lambda$ ) of 1 *N* in EtOH (50  $\lambda$ ) in the other and with 1 *N* KI (50  $\lambda$ ) in aqueous EtOH (3 cc.) in the spectrophotometer cell.

Again on adding the disulfide a considerable increase in the rate of liberation of iodine was observed.

(c) To investigate the oxidation on thiols, the sulfenic ester (10  $\lambda$ ) in EtOH (50  $\lambda$ ) and trimethylene dithiol (5  $\lambda$ ) in EtOH (50  $\lambda$ ) were introduced into the side arms. The cell contained 1 *N* NaOH (50  $\lambda$ ) in EtOH (3 cc. of 90%). After removing oxygen, the dithiol was added to the alkali; a small amount of trimethylene disulfide was formed slowly. Addition of the sulfenic ester caused an instantaneous production of trimethylene disulfide (O.D. at 3300 Å. 0.75).

(d) A similar experiment demonstrated that the sulfenic ester appears to be relatively stable to thiols under neutral conditions (Fig. 16).

(e) A similar experiment conducted with di-*t*-butyl disulfide (4  $\lambda$ ), and trimethylene dithiol (4  $\lambda$ ) also showed a production of trimethylene disulfide, but in this case the rate of formation was slow and the ultimate yield small.

**Ethyl Trichloromethylsulfenate.**—This was prepared from trichloromethylsulphenyl chloride by reaction, with sodium ethoxide under conditions similar to those used for the preparation of *t*-butyl analog. *Anal.* Calcd. for C<sub>3</sub>H<sub>5</sub>SOCl<sub>3</sub>: C, 18.4; H, 2.6; OEt, 23. Found: C, 21.4; H, 3.1; OEt, 22.4. The absorption spectra of the chloride and ester are shown in Figs. 17 and 18.

**Oxidation of Trimethylene Dithiol by the Photolysis Solution.**—In the apparatus in the diagram (Fig. 19), the Cary cell (A) was charged with ethanol (3 cc. of 90%) and 90  $\lambda$  of 1 *N* NaOH, the side arm with trimethylene dithiol/ $\lambda$  (5  $\lambda$ ) + ethanol (150  $\lambda$ ) and the photolysis cell (B) with trimethylene disulfide solution (3 cc.,  $1.2 \times 10^{-2}$  *M*) + 40  $\lambda$  of 0.95 *N* HCl ( $\cong$  1 mole prop.). Pure N<sub>2</sub> was bubbled through the capillaries for ten minutes after the effluent gas had zero oxygen content according to a Pauling oxygen analyzer and the taps were then turned. The trimethylene dithiol was dumped into the Cary cell and the spectrum taken. A small amount of trimethylene disulfide was found. The Cary cell was then wrapped in foil, the disulfide in the photolysis cell exposed to a bank of eight 4 watt tubular ultraviolet lamps at a distance of ca. 1.5" for two hours, the apparatus being kept cool by an air blast. The spectrum of the dithiol and alkali in the spectrophotometric cell was taken again but no increase in the concentration of trimethylene disulfide had taken place. The contents of the Cary cell were then tipped into the photolysis cell, mixed thoroughly and poured back into the Cary cell. The spectrum showed an increased absorption at 3300 Å. which developed with time. The ultimate increase in the height of the band corresponded to ca. 15% yield in the oxidation of trimethylene dithiol to trimethylene disulfide. Reduced pressure distillation of the acidified mixture gave a distillate containing trimethylene disulfide.

**Photolysis of Trimethylene Disulfide in the Presence of Sodium Hydroxide.**—A solution of trimethylene disulfide in ca. 95% ethanol (0.01 *M*) was treated with 70  $\lambda$  of 1 *N* NaOH, freed from oxygen and photolyzed on a Cary spectrophotometer cell before a bank of 6 watt tubular ultraviolet lamps. Figure 20 shows the progress of the photolysis and the effect of acidifying the photolysate.

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