The Effect of β-Hydrogen Atoms and Hydrocarbon Structure on the Thermal Stability of Sulfones[1]

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The effect of the β-hydrogen atoms and hydrocarbon structure on the thermal stability of sulfones has been investigated. Twelve monomeric sulfones containing from 0 to 18 β-hydrogen atoms and of varying structure were synthesized and then heated at 275° for 1 hr. under vacuum in the absence of solvent. The results indicate that the absence of β-hydrogen atoms, or their substitution by stabilizing groups and by long methylene chains or alicyclic rings, enhances the thermal stability of sulfones. Phenyl groups α to the sulfone group acting as electron-withdrawing groups also have a stabilizing effect. To test these observations, sulfone polymers containing these features were synthesized and their thermal stabilities studied.

It is well known that the sulfone group has an activating influence on the hydrogen atoms at the α-position in sulfones. Two sulfone groups on the same carbon atom make the hydrogen replaceable by alkali metals; three sulfone groups permit the hydrogen atom to ionize.[2]

The precise nature of the effect of the sulfone group on the hydrogen atoms at the β-carbon atoms is not nearly so well known. β-Disulfones appear to exhibit a high degree of instability to basic reagents. Diethyl sulfone, for instance, in the presence of potassium hydroxide decomposes at 200° to give ethylene and potassium ethylsulfinate.[3a] Fenton and Ingold found that dioctyl sulfone is stable under these conditions. This shielding effect of methylene groups on the decomposition of alkyl sulfones by β-elimination in the order of the ease of elimination of olefin was shown to be phenylethyl > ethyl, isopropyl, *sec*-butyl > propyl > *n*-butyl > *n*-amyl, *n*-hexyl, *n*-heptyl, *n*-octyl > isoamyl > isobutyl.[3b] Naylor and Anderson have shown that the decomposition rates of polymers of olefins and sulfur dioxide roughly parallel the total number of hydrogen atoms on the carbon atoms β to the sulfone linkage.[4] Whether a true β-elimination takes place has never been fully established.

The pyrolysis of aromatic sulfones containing methyl groups *ortho* and *para* to the sulfonyl group has been investigated.[5] At least one methyl group was found necessary to produce diarylmethanes by β-elimination.

In general it appears that the thermal stability of sulfones and sulfone polymers may depend on the number of β-hydrogen atoms and the hydrocarbon structures. In the present investigation an attempt was made to correlate these two factors with the thermal properties of sulfones by studying the extent of decomposition of twelve monomeric sulfones at 275° in the absence of solvent (see Table I). For this investigation, sulfones containing 0 to 18 β-hydrogen atoms and of varying structures were prepared and tested. In counting β-hydrogens, we have ignored those of an aromatic ring, since it is quite unlikely that they can participate in hydrogen-bond formation involving an *o*-carbon and a sulfone oxygen.

TABLE I

MODEL MONOMERIC SULFONES

Sulfone	Number of β-hydrogens	M.p. or b.p. (mm.), °C.	Yield, %
Diphenyl[a]	0	127–128	97
Dimethyl[b]	0	109–110	94
Dibenzyl	0	151.0–151.5	17
Isobutyl phenyl[c]	1	126 (1)	87
Benzyl butyl	2	97.0–97.5	78
Diisobutyl[d]	2	265 (750)	62
Dibutyl[e]	4	43.5–44.0	97
Didodecyl[f]	4	92.5–93.0	73
Cyclopropyl phenyl	4	120–124 (0.1)	56
Isopropyl phenyl[g]	6	112–114 (0.5)	47
Diisopropyl[d]	12	128–130 (0.5)	60
Di-*t*-butyl	18	128–129	77

[a] O. Hinsberg, *Ber.*, **43**, 290 (1910). [b] E. Fromm and J. Polma, *ibid.*, **39**, 3315 (1906). [c] *Anal.* Calcd. for $C_{10}H_{14}O_2S$: C, 60.60; H, 7.07; S, 16.16. Found: C, 60.46; H, 7.29; S, 16.29. [d] See ref 9. [e] N. Grabowsky, *Ann.*, **175**, 348 (1875). [f] P. Allen, Jr., L. S. Karger, J. D. Haygood, Jr., and J. Schresnel, *J. Org. Chem.*, **16**, 767 (1951). [g] See ref. 10.

Discussion

The decomposition of sulfones generally appears to increase with increasing number of β-hydrogen atoms but there are several exceptions. Dibutyl sulfone with four β-hydrogen atoms decomposes to a less extent than isobutyl phenyl, benzyl butyl, and diisobutyl sulfones which contain fewer β-hydrogens. The structural effects of the substituent groups on the thermal stability must therefore be considered. By examining Table II we note that two phenyl groups result in a stable sulfone, perhaps as a result of the type of β-hydrogen atoms and the high energy of activation necessary to produce the highly active phenyl radical formed on scission of the carbon–sulfur bond. Benzyl groups tend to promote instability because the stable benzyl free radical produced on bond scission provides a driving force for decomposition. Alkyl phenyl sulfones show greater stability than alkyl sulfones because of the electron-withdrawing effect of the phenyl group. Stability of alkyl sulfones decreases as the carbon attached to the sulfone group is changed from a primary to a secondary and then to a tertiary carbon atom, corresponding to the increasing stabilities of the primary, secondary, and tertiary alkyl free radicals produced. The shielding effect of a long methylene

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[1] Presented before the Division of Organic Chemistry at the 145th National Meeting of the American Chemical Society, New York, N. Y., September, 1963.

[2] C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 740, 754 ff.

[3] (a) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 3128 (1928); (b) 2338 (1929); 705 (1930).

[4] M. A. Naylor and A. W. Anderson, *J. Am. Chem. Soc.*, **76**, 3962 (1954).

[5] H. Drews, E. K. Fields, and S. Meyerson, *Chem. Ind.* (London), 1403 (1961).

chain or the steric effect of a cyclopropyl group stabilizes the sulfone by making interaction between the sulfone group and the β-hydrogens difficult. Details of a mechanism of decomposition involving β-hydrogen atoms will appear elsewhere.

TABLE II

EFFECT OF β-HYDROGEN ATOMS ON THE THERMAL STABILITY OF SULFONES AT 275° FOR 1 HR.

Sulfone	Number of β-hydrogen atoms	Pressure, mm.	Decomposition, mole %
Dimethyl	0	6	0.03
Diphenyl	0	10	0.14
Dibenzyl	0	25	0.73
Isobutyl phenyl	1	14	1.2
Benzyl butyl	2	22	1.5
Diisobutyl	2	24	3.1
Dibutyl	4	12	0.7
Didodecyl	4	4	0.21
Cyclopropyl phenyl	4	10	0.84
Isopropyl phenyl	6	36	2.8
Diisopropyl	12	76	4.5
Di-*t*-butyl	18	330	85.8

We desired to compare the thermal stability of these simple compounds with the stability of polymeric sulfones and determine whether our structural and mechanistic hypotheses had validity for similar polymers.

Therefore several sulfone polymers with the following structural features were synthesized and examined: polymers without β-hydrogen atoms or with one or more β-hydrogens substituted by stabilizing groups, polysulfones containing long methylene chains or heterocyclic rings, and sulfone polymers containing phenyl groups α to the sulfone groups. In addition, the stability of a polysulfone with three sulfone groups β to one methylene group also was investigated.

We conclude that sulfone polymers of high purity whose β-hydrogens are substituted or shielded by long carbon chains or are sterically hindered ring hydrogens should be thermally stable. Phenyl groups α to the sulfone group acting as electron-withdrawing groups should also aid in the stabilization of such polymers.

Experimental

Preparation and Purification of Sulfones.—The sulfones prepared for this investigation are listed in Table I. They were in most cases prepared by condensation of a mercaptide with a halide in ethanol. The resulting sulfide was oxidized to the sulfone with hydrogen peroxide in acetic acid. The following sulfones were synthesized by other methods.

Dibenzyl sulfone was prepared from benzyl chloride and sodium dithionite.[6] Benzyl chloride, 12.6 g. (0.10 mole) and 9.0 g. (0.50 mole) of sodium dithionite were heated with stirring for 9 hr. in 100 ml. of dimethylformamide at 110°. The product was obtained by pouring the mixture into ice and recrystallizing the crude product from ethyl alcohol, 2.0 g., 17%, m.p. 151.0–151.5° (lit.[7] m.p. 151°).

Benzyl butyl sulfone was synthesized from lithium butylsulfinate, prepared from butyllithium and sulfur dioxide, and benzyl chloride in refluxing ethyl alcohol as solvent. The product, recrystallized twice from isopropyl alcohol, melted at 97.0–97.5°, lit.[8] m.p. 95–97°, 78%.

Diisopropyl sulfone was prepared from 24.6 g. (0.20 mole) of isopropyl bromide and 11.2 g. (0.20 mole) of sodium hydrosulfide in 100 ml. of water and 100 ml. of ethanol. The mixture was refluxed 4 hr., 300 ml. of water was added, and the fraction extracted with hexane and ether was oxidized with 30% hydrogen peroxide in 100 ml. of acetic acid at 80° for 3 hr. The product, 9.0 g., 60%, was obtained by fractional distillation; it boiled at 128–130° (0.3–0.5 mm.), lit.[9] m.p. 36°.

Anal. Calcd. for $C_6H_{14}O_2S$: C, 48.00; H, 9.30; S, 21.35. Found: C, 48.01; H, 9.39; S, 21.24.

Cyclopropyl phenyl sulfone was prepared by the method of Zimmerman and Thyagarajan[10] by cyclization of 21.9 g. of γ-chloropropyl phenyl sulfone in a solution of sodium *t*-butoxide prepared from 2.76 g. of sodium and 60 ml. of *t*-butyl alcohol. The solution was stirred and refluxed for 6 hr., then cooled, diluted with 200 ml. of water, extracted with ether, dried over sodium sulfate, and concentrated at reduced pressure. Distillation of the residue gave 10.2 g. of a colorless oil, 56%, b.p. 120–124° (0.1 mm.). The product was further purified by fractional crystallization, giving a solid product m.p. 36–37°, lit.[11] m.p. 36–37.5°, b.p. 130–135° (0.5 mm.). The structure of this compound was confirmed by infrared and elemental analysis.

Anal. Calcd. for $C_9H_{10}O_2S$: C, 59.33; H, 5.53; S, 17.58. Found: C, 59.04; H, 5.92; S, 17.21.

Di-*t*-butyl sulfone was prepared *via* nucleophilic substitution of *t*-butyl mercaptan on the carbonium ion of *t*-butyl alcohol in sulfuric acid by adapting the method of Fehnel and Carmack,[12] followed by oxidation. A mixture of 225 g. of concentrated sulfuric acid and 65 g. of water was cooled in an ice bath. *t*-Butyl alcohol, 50.4 g. 0.60 mole, was added at such a rate as to control the temperature of the mixture near 10°. After the addition had been completed, 27.0 g. (0.30 mole) of *t*-butyl mercaptan was added dropwise during 30 min. The reaction mixture was allowed to warm to 25°. The product, *t*-butyl sulfide, boiling at 144–149°, was isolated by pouring the mixture over 500 g. of ice, extracting with ether, drying over anhydrous magnesium sulfate, and fractionally distilling the ether solution. The yield was 28.2 g. (88%). The sulfide, 10.2 g., was oxidized to the sulfone in 45 ml. of acetic acid with 30% hydrogen peroxide. The acid was neutralized with aqueous sodium hydroxide and extracted with ether to give 9.5 g. (77%) of sulfone, recrystallized from water, and purified by sublimation, m.p. 128–129°, lit.[13] m.p. 129–130°.

Anal. Calcd. for $C_8H_{18}O_2S$: C, 53.93; H, 10.11; S, 17.97. Found: C, 54.05; H, 10.29; S, 18.09.

Decomposition of Sulfones.—The apparatus used was that already described for the decomposition of sulfinic acids.[14] The thermal decomposition of these sulfones was carried out in tared Pyrex glass tubes containing break-seal capillary joints. Break-seal tubes were used to prevent sublimation and distillation of the sulfones as well as to permit us to determine accurate weight losses of the samples after decomposition. The tubes containing 0.001-mole samples were evacuated at 0.005 mm. for at least 16 hr. and sealed while under vacuum. They were heated to 275 ± 3°.

After 1 hr., the seals were broken by a small iron bar contained in the side arm of the tube, which was manipulated by a magnet outside the tube. The extent of decomposition was determined by the pressures, by the weight loss of the sulfones, and by infrared analysis of the condensible gaseous products collected in the cold finger of an infrared gas cell. The results (Table II) indicate that a dimethyl or a diphenyl sulfone containing no β-hydrogen atoms decomposes least while *t*-butyl sulfone with 18 β-hydrogens decomposes extensively.

Preparation and Characterization of Polysulfones.—**Polymethylene sulfone** was prepared by the oxidation of polymethylene sulfide. The polysulfide was prepared according to the procedure of Lal[15] by the condensation of bis(chloromethyl) sulfide and sodium sulfide nonahydrate in refluxing ethanol. It was oxidized to the polysulfone at 70° in formic acid by use of 30% hydrogen peroxide. The polymer, obtained as a white powder (25%), was washed with hot benzene and dried. The

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(6) E. Wellisch, E. Gipstein, and O. J. Sweeting, to be published.

(7) J. Troger and K. Artmann, *J. prakt. Chem.*, **53**, 500 (1896).

(8) S. Archer, U. S. Patent 2,682,544 (June 29, 1954).

(9) E. O. Beckmann, *J. prakt. Chem.*, **17**, 439 (1878).

(10) H. E. Zimmerman and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **82**, 2505 (1960).

(11) W. E. Truce and L. B. Lindy, *J. Org. Chem.*, **26**, 1463 (1961).

(12) E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, **71**, 84 (1949).

(13) F. G. Bordwell and W. H. McKellin, *ibid.*, **73**, 2251 (1951).

(14) E. Wellisch, E. Gipstein, and O. J. Sweeting, *J. Org. Chem.*, **27**, 1810 (1962).

(15) J. Lal, *ibid.*, **26**, 971 (1961).

polymer did not melt but sublimed with decomposition above 345°. No chloromethyl end groups were found in the polymer.

Anal. Calcd. for $(-CH_2SO_2-)_x$: C, 15.38; H, 2.56; S, 41.02. Found: C, 15.43; H, 2.83; S, 39.96.

Poly-*p*-xylylene sulfone was prepared by the addition of 18 g. (0.10 mole) of sodium dithionite to 18.0 g. (0.10 mole) of *p*-xylylene dichloride in 100 ml. of dimethylformamide at 110°.[6] The polymer was obtained as 10.0 g. of a white amorphous solid (60%), m.p. >360°, by pouring the mixture into ice-water, filtering, and washing with hot ethanol; it was insoluble in most common organic solvents.[16] The structure was confirmed by infrared analysis and found similar to that for dibenzyl sulfone: C–H stretching, 3.45 μ, strong; C–H aromatic, 6.2 and 6.6, strong; C–H deformation, 6.75 and 7.02, very strong; SO_2, 7.6 and 8.95, very strong.

Polytetra-, hexa-, and octamethylene sulfides were prepared from the corresponding dimercaptans and dibromides by condensation in refluxing ethanol in the presence of a basic catalyst. The resulting polysulfides were oxidized to the polysulfones with 30% hydrogen peroxide in formic acid.[17] Melting points and yields of the sulfones were, respectively: 265–269°, 73.0%; 212–215°, 84.5%; 199–204°, 76.7%.

Some precautions were found necessary in the oxidation step and the isolation of product. The polysulfide must be washed free of occluded sodium bromide which interferes with the oxidation of the sulfide by preferential oxidation to bromine. Stirring the polysulfide first in refluxing hot water for several hours was found satisfactory. When the polysulfone was poured into water, a colloidal suspension formed, which was hard to filter and had to be tediously centrifuged, but this could be eliminated by cooling the product in the original formic acid solvent, filtering it, and then washing the polymer free of acid on a Büchner funnel.

All three polysulfones and the *p*-xylylene polysulfone were purified by recrystallization from concentrated sulfuric acid. They were dissolved at 40–70°, recovered by dilution with ice-water, extracted with hot water in a Soxhlet extractor for 24 hr., washed with ether, and dried for 24 hr. at 100° under reduced pressure.

Anal. Calcd. for $(-C_4H_8SO_2-)_x$: C, 40.00; H, 6.72; S, 26.66. Found: C, 39.63; H, 6.63; S, 25.58.

Anal. Calcd. for $(-C_6H_{12}SO_2-)_x$: C, 48.64; H, 8.10; S, 21.62. Found: C, 48.05; H, 8.30; S, 22.03.

Anal. Calcd. for $(-C_8H_{16}SO_2-)_x$: C, 54.54; H, 9.09; S, 18.18. Found: C, 54.77; H, 9.44; S, 18.17.

Polyphenylene octamethylene sulfone was prepared by a modification of the method of Kreuchunas.[18] Bis(*p*-chlorophenyl) sulfone and lithium octamethylene dimercaptide were condensed in quinoline at 175° with copper(I) chloride as catalyst. The polysulfide–polysulfone, m.p. 120–125°, was oxidized to the polysulfone in formic acid at 80° by use of 30% hydrogen peroxide, m.p. 250–255°; yield, 90.0%.

Anal. Calcd. for $(-C_{20}H_{24}O_6S_3-)_x$: C, 52.63; H, 5.26; S, 21.05. Found: C, 52.57; H, 5.32; S, 20.71.

Polyoctamethylene *p*-xylylene sulfide was prepared by the condensation of *p*-xylylene dichloride and octamethylene dimercaptan in refluxing ethanol with sodium. The polysulfide, m.p. 79–81°, was oxidized in the usual way to give the polysulfone, m.p. 245–250°; yield, 90.0%.

Anal. Calcd. for $(-C_{16}H_{24}O_4S_2-)_x$: C, 55.65; H, 7.24; S, 18.56. Found: C, 55.56; H, 7.05; S, 18.87.

Poly-3-oxythiophene 1,1-dioxide was prepared by dissolving 8.5 g. (0.05 mole) of sulfolene chlorohydrin in 100 ml. of tetramethylene sulfone (sulfolane) at 70° and slowly adding 3.2 g. of sodium hydroxide dissolved in 15 ml. of water with stirring for 4 hr. The polymer, 1.6 g. (24%), was isolated from ice-water, extracted with hot water, and dried. A dimeric product which was obtained by Van Lohuizen and Backer[19] by a similar procedure sublimed at 287–290°, whereas our polymer sublimed with decomposition at 355°.

Anal. Calcd. for $(-C_4H_6O_3S-)_x$: C, 35.82; H, 4.47. Found: C, 35.90; H, 4.58.

The infrared spectrum showed strong absorption for SO_2 at 7.7 and 8.8 μ.

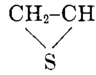
A copolymer of **divinyl sulfone** and **bis(phenylsulfonyl)methane** was prepared in carbon tetrachloride with sodium ethoxide as catalyst by a Michael addition by the procedure of Schoene,[20] m.p. 245–255°; yield, 94.0%. Infrared analysis indicated the structure $[-C(SO_2C_6H_5)_2CH_2CH_2SO_2-]$.

Anal. Calcd. for $(-C_{17}H_{18}O_6S_3-)_x$: C, 48.11; H, 4.24; S, 22.64. Found: C, 47.98; H, 4.95; S, 23.18.

Thermal Decomposition of Polymers.—The polymers were weighed into tared Pyrex glass tubes (a glass-wool plug was inserted to prevent mechanical losses during heating), the tubes were evacuated and the temperature around the samples was raised to 275°. The extent of decomposition determined as described previously is compared in Table III.

TABLE III

THERMAL DECOMPOSITION OF SULFONE POLYMERS AT 275° FOR 1 HR.

Polysulfone	Decomposition products	Decomposition, mole %
	A. No β-hydrogens	
Methylene	SO_2, C_2H_4, CH_4, CO_2, CS_2, CH_3SH, H_2S, CH_3S-CH_3, $CH_3-S-S-CH_3$,  $\underset{S}{CH_2-CH_2}$	73
p-Xylylene	SO_2, olefin	10.6
	B. Long methylene chains[a]	
Tetramethylene	SO_2, olefin, hydrocarbon	7.6
Hexamethylene	SO_2, olefin, hydrocarbon	4.8
Octamethylene	SO_2, olefin, hydrocarbon	3.7
p-Xylyleneocta-methylene	SO_2, olefin	7.5
	C. Heterocyclic	
3-Oxythiophene, 1,1-dioxide		No decomposition observed up to 300°
	D. α-Phenyl group	
Phenyleneocta-methylene	SO_2, olefin	2.5
	E. Several β-sulfone groups	
Copolymer of bis-(phenylsulfonyl)-methane and divinyl sulfone	SO_2, olefin	67

[a] The mechanism of decomposition of polytetra-, hexa-, and octamethylene sulfones is to be published in more detail.

The data of Table III agree with our previous experimental results (Table II) with one exception. The extensive decomposition observed in polymethylene sulfone may be attributed to strong hydrogen bonding between the methylene and sulfone groups associating to give stable six-membered rings within the polymer chain. A disruption of these rings is postulated to occur abruptly at 250°, resulting in rapid decomposition. From the decomposition products of Table III the possibility of a decomposition by C–S scission, occurring at high temperatures and in the absence of β-hydrogens, to produce carbene fragments giving ethylene and episulfide, is reasonable and is being further investigated.

The high instability of the copolymer of bis(phenylsulfonyl)methane and divinyl sulfone containing three sulfonyl groups can be ascribed to their positions β to one $-CH_2-$ group in the polymer repeat unit; the effect of additional sulfone groups appears to be additive.

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[16] L. A. Errede and J. M. Hoyt, *J. Am. Chem. Soc.*, **82**, 436 (1960).

[17] H. D. Noether, U. S. Patent, 2,534,366 (December 19, 1950); *Textile Res. J.*, **28**, 533 (1958).

[18] A. Kreuchunas, U. S. Patent 2,822,351 (February 4, 1958).

[19] O. E. Van Lohuizen and H. S. Backer, *Rec. trav. chim.*, **68**, 1132 (1949).

[20] D. L. Schoene, U. S. Patent 2,505,366 (April 25, 1960).