[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reaction between Sulfur Dioxide and Olefins. III.[1] Higher Olefins and Some Limitations of the Reaction

BY L. L. RYDEN AND C. S. MARVEL

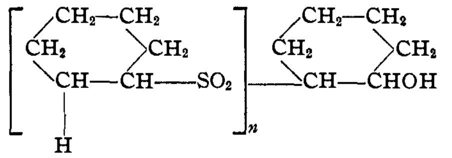
Previous investigations have shown that sulfur dioxide will combine with the simple olefins ethylene,[2] propylene,[1,2] cyclohexene[3] and methylpropene;[4] with a large number of conjugated dienes;[5] and with allyl alcohol and some of its simple ethers.[6] In order to learn more about the limitations of this addition reaction we have made this study of the formation of polysulfones from sulfur dioxide and a variety of unsaturated compounds.

Polysulfones have been obtained by the combination of sulfur dioxide and methylpropene, 1-pentene, 2-pentene, 1-nonene, 3-cyclohexylpropene and 3-methylcyclohexene. Under the same experimental conditions which were used for the production of the above polysulfones, no reaction could be obtained between sulfur dioxide and trimethylethylene, tetramethylethylene, pinene or 1,4-dihydronaphthalene. The failure of these olefins to react with sulfur dioxide indicates that increasing the number of hydrocarbon substituents on the carbon atoms which are attached by a double union will tend to block this addition reaction.

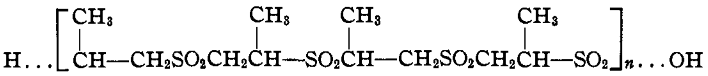
We have also treated sulfur dioxide with the following compounds which contain not only the olefin group but some other functional group as well: 1-chloropropene, trichloroethylene, allyl cyanide, 2-allyl-*p*-cresol, undecylenic acid, sodium undecylenate, ethyl undecylenate, ethyl erucate, crotonaldehyde, oleyl alcohol and undecylenyl alcohol. Of these compounds, only undecylenyl alcohol gave a polysulfone. This confirms Solonina's observation[6] that an alcoholic hydroxyl group in the olefin molecule does not interfere with the formation of a polysulfone. The failure of oleyl alcohol to combine with sulfur dioxide must be due to the fact that the double bond is in the middle of a long chain. While the negative results obtained in our other experiments must be accepted with the usual caution, they do clearly show that many simple functional groups do interfere with the addition of sulfur dioxide to an olefin group. In this connection, it may be mentioned that *d*-limonene, an unconjugated diene, also failed to combine with sulfur dioxide under the conditions of our experiments.

1-Heptyne does combine with sulfur dioxide to produce a polymeric product of the composition $(C_7H_{12}SO_2)_n$. The extension of the reaction to other acetylenes is now under investigation in this Laboratory.

In the earlier work on cyclohexene,[3] it was found that the polysulfone (I) contained an alcohol group which could be chloroacetylated.



I



$$H\ldots\left[\overset{CH_3}{CH}-CH_2SO_2CH_2\overset{CH_3}{CH}-SO_2\overset{CH_3}{CH}-CH_2SO_2CH_2\overset{CH_3}{CH}-SO_2\right]_n\ldots OH$$

II

On the other hand, it was found that propylene-polysulfone (II)[1] has a sulfonic acid group at one end of the chain. The polysulfones described in this paper are apparently of the alcohol type, as none of them are alkali soluble, and those which have been treated with an acid chloride have given acyl derivatives.

In previous work[3] an attempt was made to estimate the molecular weight of cyclohexene-polysulfone from the chlorine content of the chloroacetyl derivative. Further work on this phase of the problem has cast some doubt on the molecular weight values which are determined in this manner. It is extremely difficult to purify these compounds, and their chlorine content is

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(1) For the second paper in this series, see Hunt and Marvel, THIS JOURNAL, **57**, 1691 (1935).

(2) Staudinger and Ritzenthaler, *Ber.*, **68**, 458 (1935).

(3) Frederick, Cogan and Marvel, THIS JOURNAL, **56**, 1815 (1934).

(4) Mathews and Elder, British Patent 11,635 (1914); *C. A.*, **9**, 2971 (1915).

(5) De Bruin, *Verslag. Akad. Wetenschappen*, **23**, 445 (1914); *C. A.*, **9**, 623 (1915); Hofmann and Damm, *Chem. Zentr.*, **97**, I, 2342 (1926); Staudinger, German Patent 506,839 (1929); French Patent 698,857 (1930); *C. A.*, **25**, 522, 3360 (1931); Eigenberger, *J. prakt. Chem.*, **127**, 307 (1930); **129**, 312 (1931); Backer and Bottema, *Rec. trav. chim.*, **51**, 294 (1932); Backer and Strating, *ibid.*, **53**, 525 (1934); **54**, 170 (1935); Seyer and King, THIS JOURNAL, **55**, 3140 (1933); Sorokin and Puztizkii, *Sintet. Kauchuk*, **6**, 12–16 (1933); *C. A.*, **28**, 3339 (1934); Staudinger and Ritzenthaler, *Ber.*, **68**, 455 (1935).

(6) Solonina, *J. Russ. Phys.-Chem. Soc.*, **30**, 826 (1898).

low. We have used trichloroacetyl chloride as an acylating agent in our later experiments, but even with the threefold increase in chlorine content, the experimental error is so large that the calculated molecular weight cannot be checked closer than about 50,000. Therefore, the only conclusion we have reached concerning the molecular weights of the various polysulfones is that all are in the region of 100,000 to 200,000. We have repeated some earlier work on the estimation of the molecular weight of propylenepolysulfone by determining the nitrogen content of the anilide, and have found that this polysulfone has a molecular weight of about 50,000 instead of 6000. This new value is in better agreement with the molecular weight of propylenepolysulfone which Staudinger and Ritzenthaler[2] calculated from viscosity measurements.

The alkaline degradation of these new polysulfones has not been extensively studied. 2-Pentenepolysulfone, on heating with sodium hydroxide solution, yields 2-pentene, dipentenylsulfone and sodium sulfite. Methylpropenepolysulfone gives large amounts of methylpropene and sodium sulfite under the same conditions. No other hydrolysis products were obtained. 1-Pentenepolysulfone does not regenerate the olefin when heated with alkali. Therefore, it is probable that the polysulfones derived from all olefins of the type $RCH{=}CH_2$ will be found to be closely related to propylenepolysulfone in structure.

Experimental Part

Polysulfones from Simple Olefins.—The general method developed for the preparation of cyclohexenepolysulfone[3] was followed in this work. Ten volumes of liquid olefin and ten volumes of liquid sulfur dioxide were mixed together in a pressure flask, and one volume of 3% hydrogen peroxide and one volume of paraldehyde was added. The pressure flask was sealed and the mixture allowed to stand for about twelve hours. In most cases, the reaction was then as complete as it could be made to go under these general conditions. In the case of methylpropene, 1-pentene and 1-nonene, it was observed that better results were obtained by mixing the olefin, sulfur dioxide and hydrogen peroxide, and allowing this mixture to stand for twelve hours, then introducing the paraldehyde. Within an hour, the reaction was then finished.

In all cases, the products were isolated by pouring the reaction mixture into water, and were purified by thorough washing with alcohol and ether. The yields, melting points and analyses of the new polysulfones are recorded in Table I.

Methylpropenepolysulfone is a white, amorphous powder, quite brittle and insoluble in common organic solvents. The derivatives of 1-pentene, 2-pentene and 1-nonene were soluble in acetone, and were purified by solution in this solvent and reprecipitation with water. 1-Nonenepolysulfone is a softer and more plastic material than are the polysulfones with shorter carbon chains.

Perbenzoic acid could not be satisfactorily substituted for 3% hydrogen peroxide as a catalyst for the addition reaction.

Trichloroacetyl Derivatives and Calculated Molecular Weights.—The trichloroacetyl derivatives of the polysulfones from cyclohexene, methylpropene, 1-pentene, 2-pentene, 3-cyclohexylpropene and 1-nonene were prepared by allowing a mixture of 1 g. of polysulfone and 3 cc. of trichloroacetyl chloride to stand for about twenty-four hours. Methylpropenepolysulfone was the only one which was completely insoluble in the acid chloride. At the end of twenty-four hours the reaction mixture was poured into water and filtered. Most of the trichloroacetic acid was removed by grinding the product with alcohol, filtering and repeating the process, using ether as a solvent. The trichloroacetyl derivative was then dissolved in a solvent and reprecipitated. This product was then ground up with alcohol and washed on a filter with ether at least three times. Control experiments, using the polysulfone and trichloroacetic acid, showed that all of the chlorine could be removed by this method of purification. Methylpropenepolysulfone was most difficult to purify, since it did not dissolve in any solvent which was tried. The cyclohexene derivative was purified by dissolving in benzene and precipitation with alcohol, and the other products were dissolved in acetone and precipitated with water. The products were carefully dried and analyzed for chlorine by the Parr bomb procedure. A 0.3 to 0.4-g. sample was

Table I

Properties of Some Polysulfones

				Analyses, %					
				Calcd.		Found			
Olefin used	Yield, %	M. p. (dec.), °C. Bloc Maquenne	Formula	C	H	C		H	
Methylpropene[d]	75–90	340	$(C_4H_8SO_2)_n$	40.0	6.66	39.5	39.7	6.84	7.16
2-Pentene	75	290–300[a]	$(C_5H_{10}SO_2)_n$	44.8	7.46	44.34	44.40	7.12	7.28[b]
1-Pentene	80–90	340	$(C_5H_{10}SO_2)_n$	44.8	7.46	42.9	43.9	7.54	7.82
1-Nonene	75–80	>300[c]	$(C_9H_{18}SO_2)_n$	57.0	9.47	56.9	56.7	8.58	9.15
3-Cyclohexylpropene[e]	75	330	$(C_9H_{16}SO_2)_n$	57.5	8.50	57.2	56.7	8.34	8.78
3-Methylcyclohexene	5–10	270	$(C_7H_{12}SO_2)_n$	52.5	7.50	51.8	51.7	7.39	7.25

[a] Decomposes at 215–220° in an ordinary melting-point tube. [b] Calcd. for $(C_5H_{10}SO_2)_n$: S, 23.88. Found: S, 24.04, 23.73. [c] This polymer was quite plastic at 200°, and slowly decomposed at 300°. [d] Calcd.: S, 26.6. Found: S, 26.00, 25.85. [e] Calcd.: S, 17.00. Found: S, 17.12.

used, and 0.05 N silver nitrate and ammonium thiocyanate solutions were used. Blanks were run on the reagents in each experiment. The results are summarized in Table II.

TABLE II

POLYSULFONE TRICHLOROACETATES

Polysulfone from	Expt. no.	Chlorine, %	Calcd. mol. wt.
Cyclohexene	1	0.107	99,200
Cyclohexene	2	.075	142,000
		.075	142,000
Cyclohexene	3[a]	.109	98,000
		.065	164,000
1-Pentene	4	.077	139,000
		.045	237,000
2-Pentene	5	.045	237,000
	6	.086	124,000
Methylpropene[b]	7	.041	260,000

[a] This sample was prepared by allowing the solution of cyclohexenepolysulfone in trichloroacetyl chloride to stand for ten days.

[b] This derivative was purified by repeated washing with alcohol and ether.

The polysulfones prepared from 1-nonene and 3-cyclohexylpropene reacted with trichloroacetyl chloride to liberate hydrogen chloride. The resulting products were sticky, insoluble materials of such a nature that purification was very unsatisfactory, and hence no attempt has been made to estimate molecular weights from the chlorine content of these esters.

Propylenepolysulfonanilide. — Propylenepolysulfonanilide was prepared as described previously.[1] The product was ground up with 5% hydrochloric acid and filtered, and this process repeated four times. Sample AI was then collected. The hydrochloric acid treatment was repeated five more times, and sample AII was collected. After five more washings, sample AIII was collected. Then the remaining product was suspended in water, exactly neutralized and boiled for thirty minutes (in order to steam distill any remaining aniline). The propylenepolysulfonanilide was then washed with alcohol and ether to give sample AIV. For comparison, a mixture of propylenepolysulfone and aniline were similarly treated, and B samples I′ to IV′ were collected. Nitrogen in these samples was determined by the Kjeldahl method. The results of these experiments are given in Table III.

TABLE III

NITROGEN CONTENT AND MOLECULAR WEIGHT OF PROPYLENEPOLYSULFONANILIDE

Sample A	N, %	Sample B	N, %	N, % A − B	Calcd. mol. wt.
I	0.065	I′	0.029	0.036	38,880
II	.043	II′	.013	.030	46,600
III	.040	III′	.0076	.032	43,750
IV	.0175	IV′	.0022	.015	93,300

The fact that the nitrogen content of the polymer after correction remains fairly constant through the first three samples seems significant. The low value for nitrogen in sample IV indicates that steam distillation has caused some complex decomposition of the molecule.

Alkaline Degradation of Polysulfones

2-Pentenepolysulfone.—A mixture of 50 g. of 2-pentenepolysulfone and 160 cc. of 20% sodium hydroxide was heated under a reflux condenser for about an hour and a half. During this heating period a considerable amount of 2-pentene was formed. This was collected in a cooled trap at the upper end of the reflux condenser. The olefin was identified by its boiling point (36–37°) and by the boiling point of its dibromo derivative (176°). During the period of refluxing, an oil appeared on the alkaline solution. This product was separated and distilled under reduced pressure. It boiled at 132° at 4–5 mm., decolorized an aqueous solution of potassium permanganate, but did not take up bromine from carbon tetrachloride. It is apparently a diamylenesulfone.

Anal. Calcd. for $C_{10}H_{18}SO_2$: C, 59.04; H, 8.91; S, 15.83; mol. wt., 202. Found: C, 58.5, 58.7; H, 9.52, 9.47; S, 16.9, 16.7; mol. wt. (Rast), 206, 218.

From the alkaline solution considerable sodium sulfite was isolated. No organic sulfonic or sulfinic acid salts could be extracted from these residues.

Methylpropenepolysulfone.—A mixture of 40 g. of methylpropenepolysulfone and 150 cc. of 10% sodium hydroxide solution was heated to boiling. Within fifteen minutes over 35% of the theoretical amount of methylpropene was liberated. The olefin was identified as the dibromide, b. p. 148–149°. Sodium sulfite was produced in large quantities, but no other hydrolysis products were isolated.

1-Pentenepolysulfone.—A mixture of 35 g. of 1-pentenepolysulfone and 100 cc. of 20% sodium hydroxide solution was heated under a reflux condenser. The polysulfone dissolved in a short time producing a red-colored solution. No 1-pentene was regenerated. After about fifteen minutes a small amount of oily material separated on the surface of the solution. However, no definite products were isolated from the amount of material which was available.

Undecylenyl Alcohol Polysulfone.—Undecylenyl alcohol and sulfur dioxide combine very easily under the general conditions mentioned above, and the paraldehyde can be omitted from the reaction mixture without affecting the yield of product. The polysulfone is at first a jelly-like mass, but soon turns to a semi-transparent, crumbly substance which is insoluble in all common organic solvents, and is also insoluble in dilute aqueous alkalies. The product darkened at 330°, but did not appear to soften or liberate gas.

Anal. Calcd. for $(C_{11}H_{22}SO_3)_n$: C, 54.26; H, 9.86. Found: C, 55.91, 55.54; H, 8.99, 9.19.

The product was converted to a chloroacetyl derivative, but the properties were not changed in any noticeable fashion.

Anal. Calcd. for $(C_{11}H_{21}OCOCH_2ClSO_2)_n$: Cl, 11.4. Found: Cl, 10.8, 10.5.

1-Heptyne Polysulfone.—When 1-heptyne and sulfur dioxide were allowed to react in the presence of 3% hydrogen peroxide and paraldehyde, a 50–60% yield of a polymer was obtained after three days. The product was soluble in acetone and insoluble in alcohol, ether and cold dilute sodium hydroxide solution. It melted at 160–169°.

Anal. Calcd. for $(C_7H_{12}SO_2)_n$: C, 52.5; H, 7.50; S, 20.00. Found: C, 52.38, 52.32; H, 7.55, 7.62; S, 19.5, 19.4.

Summary

1. Methylpropene, 1-pentene, 2-pentene, 1-nonene, 3-cyclohexylpropene and 3-methylcyclohexene give polysulfones by the addition of sulfur dioxide. These polysulfones are all neutral products and the first five of them have alcohol groups at the ends of the chains. Evidence has been obtained to indicate that 1-pentenepolysulfone is degraded with alkali in a manner which is like that reported for propylenepolysulfone, whereas the methylpropene and 2-pentene derivatives are degraded more nearly after the manner of the cyclohexene derivative. The molecular weights of these polysulfones are in the range of 100,000 to 200,000.

2. Highly substituted olefins do not add sulfur dioxide under the experimental conditions used in our work.

3. Polysulfones have been obtained from 1-heptyne and from undecylenyl alcohol. No evidence of addition of sulfur dioxide to typical olefins containing chloro, cyano, phenolic hydroxyl, aldehydo, carboethoxy, carboxyl or salt of carboxyl groups could be obtained.

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Arsenicals Containing the Furan Nucleus. II. Action of Chlorine. Some Substituted Furan Arsenicals

BY WESLEY G. LOWE[1] AND CLIFF S. HAMILTON

The action of chlorine on furyldichloroarsine, difurylchloroarsine and trifurylarsine in chloroform or carbon tetrachloride solution leads in every instance to the formation of 2-chlorofuran tetrachloride. This reaction can be carried out at room temperature or by introducing dry chlorine gas into a chloroform solution of the arsenical at −78° followed by evaporation of the solvent at room temperature. 2-Chlorofuran, prepared from Hill's 5-chloropyromucic acid[2] by decarboxylation in aqueous mercuric chloride,[3] adds four atoms of chlorine under the same conditions and the 2-chlorofuran tetrachloride thus obtained is identical with that prepared from the furan arsenicals.

In agreement with the observation made by Hill and Hartshorn[4] that 2,5-dibromofuran tetrabromide in alcoholic potassium hydroxide solution loses two molecules of hydrogen bromide to yield tetrabromofuran, we have found that from a similar solution of 2-chlorofuran tetrachloride 40% of the total chlorine can be precipitated with silver nitrate, indicating the loss of two molecules of hydrogen chloride and the formation of a trichlorofuran. The action of aqueous silver nitrate on an alcoholic solution of 2-chlorofuran tetrachloride is complex, varying conditions of temperature and acidity leading to a precipitation of 60, 70 and 75% of the total chlorine as silver chloride. Hydrolysis of the symmetrical molecule, 2,5-dibromofuran tetrabromide, involves a loss of five-sixths of the total bromine yielding bromomaleic acid as a final product.[4] This stepwise loss of chlorine is the same for chlorofuran tetrachloride prepared by either of the methods mentioned and is further proof of identity of structure.

Efforts to isolate a second product from the chlorination of furyldichloroarsine were unsuccessful. However, in each of six chlorinations of difurylchloroarsine it was possible to isolate a white solid which on exposure to air gave off hydrogen chloride gas. This compound was not identified as such, but on hydrolysis with cold water it yielded difurylarsinic acid which was purified by crystallization from hot water. Although it is not necessary to fractionate difurylchloroarsine to purity before chlorination in order to obtain this acid, efforts to prepare it from the mixture of arsenicals before distillation were unsuccessful. The acid, when pure, is stable to air and light, but it is more sensitive to sulfuric acid than is furoic acid and can be detected in very dilute solution by the formation of a dark ring at the water–sulfuric acid interface.

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(1) Parke, Davis and Company Fellow.

(2) Hill and Jackson, *Proc. Am. Acad. Arts Sci.*, **24**, 320 (1889).

(3) Gilman and Wright, THIS JOURNAL, **55**, 3302 (1933).

(4) Hill, *Ber.*, **16**, 1132 (1883); Hill and Hartshorn, *ibid.*, **18**, 449 (1885).