

THE POLYMERIZATION OF 1,3-OXATHIOLANE  
AND RELATED COMPOUNDS

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AND RELATED COMPOUNDS

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## INTRODUCTION

This work was undertaken to find new copolymers containing the ethylene sulfide linkage, (-CH<sub>2</sub>-CH<sub>2</sub>-S-). More specifically, the aim has been to find monomeric cyclic compounds containing this unit and capable of ring-scission polymerization, and to produce and study their polymers.

Obviously the simplest such cyclic compounds would contain four-membered rings such as  $\begin{array}{c} \text{CH}_2\text{-CH}_2 \\ | \quad | \\ \text{CH}_2\text{-S} \end{array}$ ,  $\begin{array}{c} \text{CH}_2\text{-O} \\ | \quad | \\ \text{CH}_2\text{-S} \end{array}$ , and  $\begin{array}{c} \text{CH}_2\text{-S} \\ | \quad | \\ \text{CH}_2\text{-S} \end{array}$ . Of these the first is known, and known to polymerize; the second is unknown; and the third has been sought in vain as a monomer.

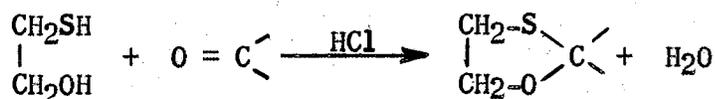
The next larger rings, five-membered ones, would be expected on the basis of ring strain to polymerize less readily if at all; and indeed most five-membered ring compounds do not polymerize. However, both tetrahydrofuran and 1,3-dioxolane are polymerized by acid catalysts; and this suggested extension of the reaction to 1,3-oxathiolanes and 1,3-dithiolanes, both unstudied in this respect.

The polymerization of six-membered rings containing the -CH<sub>2</sub>-CH<sub>2</sub>-S- unit was considered hopeless, but since an eight-membered ring, 1,3,6-trioxocane, has been made and shown polymerizable, the preparation of 6-thio-1,3-dioxocane was tried for the same purpose.

## HISTORICAL

### Preparation and Properties of 1,3-Oxathiolanes

A number of 2-substituted-1,3-oxathiolanes have been prepared by the reaction of aldehydes or ketones with 2-mercaptoethanol.



Also several 1,3-oxathiolane derivatives of keto groups in steroid-type compounds have been reported.<sup>12, 29, 42, 43</sup> The known non-steroid 1,3-oxathiolanes are listed in Table I.

TABLE I

#### LIQUID 1,3-OXATHIOLANES

<u>Parent Carbonyl Compound</u>	<u>B.P., °C</u>	<u>Yield, %</u>	<u>Reference</u>
Formaldehyde	125-6.5 (746 mm)	67	11
Acetaldehyde	129	--	7
Propionaldehyde	149.5 (743 mm)	49	11
Acetone	70 (65 mm)	85	3, 12
Methyl ethyl ketone	42 (8 mm)	79	12
Methyl isobutyl ketone	41 (2 mm)	70	3, 12
Cyclohexanone	47 (0.6 mm)	62	12
Acetophenone	132-2 (16 mm)	78	12, 38
Benzaldehyde	86-7 (5 mm)	76.6	32
Isobutyraldehyde	29 (2.5 mm)	60	32
Ethyl acetoacetate	117 (20 mm)	77	12
3,4-Dioxymethylenebenz- aldehyde	118 (1.5 mm)	50	32

Oxathiolanes also have been prepared from benzil<sup>16</sup> and cyclohexane-1,2-dione<sup>31</sup> in connection with some steroid derivatives. Sjoberg<sup>45</sup> prepared a 5-substituted-1,3-oxathiolane from 1-mercapto-2-propanol and acetone. The alcohol was prepared indirectly from propylene oxide and thioacetic acid.

The preparations were carried out by various methods. Dermer and Sinclair<sup>11</sup> first prepared 1,3-oxathiolane in good yields by refluxing 2-mercaptoethanol and paraformaldehyde in an apparatus with a Barrett water trap. Concentrated hydrochloric acid, ferric chloride, or zinc chloride was used as catalyst. Djerassi and Gorman<sup>12</sup> prepared oxathiolanes by the method described, and by an alcohol exchange reaction.

The steroid 1,3-oxathiolanes are used in blocking ketone groups in steroids while other operations are being carried out.

The compounds are soluble in most organic solvents and insoluble in polar solvents. They have a strong odor and are colorless.

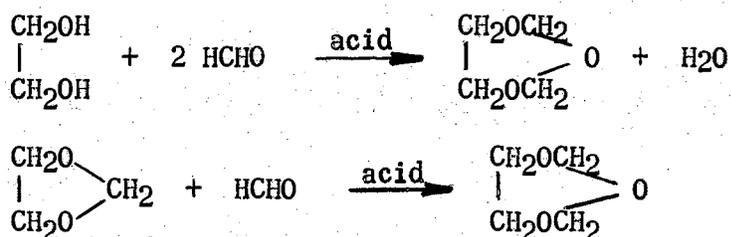
Pinder and Smith<sup>38</sup> reduced 2-methyl-2-phenyl-1,3-oxathiolane with sodium in methanol to obtain ethylbenzene as the chief product, along with traces of 1-ethyl-1,4-cyclohexadiene.

#### Preparation of Poly-1,3-Dioxolanes

According to Gresham<sup>19</sup> 1,3-dioxolane may be polymerized by proton and Lewis acids. Friedel-Crafts catalysts at 0 - 150° give poly-1,3-dioxolanes,  $(-OCH_2OCH_2CH_2-)_x$ , with molecular weights of about 1000 to greater than 10,000. If fewer than ten monomer units are linked the polymer is liquid; if the chain has more than ten units, the polymer is solid. At a molecular weight greater than 10,000 the polymer is a tough, cold-drawable solid. Poly-

dioxolane was prepared by refluxing 417 parts of 1,3-dioxolane with two parts of concentrated sulfuric acid for various times. Polymers<sup>19</sup> formed with boron trifluoride at 6° and further at 75 - 90° had molecular weights of 1000 - 200,000. The elasticity and high tensile strength of the solid polymers disappeared after one week. This was caused by peroxidation and was prevented by addition of hydroquinone. Gresham<sup>21</sup> also polymerized 1,3-dioxolane in solution in toluene using boron trifluoride as a catalyst, and made the polymer<sup>22</sup> directly from paraformaldehyde, ethylene oxide, and boron trifluoride catalyst. The polymer, partially water-soluble, is said to be useful as a plasticizer.

Formaldehyde has been condensed with both 1,3-dioxolane and ethylene glycol to yield 1,3,5-trioxepane<sup>24, 25</sup>.



As expected, this seven-membered ring is readily converted to a polymer of the type  $\text{H}(-\text{OCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2-)_x\text{OH}$ . This poly-1,3,5-trioxepane has a structure equivalent to a copolymer of 1,3-dioxolane and formaldehyde. Similarly, 1,3-dioxolane has been copolymerized<sup>23</sup> with various formals to give clear viscous polymers containing at least two dioxolane residues  $(-\text{OCH}_2\text{OCH}_2\text{CH}_2\text{O}-)$  per formal unit  $(-\text{OCH}_2\text{O}-)$ ; the copolymerization was catalyzed by sulfuric acid. Also using acid catalysts Loder and Gresham<sup>34</sup> copolymerized 1,3-dioxolane or its 2-substituted derivatives with olefins, esters, nitriles, amides, and other compounds containing functional groups.

Wood<sup>47</sup> reported the free-radical copolymerization of 1,3-

dioxolane with vinyl acetate. Solid copolymers, melting below 90 - 100°, were formed at 77 - 85° with benzoyl peroxide as catalyst.

### Preparation and Properties of 1,3-Dithiolanes

Fasbender<sup>14</sup> in 1887 first prepared 1,3-dithiolane by heating 1,2-ethanedithiol with formaldehyde using an acid catalyst.

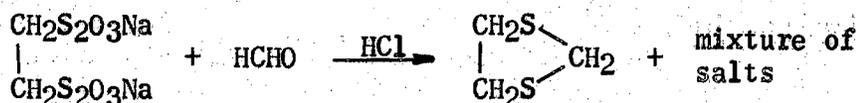


In 1888 he reported preparing eight 2-substituted-1,3-dithiolanes<sup>15</sup>. The substituents were derived from acetaldehyde, propionaldehyde, benzaldehyde, anisaldehyde, glyoxal, benzophenone, acetone, and pyruvic acid.

The dithiolanes<sup>16,27,31</sup> are also being used as carbonyl-blocking compounds in steroid chemistry. In connection with steroids, dithiolanes have been prepared from cyclohexanone<sup>27</sup>, cyclohexa-1,2-dione<sup>31</sup>, menthone<sup>27</sup>, and camphor<sup>27</sup>. Dithiolanes also have been prepared<sup>4</sup> from ethanedithiol and many-membered cyclic diketones.

Hach<sup>26</sup> prepared 3-chloromethyl-1,3-dithiolanes as intermediates in some preparative work.

Gibson<sup>18</sup> prepared 1,3-dithiolane in 50 - 60% yields by causing formaldehyde to react with sodium ethylene thiosulfate using hydrochloric acid as a catalyst.



Some polymers were obtained. This dithiolane was also prepared<sup>46</sup> from 1,2-ethanedithiol and dichloromethane in presence of base. The yields were poor and a large portion of the reactants went to polymers. Mazover<sup>36</sup> has used the Bunte salt method of Gibson<sup>18</sup>

to prepare dithiolanes in good yields.

In 1950 Reid and Jelinek<sup>39</sup> reported the preparation and physical properties of nineteen dithiolanes. The preparations were accomplished by mixing 1,2-ethanedithiol with the carbonyl compound, saturating with hydrogen chloride, and letting the mixture stand overnight. The dithiolanes were purified by vacuum distillation. In the same year, Hauptmann and Wladislaw<sup>28</sup> reported 2-methyl-2-phenyl-1,3-dithiolane prepared from acetophenone and 1,2-ethanedithiol with acetic and hydrochloric acids as catalysts. The dithiolanes are generally soluble in non-polar solvents such as benzene and ether and insoluble in water.

In the literature there are reports of polymers of the dithiolane type<sup>35,41</sup>, but none were prepared directly from 1,3-dithiolanes. Marvel and co-workers<sup>35</sup> obtained polymers by treating various aldehydes with molecules of the type  $(\text{H}_2\text{C})_n(\text{SH})_2$  in the presence of acid. Polymers thus produced are of the character  $(-\underset{\text{R}}{\text{C}}\text{H}-\text{S}-(\text{CH}_2)_n\text{S}-)_x$ , with molecular weights of 1100 - 76,000 by viscosity measurements. Polymers were produced only for  $n = 6$  and  $n = 10$ ; other dithiols are not believed to yield such products unless  $n > 3$ . Patrick<sup>37</sup> prepared polymeric chlorinated 1,3-dithiolanes but did not characterize polymers so produced.

#### Preparation and Properties of 6-Thio-1,3-dioxocane

Astle and co-workers<sup>1</sup> prepared 1,3,6-trioxocane using cation-exchange resins as catalyst. The 2,2-oxydiethanol was mixed with formaldehyde and refluxed over Dowex-50 ion-exchange resin. The 1,3,6-trioxocane thus produced was polymerized to a water-soluble wax by the action of acids. The polymer depolymerized readily.

It was reported that 2,2'-thiodiethanol and pentaerythritol form polymers that are useful as plasticizers and lubricants. Other hydroxyl compounds<sup>40, 41</sup> and organic acids<sup>8</sup> have been condensed with 2,2'-thiodiethanol to give ethers and esters. In the ether preparation linear polymeric ethers with -OR end-groups were produced as a major side reaction. The preparation of monoethers did not give good yields, but in acid conditions at 70° polymerization predominated.

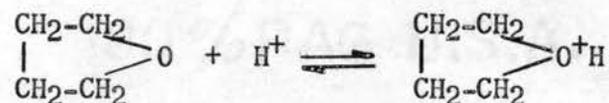
#### Ring-Scission Polymerization

Carothers<sup>5</sup> studied the competition of ring formation versus chain polymerization in condensation polymerization. Evidence was presented to indicate that for a bifunctional reaction, if a five- or six-member ring could be formed, it would appear in preference to the polymer. Polymers form almost exclusively when the repeating unit is greater than six.

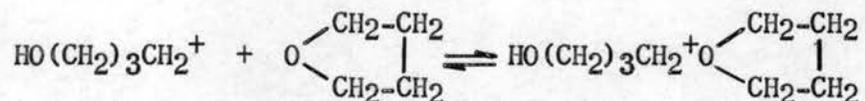
The most important factor governing ring formation is the size of the ring produced<sup>17</sup>, but also the chemistry of the ring must be considered<sup>9</sup>. Five-member rings are formed exclusively; six-member rings are generally formed, but some go to polymer by exchange mechanisms. Attempts to create rings in a polyfunctional reaction fail if the desired rings contain below five or above six members. Rings of this nature are known, but are prepared by different methods. Little is known about the polymerization of five-member polyfunctional rings. Floxy<sup>17</sup> lists a series of monomers that condense exclusively to form five-member rings. Thus  $\gamma$ -hydroxy acids condense to lactones,  $\gamma$ -amino acids give lactams, succinic acid yields the anhydride, and ethylene carbonate and ethylene formal

(1,3-dioxolane) occur only in the cyclic forms. Flory is in error in the case of ethylene formal, for Gresham<sup>19,20,21</sup> polymerized 1,3-dioxolane under various conditions in 1945, and portions of the work were duplicated by the author.

The ring-scission polymerization of tetrahydrofuran was reported in 1941 by Delfs<sup>10</sup> in a progress report at the Leverkusen Works of I. G. Farbenindustrie A. G. It was shown that on treatment with acids tetrahydrofuran forms an oxonium ion.



In presence of a large amount of tetrahydrofuran the oxonium ion rearranges to a linear carbonium ion,  $\text{HOCH}_2\text{CH}_2\text{CH}_2\overset{+}{\text{C}}\text{H}_2$ , which can attack another molecule of monomer to give an oxonium ion.



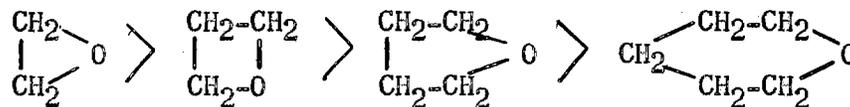
In turn, this oxonium ion can rearrange by ring scission to form a linear ion with the terminal carbon positively charged. The acids used to initiate this polymerization must be complex acids which form anions of the  $(\text{AlCl}_4)^-$ ,  $(\text{BF}_4)^-$ ,  $(\text{ClSO}_3)^-$ , or  $(\text{ClO}_4)^-$  type. Common anions such as  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{F}^-$  form covalent bonds readily and act as chain terminators.

Copolymerization of tetrahydrofuran was accomplished with other monomers of a similar nature. Compounds which copolymerize with it are:

ethylene oxide	butadiene oxide
propylene oxide	resorcin-di-glycidether
epoxybutane	phenoxypropene oxide
epichlorohydrin	trimethylene oxide

Delfs<sup>10</sup> also gave a series of reactivities of the various mono-oxygen

heterocyclics. The ease of polymerization is:



This is readily explained by the strain theory. du Pont<sup>13</sup> has patented the polymerization of six-membered cyclic formals. The ring-scission polymerization was caused by acid halides and Friedel-Crafts catalysts.

## EXPERIMENTAL

### Preparation of 1,3-Oxathiolanes

The 2-mercaptoethanol was practical grade and was used without further purification. The source of formaldehyde used was practical paraformaldehyde. The catalysts were reagent grade, with the exception of the ion-exchange resin.

Dermer and Sinclair<sup>11</sup> prepared 1,3-oxathiolane by various methods, of which the most productive is described here. One mole (35.0 g.) of paraformaldehyde was mixed thoroughly with one mole (78.0 g.) of 2-mercaptoethanol in a 200-ml. round-bottom flask. The flask was fitted for distillation and 2 ml. of concentrated hydrochloric acid were added. The reaction was immediate, and water and product were distilled without external heat. After part of the water was collected and the reaction subsided, heat was applied to distill the remaining product. Fractions were collected at 95 - 105° and 105 - 150°. The water was separated and the fractions were mixed and dried over anhydrous calcium chloride. The dry oil was distilled in a Snyder three-ball column, and a fraction was collected at 125.0° - 126.5°. If a pear-shaped flask is used and the product rapidly distilled, yields of 67% or higher can be obtained.

This method was used to prepare all 1,3-oxathiolane used as monomer in subsequent polymerizations. Oxathiolanes can also be prepared using Lewis acids<sup>11</sup> as catalyst. When Dowex-50 cation-

exchange resin was used as a catalyst<sup>1</sup> a yield of 63% was obtained.

The infrared spectrum was run on 1,3-oxathiolane using a Perkin-Elmer model 12C infrared spectrometer. The sample was placed in a liquid cell using a 0.006-inch lead spacer, and operational methods were normal using the full wave length range of the instrument. Assignment of absorption characteristics is given in Table II. Bands at 3.25  $\mu$  and 6.25  $\mu$  are believed due to the oxathiolane ring.

Butanal combined with 2-mercaptoethanol in a manner similar to the preparation of 1,3-oxathiolane gives 2-propyl-1,3-oxathiolane, a novel compound. One-half mole (39.0 g.) of 2-mercaptoethanol, one-half mole (36.0 g.) of butanal, and 2 ml. of concentrated hydrochloric acid were mixed thoroughly and heated. Heating was maintained at a level that permitted the product to be distilled as formed. First water came over, then water and product. Propyloxathiolane was collected at 170° - 180°; when the pot liquor began to char at 200° the heat was removed. The oil was dried and distilled in a Snyder three-ball column, the fraction at 167° - 168° being collected. A considerable amount of decomposition occurred during distillation and only 5 g. of product was collected (7.6% theoretical). The oil is clear and has a very penetrating odor. The compound was not characterized further.

#### Preparation and Attempted Preparation of 1,3-Dithiolanes.

The 1,2-ethanedithiol used in the preparation of 2,2-dimethyl-1,3-dithiolane was prepared according to Cope<sup>6</sup>. Only a small yield of the dithiol was obtained, and repeated attempts gave only yellow sticky polymers.

TABLE II

THE ABSORPTION CHARACTERISTICS OF THE INFRARED SPECTRUM  
OF 1,3-OXATHIOLANE

<u>WAVE LENGTH IN MICRONS</u>	<u>INTENSITY</u>	<u>RESOLUTION</u>	<u>ASSIGNMENT</u>
2.7	Weak	Sharp	Unassigned
3.25	Medium	Sharp	C-O-C; ring
4.0	Strong	Sharp	C-S-C
5.4	Weak	Sharp	Unassigned
6.25	Strong	Sharp	Oxathiolane ring
7.35	Weak	Not resolved	C-S-C
7.90	Medium	Just defined	C-S-C
8.1-11.3	Strong	Broad band	CH <sub>2</sub> and C-C
11.9	Weak	Not resolved	Unassigned
13.9-14.2	Strong	Broad band	C-S-C (Others)

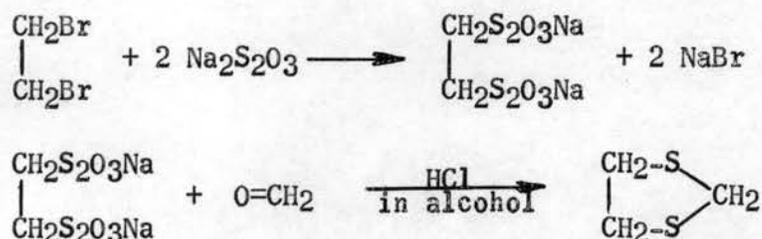
TABLE III

THE ABSORPTION CHARACTERISTICS OF THE INFRARED SPECTRUM  
OF POLY-1,3-OXATHIOLANE

<u>WAVE LENGTH IN MICRONS</u>	<u>INTENSITY</u>	<u>RESOLUTION</u>	<u>ASSIGNMENT</u>
4.0	Strong	Sharp	C-S-C
7.2	Medium	Sharp	C-S-C
8.75	Medium	Sharp	Unassigned
9.0	Strong	Not resolved	C-O-C
9.5-10.5	Strong	Band	CH <sub>2</sub> and C-C
10.75	Strong	Broad	C-O-C
12.3	Medium	Broad	Unassigned
13.1	Weak	Broad	Unassigned
14.1	Medium	Broad	R-S-R

A 100-ml. solution of 15.0 g. (0.16 moles) of 1,2-ethanedithiol, 15.8 g. (0.27 moles) of acetone, and 2 ml. of hydrochloric acid in benzene was refluxed for six hours in an apparatus fitted with a Barrett water trap. After two hours at 62°, only 1.3 ml. of water had been collected, and 1 ml. of hydrochloric acid was added to the reaction mixture. The total amount of water collected was 2.1 ml., which is 52.5% of the theoretical yield. The solution was distilled in a Snyder three-ball column and a 12.0 g. fraction boiling at 171-3° was collected. The yield of 2,2-dimethyl-1,3-dithiolane, based on 1,2-ethanedithiol, was 55.4%.

Attempts were made to reproduce the preparation of 1,3-dithiolane as described by Gibson<sup>18</sup>.



In trying to isolate 1,3-dithiolane from the oil layer, only ethyl alcohol and a charred residue were obtained.

An attempt to condense formaldehyde, saturated with hydrogen sulfide, with ethylene oxide failed to produce any characterizable products.

#### Attempted Preparation of 6-Thio-1,3-dioxocane.

The condensation of thiodiglycol with formaldehyde using acid catalyst was attempted. No 6-thio-1,3-dioxocane was obtained though approximately the theoretical amount of water was collected. Extensive decomposition of the pot liquor occurred upon distillation and no product was obtained. Also, the same condensation was tried

using Dowex-50 sulfonic acid-type cation-exchange resins<sup>1</sup>, and decomposition occurred just as in the trial using acid catalyst. Vacuum distillation in a subsequent run yielded a portion of oil which proved to be unreacted thiodiglycol.

#### Polymerization of 1,3-Oxathiolane.

Polymerization of 1,3-oxathiolane proceeds readily with acid catalysts. Polymers were formed by heating 5 ml. of 1,3-oxathiolane with a trace of concentrated sulfuric acid at 70° for 12 or more hours. The polymers are clear viscous syrups which are soluble in pyridine, benzene, nitrobenzene, and other organic solvents. The crude polymer contained 0.1% sulfuric acid and 2% formaldehyde. Cryoscopic molecular weight of the crude polymer in nitrobenzene, purified by distillation through a Todd column, gave varied results as shown in Table IV.

Purification of polyoxathiolane was accomplished by dissolving 2 g. of polymer in 5 ml. of pyridine and adding 5 ml. of water to precipitate the polymer. The mixture was then centrifuged for five minutes and the liquids decanted. The polymer was dried under vacuum at room temperature overnight. Cryoscopic molecular weights of the purified polymer are also given in Table IV. The molecular weight increase of the purified polymer is probably due to fractionation during purification as well as the removal of free formaldehyde, sulfuric acid, and other impurities. As shown, the reaction mixtures were heated for times varying from 12 to 72 hours and no significant variation of molecular weight was noted. Sulfur analysis of the purified polymer by a combustion method similar to ASTM method D90-41T as modified by J. K. Bobst of this

TABLE IV  
MOLECULAR WEIGHTS OF POLY-1,3-OXATHIOLANE

<u>Run</u>	<u>Hours Polymerized</u>	<u>Polymer Type</u>	<u>Molecular Weight</u>
1	72	Crude	192
2	72	Crude	179
3	72	Crude	317
4	72	Crude	300
5	76	Crude	229
6	76	Crude	268
7	16	Crude	552
8	16	Crude	595
9	24	Purified	1030
10	24	Purified	1480
11	24	Purified	1050
12	24	Purified	1570
13	72	Polymerized in C <sub>6</sub> H <sub>6</sub>	1454
14	72	Polymerized in C <sub>6</sub> H <sub>6</sub>	1237

laboratory gave 34.2% as compared to 35.6% theoretical. Such low values are not uncommon for polymers. The pure polymer upon an amperometric titration of thiol end-groups with silver nitrate it showed only six such endgroups per 1000 chains.

The infrared spectrum of the polymer using silver chloride windows and no spacer was determined with bands characterized and assigned as shown in Table II.

The poly-1,3-oxathiolane was also prepared in inert solvents (benzene, toluene, phenetole) by heating at 70° with 0.1% concentrated sulfuric acid. The polymers are substantially identical to those prepared without diluent.

#### Attempted Polymerization of 2,2-Dimethyl-1,3-Oxathiolane.

A 5-ml. portion of 2,2-dimethyl-1,3-oxathiolane was heated with a trace of sulfuric acid for 24 hours at 70°. A white solid was formed in the liquid; additional heating at 70° resulted in more solid white polymer. The liquid was unreacted monomer and the insoluble solid proved to be essentially polyethylene sulfide by sulfur content (calcd., 53.33%: found, 47.79%). Theoretical sulfur content for the expected polymer is 27.13%.

#### Attempted Polymerization of 2-Substituted-1,3-Oxathiolanes.

The 2-ethyl, 2-propyl, and 2-methyl-2-ethyl-1,3-oxathiolane decompose as does the dimethyl derivative. Attempts to polymerize these monomers in solution also yielded polyethylene sulfide.

#### Copolymerization of 1,3-Oxathiolane with Similar Monomers.

Under conditions like those used with 1,3-oxathiolane, 2,2-dimethyl-1,3-oxathiolane did not copolymerize with 1,3-oxathiolane.

After 72 hours a white solid was found dispersed in a viscous sirup. The white solid proved to be polyethylene sulfide and the sirup proved to be polyoxathiolane. No copolymers were found. Also 2-ethyl-1,3-oxathiolane failed to copolymerize with its unsubstituted parent. Only brown solid residues were obtained after heating 20 hours at 70°.

Attempts to copolymerize 1,2-oxathiolane with olefin sulfide monomers were only partly successful. Ethylene sulfide and 1,3-oxathiolane yielded only polyethylene sulfide after 16 hours at 70°. Equimolar portions of propylene sulfide and 1,3-oxathiolane copolymerized in 20 hours at 70° in the presence of a trace of sulfuric acid to give viscous polymers whose sulfur content was 36.5% as compared to 39.0% for the 1:1 adduct and 35.6% for poly-1,3-oxathiolane. Since sulfur results are usually low, this shows evidence of copolymerization.

Similarly equimolar portions of acidified 1,3-dioxolane and 1,3-oxathiolane were heated at 70° for 90 hours, and a very viscous copolymer was formed having solubilities which are different from those of either poly-1,3-oxathiolane or poly-1,3-dioxolane. The copolymer was slightly soluble in water and readily soluble in acetone. This was considered sufficient evidence to establish copolymer formation.

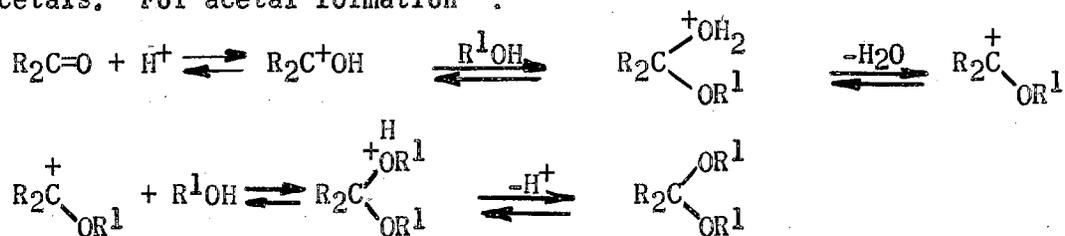
Equimolar quantities of trioxane (1.1 g.) and 1,3-oxathiolane (3.6 g.) were mixed and heated with 0.04 g. of sulfuric acid for 24 hours. A viscous copolymer similar to those in previous experiments was obtained; it was purified by the method described for poly-1,3-oxathiolane. Sulfur analysis of the copolymer gave 30.55%

sulfur as compared to 23.9% for 1:1 adduct and 35.6% for poly-1,3-oxathiolane. These results indicate a copolymer with a 2:1 ratio of oxathiolane to formaldehyde.

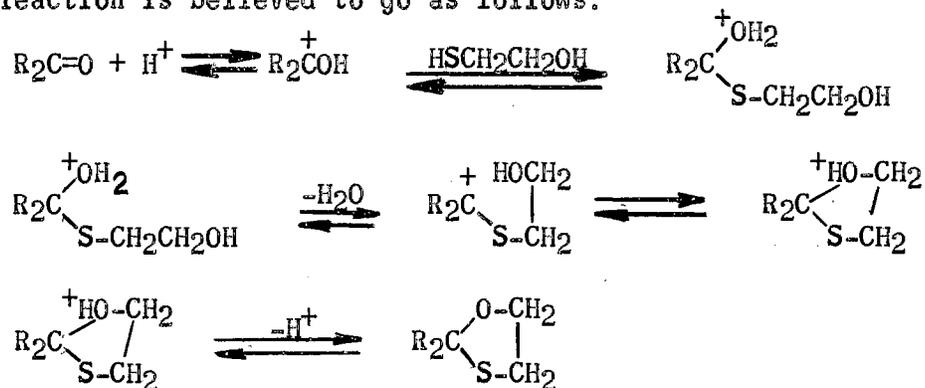
Ethylene sulfide and 1,3-dioxolane yielded only polyethylene sulfide under similar conditions.

## DISCUSSION

The formation of 1,3-oxathiolanes is similar to the formation of acetals. For acetal formation<sup>44</sup>:

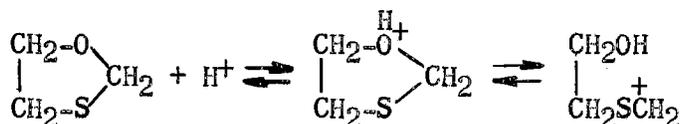


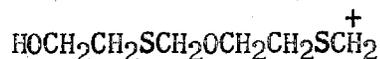
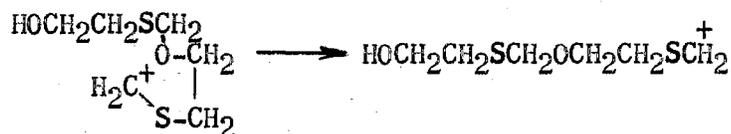
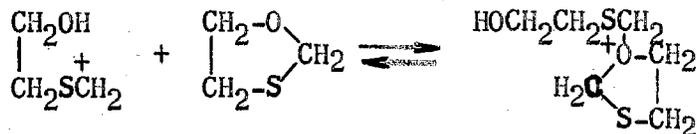
When 2-mercaptoethanol is substituted for two molecules of ROH the reaction is believed to go as follows:



In the mechanism it is assumed, owing to the greater ease of rupture of the sulfur-hydrogen bond, that the mercaptan end of the molecule is involved in the initial attack.

The polymerization of 1,3-oxathiolane proceeds through the cleavage of a carbon-to-oxygen bond by the action of acid. The predominance of -OH endgroups verify this postulate. Following is the suggested mechanism of polymerization:





plus more molecules of 1,3-oxathiolane  $\rightarrow$  higher polymers; reaction stopped by addition of  $\text{OH}^-$  from  $\text{H}_2\text{O}$



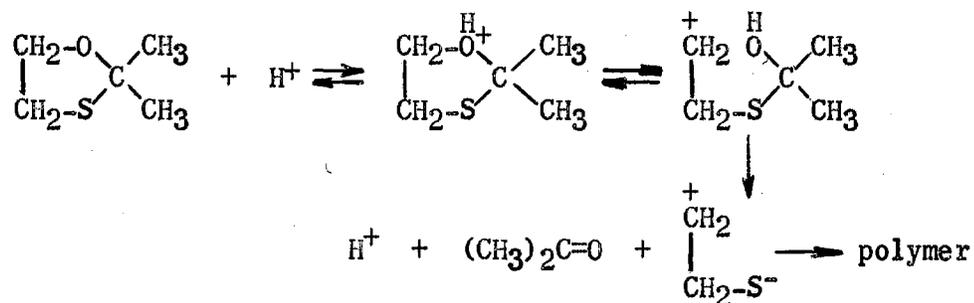
From existing data and this work, a generalization can be made on the relative ease of polymerization. As stated earlier, 1,3-dioxolane polymerizes readily to give solid polymers with a molecular weight up to 200,000. In this work it has been shown that 1,3-oxathiolane polymerizes to give only sirups of low molecular weight, and that the 2-substituted homologs do not polymerize as such. As reported by Marvel and co-workers<sup>35</sup>, 1,3-dithiolane is not believed to polymerize upon treatment with acids. Therefore, it can be concluded that for monomers of the type  $\begin{array}{c} \text{CH}_2\text{-y} \\ | \quad \diagdown \\ \text{CH}_2\text{-y} \quad \text{CH}_2 \end{array}$  the tendency to polymerize decreases as the number of sulfur atoms increases. This may be explained by the difference in basicity of oxygen and sulfur<sup>30</sup>. The more basic oxygen would tend to add a proton to form an oxonium ion which upon heating would lead to ring opening and subsequent polymerization. The formation of a sulfonium ion is not likely since the sulfur is so feebly basic.

These results are contrary to the ideas of Carothers<sup>15</sup> on stability of five-member bifunctional rings. Since the rings are practically strainless, the tendency to polymerize must be

due to the basicity of the formal oxygen atoms. This also accounts for the failure of the 1,3-dithiolanes to polymerize.

The failure of the attempted preparation of 6-thio-1,3-dioxocane is predictable by application of Carothers' observations.

The failure of the 2-substituted-1,3-oxathiolanes to polymerize can be explained by showing the influence of the inductive effects of the substituents. In the case of 2,2-dimethyl-1,3-oxathiolane, the attack would be expected to go as follows:



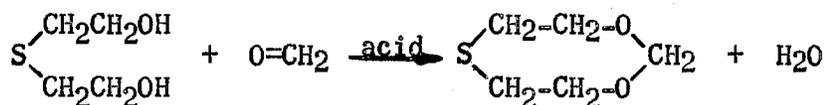
The additional electron density from the inductive effect of the two methyl groups in the 1,2 bond prevents ring rupture at that point, and causes splitting at the 1,5 bond. At this point, decomposition takes place regenerating protons and yielding acetone and a polar form of ethylene sulfide. The polar form of ethylene sulfide can react with the oxathiolane monomer to propagate the polymerization of ethylene sulfide.

### SUMMARY

When heated with acid catalysts, aldehydes or ketones condense with 2-mercaptoethanol to form 1,3-oxathiolanes. The catalysts may be Lewis acids, ion-exchange resins, or mineral acids. Concentrated hydrochloric acid gave good yields and was used in most preparations. The reaction proceeded readily at the reflux temperature; formaldehyde and 2-mercaptoethanol react exothermically. A number of 1,3-oxathiolanes were prepared by this method.

Analogous to the 1,3-oxathiolanes are the 1,3-dithiolanes. Difficulty was encountered in the preparation and isolation of 1,2-ethanedithiol. Repeated attempts to get workable quantities failed. The 1,3-dithiolanes also persistently resisted preparation by methods not involving the isolation of 1,2-ethanedithiol.

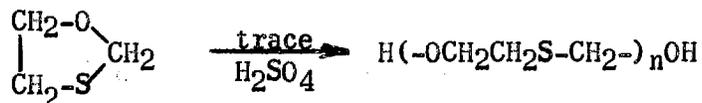
An attempt was made to prepare 6-thio-1,3-dioxocane by the method shown:



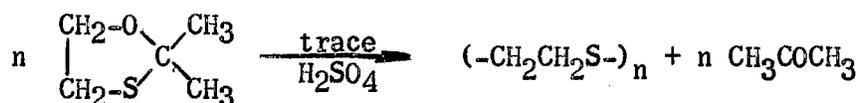
No reasonable quantity of characterizable product except water was obtained.

Polymerization of 1,3-oxathiolane was accomplished by heating the monomer at 70° for 12-72 hours with a trace of concentrated sulfuric acid. The polymer resembles those of the 1,3-dioxolane polymers of similar molecular weights.

A difference was noted in the solubility; the sulfur-containing compound is insoluble in water and soluble in aromatic hydrocarbons. The polymer is believed to be linear, with hydroxyl end-groups, as shown in the reaction:



The 2,2-dimethyl-1,3-oxathiolane did not polymerize as did the unsubstituted oxathiolane, but yielded polyethylene sulfide and acetone:



Other 2-substituted oxathiolanes reacted in a similar manner.

Copolymerization of 1,3-oxathiolane was accomplished with propylene sulfide, 1,3-dioxolane and formaldehyde, but not with ethylene sulfide. 2-Ethyl- and 2,2-dimethyl-1,3-oxathiolanes failed to copolymerize with the unsubstituted form.

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