inactive halogen compounds, a better reading can usually be obtained with the platinum black electrode as would be expected from the use of palladium for the specific purpose of the catalytic reduction of halogen compounds. Numerous attempts to use the glass electrode have failed. Dole[14] also points out that the glass electrode cannot be used in non-aqueous solutions where the activity of the water is very low.

In using the hydrogen electrode in alcoholic solutions, difficulties of the type indicated are readily recognized by the behavior of the electrode during measurements. If reduction takes place, duplicate electrodes will not agree to 0.5 millivolt and interruption of the hydrogen stream will cause a rapid change in voltage. Also, a change in the rate at which hydrogen is being bubbled into the solution will cause a fluctuation in the voltage. With these criteria as a guide, it seems probable

(14) Dole, THIS JOURNAL, **54**, 3095 (1932).

that all of the measurements reported are accurate to within 0.1 pK unit with the possible exception of the value for m-chloroaniline in ethyl alcohol. The value for this compound is close to the value obtained by Goldschmidt but it is doubtful if the maximum voltage was ever reached.

Summary

1. The dissociation constants have been measured by means of the hydrogen electrode for a series of acids and amines in ethanol.

2. The mercury–mercuric iodide half cell was found to be easily reproducible and stable as a reference electrode for both methyl and ethyl alcohols.

3. The behavior of the platinum black and the palladium black electrodes as well as the glass electrode in alcoholic solutions has been discussed.

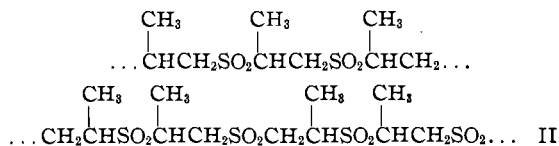AMES, IOWA   RECEIVED JANUARY 22, 1935

The Reaction between Sulfur Dioxide and Olefins. II. Propylene

BY MADISON HUNT AND C. S. MARVEL

Sulfur dioxide and propylene combine to give a product $(C_3H_6SO_2)_n$ which differs markedly in physical and chemical properties from the polysulfone which has been obtained from cyclohexene and sulfur dioxide.[1] The propylene derivative is unusual in that it is quite insoluble in all organic solvents and is soluble in dilute aqueous alkalies; but it is very easily decomposed by the alkalies to yield fairly simple products. Staudinger and Ritzenthaler[2] have recently described polypropylenesulfone, but apparently have not noticed that it differs considerably from the other olefin sulfur dioxide addition compounds that have been described.

The addition of sulfur dioxide to propylene might lead to either of two polymeric sulfones, I or II. It is also possible that the polymeric sul-

$$\begin{array}{ccccc} CH_3 & & CH_3 & & CH_3 \\ | & & | & & | \\ \ldots CHCH_2SO_2 & & CHCH_2SO_2 & & CHCH_2 \ldots \end{array}$$

$$\begin{array}{ccccccc} CH_3 & CH_3 & & & CH_3 & CH_3 \\ | & | & & & | & | \\ \ldots CH_2CHSO_2 & CHCH_2SO_2 & CH_2CHSO_2 & CHCH_2SO_2 \ldots & \text{II} \end{array}$$

(1) Frederick, Cogan and Marvel, THIS JOURNAL, **56**, 1815 (1934).
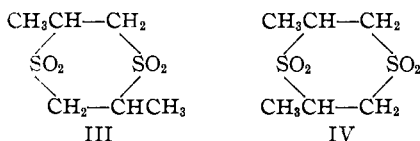(2) Staudinger and Ritzenthaler, *Ber.*, **68**, 455 (1935).

fone might contain both of these type structures mixed together in a single molecule. Such a mixed structure would not be expected, nor is it supported by the work described in this communication.

A molecule of type I would be expected on the basis of the structures which have been assigned to other polymers formed by addition reactions. Each sulfone linkage in this type is like every other sulfone linkage and alkaline degradation of a molecule of this structure should yield multiples of the building unit $\begin{array}{c} CH_3 \\ | \\ -CHCH_2SO_2- \end{array}$ or simple derivatives of it. On the other hand, the second type of structure (II) contains two types of sulfone linkages, one between secondary alkyl groups, the next between primary alkyl groups, and so on alternately throughout the chain. Fenton and Ingold[3] have shown that a sulfone linkage between two secondary alkyl groups is more easily cleaved by alkali than is such a linkage between two primary alkyl groups, hence a polymeric sulfone of type II should be degraded by alkalies to produce

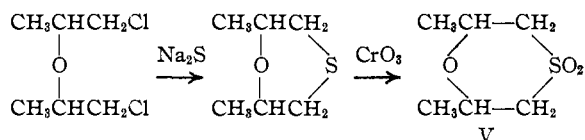(3) Fenton and Ingold, *J. Chem. Soc.*, 2338 (1929).

the unit

$$\begin{matrix} CH_3 & & CH_3 \\ | & & | \\ -CHCH_2SO_2CH_2CHSO_2- \end{matrix}$$

or simple derivatives of this unit.

It has been found that the hydrolysis of polypropylenesulfone with alkali furnishes conclusive evidence that this second type (II) of structure is the correct one. When the polymer is dissolved in normal alkali and the cold alkaline solution is slowly acidified, a product $C_6H_{12}S_2O_4$ is precipitated in almost quantitative yields. Staudinger and Ritzenthaler[2] have obtained the same product by treating the polysulfone with barium hydroxide solution, and have tentatively suggested that it is a cyclic disulfone with the structure represented in formula III. For reasons which will be presented later, we believe formula IV represents the structure of this compound.

$$\begin{matrix} CH_3CH-CH_2 \\ \diagup \qquad \diagdown \\ SO_2 \qquad SO_2 \\ \diagdown \qquad \diagup \\ CH_2-CHCH_3 \\ III \end{matrix} \qquad \begin{matrix} CH_3CH-CH_2 \\ \diagup \qquad \diagdown \\ SO_2 \qquad SO_2 \\ \diagdown \qquad \diagup \\ CH_3CH-CH_2 \\ IV \end{matrix}$$

The important point, however, is that the polysulfone is cleaved to yield six-carbon units exclusively.
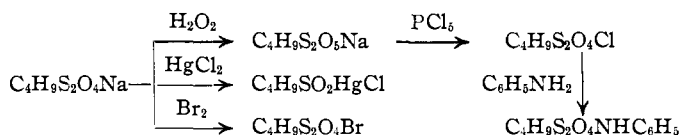
Treatment of the polysulfone with hot 5% sodium carbonate solution produced in small yield another six-carbon unit, $C_6H_{12}SO_3$, which proved to be the cyclic sulfone ether V. The structure of this compound was established by the synthesis outlined below.

$$\begin{matrix} CH_3CHCH_2Cl \\ | \\ O \\ | \\ CH_3CHCH_2Cl \end{matrix} \xrightarrow{Na_2S} \begin{matrix} CH_3CHCH_2 \\ | \qquad \diagdown \\ O \qquad S \\ | \qquad \diagup \\ CH_3CHCH_2 \end{matrix} \xrightarrow{CrO_3} \begin{matrix} CH_3CH-CH_2 \\ \diagup \qquad \diagdown \\ O \qquad SO_2 \\ \diagdown \qquad \diagup \\ CH_3CH-CH_2 \\ V \end{matrix}$$
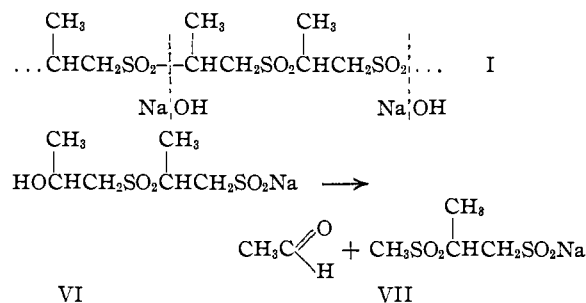
Boiling a solution of the polysulfone in 10% aqueous sodium hydroxide produced no propylene, and only traces of sodium sulfite. The polysulfones prepared from cyclohexene,[1] isobutylene,[4] and 2-pentene[4] are broken down by similar treatment to regenerate the olefin and to give sodium sulfite in considerable quantities. The polypropylenesulfone does hydrolyze smoothly under this treatment to give two products in excellent yields. One of these products separates from the alkaline solution as a red resinous substance which has been identified as a slightly contaminated sample of the resin which is formed by boiling acetaldehyde with aqueous
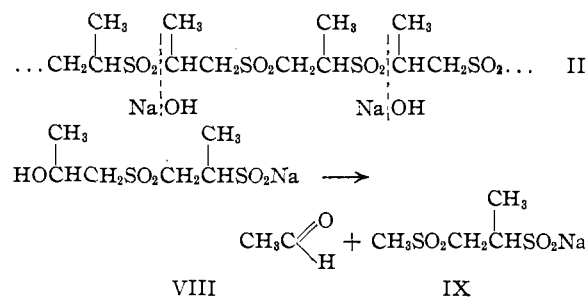
(4) Unpublished data of L. L. Ryden.

alkali.[5] The amount of resin produced indicates that two carbons out of every six carbon atoms in the polysulfone are converted to acetaldehyde during hydrolysis. The second product of this hydrolysis is a water-soluble salt with the composition $C_4H_9S_2O_4Na$. The yield of this salt is sufficient to account for the remaining four carbon atoms out of every six carbon atoms in the polysulfone. This salt gave the following reactions which indicate that it is a sodium sulfonesulfinate.

$$C_4H_9S_2O_4Na \begin{cases} \xrightarrow{H_2O_2} C_4H_9S_2O_5Na \xrightarrow{PCl_5} C_4H_9S_2O_4Cl \\ \xrightarrow{HgCl_2} C_4H_9SO_2HgCl \qquad \quad C_6H_5NH_2 \downarrow \\ \xrightarrow{Br_2} C_4H_9S_2O_4Br \qquad \quad C_4H_9S_2O_4NHC_6H_5 \end{cases}$$

A satisfactory explanation of the formation of acetaldehyde and a four carbon atom sulfonesulfinate from the polysulfone, can be offered on the basis of either structure I or II. In the case of structure I, it is necessary to assume that the compound is hydrolyzed at alternate sulfone linkages to give the six carbon atom hydroxysulfone-sulfinate (VI) indicated in the following scheme. This compound has an hydroxyl group beta to a sulfone linkage and a retrograde aldol reaction would cleave the molecule to yield acetaldehyde and the sodium sulfone-sulfinate VII.

$$\begin{matrix} CH_3 & CH_3 & CH_3 \\ | & | & | \\ \ldots CHCH_2SO_2-|-CHCH_2SO_2CHCH_2SO_2|\ldots & I \\ Na|OH & Na|OH \end{matrix}$$

$$\begin{matrix} CH_3 & CH_3 \\ | & | \\ HOCHCH_2SO_2CHCH_2SO_2Na \longrightarrow \end{matrix}$$

$$CH_3C\diagup^O_{\diagdown H} + \begin{matrix} CH_3 \\ | \\ CH_3SO_2CHCH_2SO_2Na \end{matrix}$$

VI $\qquad\qquad$ VII

On the other hand, alkaline cleavage of the sulfone linkages between secondary alkyl groups in structure II would lead to the hydroxysulfone-

$$\begin{matrix} CH_3 & CH_3 & CH_3 & CH_3 \\ | & | & | & | \\ \ldots CH_2CHSO_2|CHCH_2SO_2CH_2CHSO_2|CHCH_2SO_2\ldots & II \\ Na|OH & Na|OH \end{matrix}$$

$$\begin{matrix} CH_3 & CH_3 \\ | & | \\ HOCHCH_2SO_2CH_2CHSO_2Na \longrightarrow \end{matrix}$$

$$CH_3C\diagup^O_{\diagdown H} + \begin{matrix} CH_3 \\ | \\ CH_3SO_2CH_2CHSO_2Na \end{matrix}$$
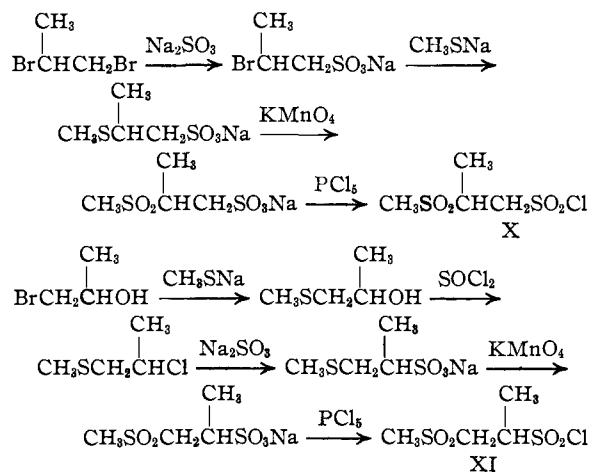
VIII $\qquad\qquad$ IX

(5) Puchot, Ann. chim., [6] 9, 422 (1886).

sulfinate VIII, and eventually to the sodium sulfone-sulfinate IX.

The reactions of the compound $C_4H_9S_2O_4Na$ which is produced by the hydrolysis of the polysulfone can be accounted for on the basis of either structure VII or IX. In order to decide between these two structures, it became necessary to use synthetic methods. The only derivative of the product of hydrolysis which was easy to purify and which had a sharp melting point was the acid chloride of the sulfonic acid which was formed by oxidation of the sulfone-sulfinate.
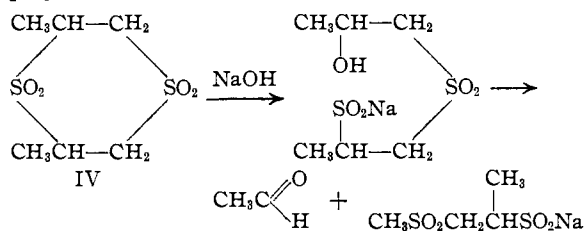
This sulfonyl chloride corresponds to either formula X or XI, depending on the structure of the hydrolysis product of the polysulfone VII or IX. Both of these sulfonyl chlorides were synthesized. The reactions used were as follows.

$$\underset{BrCHCH_2Br}{\overset{CH_3}{|}} \xrightarrow{Na_2SO_3} \underset{BrCHCH_2SO_3Na}{\overset{CH_3}{|}} \xrightarrow{CH_3SNa}$$

$$\underset{CH_3SCHCH_2SO_3Na}{\overset{CH_3}{|}} \xrightarrow{KMnO_4}$$

$$\underset{CH_3SO_2CHCH_2SO_3Na}{\overset{CH_3}{|}} \xrightarrow{PCl_5} \underset{CH_3SO_2CHCH_2SO_2Cl}{\overset{CH_3}{|}}$$
X

$$\underset{BrCH_2CHOH}{\overset{CH_3}{|}} \xrightarrow{CH_3SNa} \underset{CH_3SCH_2CHOH}{\overset{CH_3}{|}} \xrightarrow{SOCl_2}$$

$$\underset{CH_3SCH_2CHCl}{\overset{CH_3}{|}} \xrightarrow{Na_2SO_3} \underset{CH_3SCH_2CHSO_3Na}{\overset{CH_3}{|}} \xrightarrow{KMnO_4}$$

$$\underset{CH_3SO_2CH_2CHSO_3Na}{\overset{CH_3}{|}} \xrightarrow{PCl_5} \underset{CH_3SO_2CH_2CHSO_2Cl}{\overset{CH_3}{|}}$$
XI

The sulfonyl chloride (X) from the first series of reactions melted at 65°. The sulfonyl chloride (XI) from the second series of reactions melted at 100°. The sulfonyl chloride prepared by oxidizing $C_4H_9S_2O_4Na$ and treating the oxidation product with phosphorus pentachloride melted at 100°. A mixture of the synthetic material (XI) with the compound prepared from the product of hydrolysis of this polysulfone melted at 100°. Both of these sulfonyl chlorides gave the same anilide on treatment with aniline.
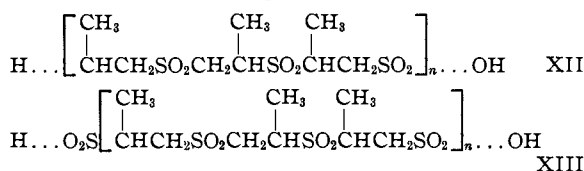
From this structure of the sulfonyl chloride, it follows that the salt $C_4H_9S_2O_4Na$ has the structure indicated in formula IX. The reaction product of this salt and mercuric chloride has the structure $\underset{CH_3SO_2CH_2CHHgCl}{\overset{CH_3}{|}}$ and the bromination product of the salt probably has the structure $\underset{CH_3SO_2CH_2CBrSO_2H}{\overset{CH_3}{|}}$.

The structure (IV) which has been assigned to the cyclic disulfone which is formed by mild hydrolysis of the polysulfone has been definitely established since hydrolysis of the cyclic product with aqueous alkalies gives the same products which are formed by hydrolysis of the original polysulfone.

$$\underset{\underset{CH_3CH—CH_2}{\diagdown}}{\overset{CH_3CH—CH_2}{\diagup}} \underset{\underset{SO_2}{\diagup}}{\overset{SO_2}{\diagdown}} \xrightarrow{NaOH} \underset{\underset{SO_2Na}{CH_3CH—CH_2}}{\overset{\overset{OH}{|}}{CH_3CH—CH_2}} \overset{\diagdown}{\underset{\diagup}{SO_2}} \longrightarrow$$
IV

$$CH_3C{\overset{O}{\diagdown_H}} + \underset{CH_3SO_2CH_2CHSO_2Na}{\overset{CH_3}{|}}$$

If the cyclic product had the structure previously suggested,[2] it would not give these products on hydrolysis.

The polypropylenesulfone is soluble in aqueous alkalies, and must, therefore, be an acidic compound. If water should add to the ends of the polysulfone molecule (II), it would be possible to produce either a monosulfonic acid (XII) or a sulfinic acid–sulfonic acid polymer (XIII), either of which would be expected to be alkali-soluble.

$$H\ldots\left[\underset{CHCH_2SO_2CH_2CHSO_2CHCH_2SO_2}{\overset{CH_3}{|}\quad\overset{CH_3}{|}\quad\overset{CH_3}{|}}\right]_n\ldots OH \quad XII$$

$$H\ldots O_2S\left[\underset{CHCH_2SO_2CH_2CHSO_2CHCH_2SO_2}{\overset{CH_3}{|}\quad\overset{CH_3}{|}\quad\overset{CH_3}{|}}\right]_n\ldots OH$$
XIII

The polypropylene sulfone does react with phosphorus pentachloride to give a sulfonyl chloride which reacts with aniline to produce an anilide. Preliminary oxidation of the polymer by treatment with hydrogen peroxide does not change the nature of the products of this series of reactions. These facts lead us to believe that formula XII represents the structure of polypropylene sulfone. The nitrogen content of the anilide indicates that the molecular weight of the polymer is about 6000 and hence n in formula XII has an average value of 19 to 20. This molecular weight is much lower than that suggested by Staudinger and Ritzenthaler[2] on the basis of viscosity measurements.

It should be noted here that the reactions of polypropylene sulfone can also be accounted for on the assumption that primary alkyl groups are linked as sulfones and the secondary alkyl groups as sulfinic esters, thus..$\left(\underset{CHCH_2SO_2CH_2CH—S{\overset{O}{\diagdown_O}}}{\overset{CH_3}{|}\qquad\overset{CH_3}{|}}\right)_n$....

Such a formula has not been rigidly excluded by the experiments which have been described above. However, it seems unlikely that sulfone linkages should alternate with sulfinic ester linkages in this polymer when there is no indication of the existence of sulfinic ester linkages in other olefin sulfur dioxide polymers. The stability of the polymer toward oxidation also favors this point of view.

Experimental

Polypropylene Sulfone.—Preliminary experiments indicated that propylene and sulfur dioxide reacted with each other rapidly in the presence of hydrogen peroxide as a catalyst, but that this reaction mixture was hard to hold in sealed glass containers. The polymer used in the experiments subsequently described was prepared by the following method. A mixture of 33 cc. of liquid sulfur dioxide and 33 cc. of liquid propylene was placed in a well-cooled pressure bottle, and about 4 cc. of paraldehyde was added. The pressure bottles were sealed and allowed to warm up to room temperature. After about two hours, the containers were cooled and opened. The material was ground finely in a mortar, washed with two 50-cc. portions of ether and dried. The yield was about 40 g. (80%) of a white amorphous solid.

Anal. Calcd. for $(C_3H_6SO_2)_n$: C, 33.96; H, 5.66; S, 30.19. Found: C, 30.63, 31.35; H, 4.81, 4.95; S, 30.14, 30.05.

The carbon and hydrogen determinations were never satisfactory as the compound decomposed to propylene and sulfur dioxide at elevated temperatures, and some propylene escaped oxidation.

The polymer began to decompose at about 250°, and was charred completely at 270°. It was insoluble in chloroform, carbon tetrachloride, dioxane, ether, acetone, alcohol, ethyl acetate, acetyl chloride and benzene. It dissolved slowly in concentrated nitric acid or concentrated sulfuric acid, and was apparently recovered unchanged by pouring these solutions into a large volume of water. The polymer dissolved in 0.1 N alkali, but upon acidification the original compound was not recovered. Hence, direct titration to determine molecular weight could not be used.

Polypropylene Sulfone-anilide.—Five grams of the polymer was ground in a mortar with 1 g. of phosphorus pentachloride. This mixture was then treated with 200 cc. of ice water and filtered. The insoluble material was treated with 5 cc. of aniline. After a few minutes this mixture was washed twelve times with 30-cc. portions of dilute hydrochloric acid to remove the excess aniline. The product was then washed five times with water and dried. This product melted, with decomposition, at 240–255°.

Anal. Calcd. for $H(C_3H_6SO_2)_{66}NHC_6H_5$: N, 0.23. Found: N, 0.23, 0.24, 0.22; mol. wt., approx. 6000.

A 5-g. sample of the polymer was treated with 20 cc. of 30% hydrogen peroxide and, after some time, the polymer was isolated and treated as above. The anilide thus obtained checked with the one previously described.

Alkaline Degradation of Polypropylene Sulfone

(a) **With Cold 0.1 N Alkali.**—In 44 cc. of 0.117 N sodium hydroxide 1.016 g. of the polymer was dissolved. Addition of acid to this solution caused a slow precipitation of a product which melted at 320°. The yield was 1.0 g.

Anal. Calcd. for $C_6H_{12}S_2O_4$: C, 33.96; H, 5.66; S, 30.19. Found: C, 33.81, 33.77; H, 5.72, 5.70; S, 30.19, 30.24.

Our molecular weight determinations were unsatisfactory.

This product is identical with the $C_6H_{12}S_2O_4$ obtained by Staudinger and Ritzenthaler by the treatment of polypropylene sulfone with barium hydroxide[2] and is a cyclic disulfone.

(b) **With Hot 5% Sodium Carbonate.**—A solution of 25 g. of the polymer in 250 cc. of 5% sodium carbonate solution was refluxed for twenty-four hours. A small amount of insoluble material separated and was filtered off. The insoluble material (2 g.) melted at 320°, and was identical with the cyclic disulfone described above.

The filtrate was extracted with ether, and evaporation of the ether yielded 3 g. of a white crystalline compound, m. p. 102°.

Anal. Calcd. for $C_6H_{12}SO_3$: C, 43.90; H, 7.32; S, 19.51; mol. wt., 164. Found: C, 43.41, 43.96; H, 7.33, 7.50; S, 19.21, 19.03; mol. wt. (Rast), 162.

This product is a cyclic ether sulfone, and its synthesis is recorded later.

(c) **With Hot 10% Aqueous Sodium Hydroxide.**—A solution of 50 g. of the polymer in 250 cc. of 10% sodium hydroxide was refluxed for eight hours. A bromine trap was provided to catch any propylene which might escape through the condenser, but no trace of propylene bromide was formed. During the period of boiling, a red solid separated. Experiment indicated that hydrolysis was complete after eight hours.

The reaction mixture was filtered, and the red amorphous material was air dried. The yield varied from 5–7 g. This product was so insoluble that it could not be purified satisfactorily. It was dried in an Abderhalden drier over boiling toluene and analyzed. It contained about 68.5% carbon and 7.15% hydrogen. This material agrees in properties with Puchot's[5] aldehyde resin from acetaldehyde which has the same physical appearance and solubility, and contains about 69.5% carbon and 8% hydrogen. Our product had some sulfur-containing compound as an impurity, and this accounts for the low values for carbon and hydrogen which we obtained.

The alkaline filtrate from the aldehyde resin was extracted with ether, but no product was thus separated. No product volatile with steam could be separated. Acidification with phosphoric acid followed by steam distillation showed no volatile product. This solution was again made alkaline and evaporated on a steam-bath. The residue solidified. Repeated extraction with hot 95% ethyl alcohol yielded 35 g. of a white crystalline salt. This salt contained water of crystallization which could be removed by drying in an Abderhalden dryer over boiling toluene.

Anal. Calcd. for $C_4H_9S_2O_4Na\cdot2H_2O$: H₂O, 15.5. Found: H₂O, 14.6, 14.7.

The remaining analyses were made on the anhydrous salt.

Anal. Calcd. for $C_4H_9S_2O_4Na$: C, 23.3; H, 4.37; S, 31.06; Na, 11.17. Found: C, 22.14, 22.26; H, 4.93, 4.79; S, 30.6, 30.7; Na, 10.23 10.4.

Reactions of the Salt $C_4H_9S_2O_4Na$

(a) **With Mercuric Chloride.**—To 200 cc. of a saturated water solution of mercuric chloride was added 2 g. of the salt. The mixture was then diluted to 300 cc. and heated at about 90° for an hour. A white crystalline compound which separated was filtered from the hot solution and washed thoroughly with hot water. The yield was 3 g. (88%) of a product which was extremely insoluble, and did not melt below 200°.

Anal. Calcd. for $C_4H_9SO_2HgCl$: Hg, 56.16. Found: Hg, 54.03, 55.29.

(b) **With Bromine.**—A solution of bromine in carbon tetrachloride was added to a suspension of 4 g. of the dry salt in 40 cc. of carbon tetrachloride until the bromine color persisted for a short time. The mixture was then heated to boiling and filtered. On concentrating the filtrate to about 20 cc., a crystalline compound separated. After three crystallizations from carbon tetrachloride it melted at 76°. The yield was 3 g. (59%). This product was insoluble in water, but dissolved in 5% sodium carbonate solution. Titration with alkali did not give a good end-point.

Anal. Calcd. for $C_4H_9S_2O_4Br$: C, 18.11; H, 3.40; S, 24.15; Br, 30.19. Found: C, 18.13, 18.12; H, 3.60, 3.52; S, 24.24; Br, 30.94.

(c) **With Hydrogen Peroxide.**—To a solution of 10 g. of the salt in 20 cc. of water was added slowly 30 cc. of 30% hydrogen peroxide. Considerable heat was liberated during the oxidation. The reaction mixture was evaporated nearly to dryness, and then taken up in 200 cc. of hot 95% alcohol. On cooling, a white crystalline solid separated. The yield was 7 g. (65%). The product was dried in an Abderhalden dryer over boiling toluene before it was analyzed.

Anal. Calcd. for $C_4H_9S_2O_5Na$: C, 21.62; H, 4.05; S, 28.83. Found: C, 20.37; H, 3.40; S, 28.19, 28.24.

The carbon and hydrogen determination was complicated by the fact that the salt did not burn well, and a dark residue was left in the boat.

A mixture of 4 g. of this salt with 4 g. of phosphorus pentachloride was ground in a mortar and the excess phosphorus pentachloride was destroyed by treatment with 250 cc. of ice water. The product which remained was recrystallized five times from benzene to yield 2.5 g. (62%) of a white crystalline solid melting at 100°.

Anal. Calcd. for $C_4H_9S_2O_4Cl$: C, 21.77; H, 4.08; S, 29.02; Cl, 16.09; mol. wt., 220.5. Found: C, 21.83, 21.84; H, 4.18, 4.24; S, 28.67; Cl, 16.30; mol. wt. (Rast), 220, 200.

One gram of the sulfonyl chloride was treated with 3 cc. of aniline, and after a few minutes the excess aniline was removed by adding 30 cc. of dilute hydrochloric acid. The anilide separated from this solution and was recrystallized four times from alcohol. The yield was 0.5 g. (49%) of white needles, m. p. 105°.

Anal. Calcd. for $C_4H_9S_2O_4NHC_6H_5$: C, 43.32; H, 5.42; S, 23.11; N, 5.06. Found: C, 42.93, 43.23; H, 5.47, 5.36; S, 23.40, 23.33; N, 5.39.

Synthesis of 2-Methylsulfonepropane-1-sulfonyl Chloride

Sodium 2-Bromopropane-1-sulfonate.—This product was prepared from propylene dibromide according to the method described for the preparation of sodium 2-bromo-ethanesulfonate.[6] A solution of 110 g. of propylene dibromide in 209 cc. of 95% alcohol and 75 cc. of water was treated with a solution of 21 g. of sodium sulfite in water. The product was recrystallized from alcohol. The yield was 25 g. (67%).

Anal. Calcd. for $C_3H_6SO_3BrNa$: Br, 35.55. Found: Br, 36.2.

Sodium 2-Methylthiolpropane-1-sulfonate.—An alcoholic solution of sodium methyl mercaptan was prepared by the method described by Windus and Shildneck.[7] A stirred mixture of 68 cc. of this solution and 20 g. of sodium 2-bromopropanesulfonate was refluxed for about twelve hours, 100 cc. of 95% alcohol was added, and the boiling mixture was filtered. On cooling, 8 g. (47%) of the desired salt separated.

Anal. Calcd. for $C_4H_9S_2O_3Na$: S, 33.33. Found: S, 32.82.

2-Methylsulfonepropane-1-sulfonyl Chloride.—To a solution of 3 g. of the above salt in 10 cc. of water was added one drop of 10% sodium hydroxide solution, and enough 5% potassium permanganate solution so that the color persisted after boiling. The hot solution was filtered and the excess permanganate was destroyed by hydrogen peroxide. The reaction mixture was evaporated to dryness and the residue was ground with 5 g. of phosphorus pentachloride. The product was isolated by adding 200 cc. of ice water and filtering the mixture. After four crystallizations from benzene, the white product weighed 0.5 g. (14%) and melted at 65°.

Anal. Calcd. for $C_4H_9S_2O_4Cl$: Cl, 16.09. Found: Cl, 16.55.

Synthesis of 1-Methylsulfonepropane-2-sulfonyl Chloride

1-Methylthiol-2-hydroxypropane.—The directions for making methylthiolethyl alcohol[7] were followed in this preparation. From 100 g. of propylene bromohydrin and 290 cc. of alcoholic sodium methyl mercaptan there was obtained 52 g. (68%) of product boiling at 67° (20 mm.); d^{20}_{20} 1.039; n^{20}_D 1.4869.

Anal. Calcd. for $C_4H_{10}SO$: S, 30.19. Found: S, 29.98.

1-Methylthiol-2-chloropropane.—The directions for preparing β-chloroethylmethyl sulfide[8] were adapted for this preparation. From 40 g. of the hydroxy compound and 53 g. of thionyl chloride, 20 g. (42%) of a product boiling at 67° (37 mm.); d^{20}_{20} 1.078; n^{20}_D 1.4905 was obtained.

Anal. Calcd. for C_4H_9SCl: Cl, 28.51. Found: Cl, 29.82.

(6) Marvel and Sparberg, "Organic Syntheses," John Wiley and Sons, Inc., New York City, 1930, Vol. X, p. 96.

(7) Windus and Shildneck, *ibid.*, 1934, Vol. XIV, p. 54.

(8) Kirner and Windus, "Organic Syntheses," John Wiley and Sons, Inc., New York City, 1934, Vol. XIV, p. 18.

A small fraction of a chlorine-rich compound which boiled higher was also obtained. It was not identified.

Sodium-1-methylthiolpropane-2-sulfonate.—To a boiling solution of 28 g. of sodium sulfite in 100 cc. of water, 25 g. of 1-methylthiol-2-chloropropane was added over a period of two hours. The mixture was stirred with a mechanical stirrer, and the heating was continued for two hours after all of the chloro compound had been added. The water was removed under reduced pressure, and the residue was recrystallized from 40 cc. of hot 95% alcohol. The yield was 16 g. (41%).

Anal. Calcd. for $C_4H_9S_2O_2Na$: Na, 33.33. Found: Na, 32.82, 32.65.

1-Methylsulfonepropane-2-sulfonyl Chloride.—A solution of 3 g. of sodium 1-methylthiolpropane-2-sulfonate in 10 cc. of water was oxidized with potassium permanganate, and the acid chloride was prepared in a manner exactly analogous to the procedure described above for the isomer. The yield was 0.5 g. (14%) of a product which melted at 100°.

This compound was mixed with the acid chloride obtained from the hydrolysis product of the polymer, and the mixture melted at 100°. A sample of the above acid chloride was converted to the anilide which melted at 105°, and showed no depression in melting point when mixed with a sample of anilide prepared from the product of hydrolysis of the polysulfone.

Hydrolysis of the Cyclic Disulfone $C_6H_{12}S_2O_4$ (IV).— A mixture of 3 g. of the cyclic disulfone (m. p. 320°) which was isolated from the mild hydrolysis of the polypropylenesulfone was boiled with 25 cc. of 10% aqueous sodium hydroxide for twelve hours. During this period the same red amorphous compound which was obtained by hydrolysis of the polysulfone separated. The mixture was filtered, and the soluble sodium salt was isolated from the water. On oxidation with hydrogen peroxide and treatment with phosphorus pentachloride it yielded 1-methylsulfonepropane-2-sulfonyl chloride, m. p. 100°.

Synthesis of the Cyclic Sulfone Ether $C_6H_{12}SO_3$ (V). 2,6-Dimethyl-p-thioxane.—An alcoholic solution of sodium sulfide was prepared as described by Bost and Conn[9] 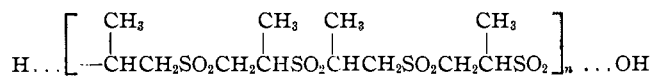in connection with the preparation of n-propyl sulfide. A solution of 240 cc. of this alcoholic sodium sulfide in 200 cc. of absolute alcohol was heated to boiling in a 1-liter, three-necked flask fitted with a dropping funnel, mechanical stirrer and reflux condenser. The stirrer was started and 35 g. of dichloroisopropyl ether[10] was added through the dropping funnel. The mixture was refluxed for about eight hours and then the alcohol was distilled. The residue was extracted twice with 50 cc. of ether, and the ether evaporated from the extract. The oil which remained was distilled. The yield was 20 g. (74%) of a product of b. p. 162°.

Anal. Calcd. for $C_6H_{12}SO$: S, 24.28. Found: S, 24.28.

Oxidation of 2,6-Dimethyl-p-thioxane.—The oxidation of the thioxane derivative to the sulfone did not run well. Neither aqueous potassium permanganate nor perhydrol in acetic acid gave satisfactory results. Chromic oxide in acetic acid yielded the sulfone in rather poor yields. To a solution of 3 g. of 2,6-dimethyl-p-thioxane in 20 cc. of glacial acetic acid was added in very small portions 2.5 g. of chromic oxide. Considerable heat was generated and occasionally the reaction mixture exploded. After the addition of the oxidizing agent, the solution was made alkaline with potassium carbonate and the sulfone was extracted with ether. Evaporation of the ether left an oily residue from which a few crystals separated after a few days. These crystals were separated and recrystallized from alcohol; m. p. 101°. A mixture of this synthetic product with the compound $C_6H_{12}SO_3$ obtained by action of 5% sodium carbonate on propylene polysulfone melted at 102°.

Summary

Polypropylenesulfone has been prepared by the interaction of propylene and sulfur dioxide, and its structure has been shown to be

$$H\cdots\left[-\underset{\underset{\displaystyle CH_3}{|}}{CH}CH_2SO_2CH_2\underset{\underset{\displaystyle CH_3}{|}}{CH}SO_2\underset{\underset{\displaystyle CH_3}{|}}{CH}CH_2SO_2CH_2\underset{\underset{\displaystyle CH_3}{|}}{CH}SO_2\right]_n\cdots OH$$

(9) Bost and Conn, "Organic Syntheses," John Wiley and Sons, Inc., New York City, 1935, Vol. XV, p. 72.

(10) The product marketed by Carbide and Carbon Chemicals Corporation was used.