[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Copolymerization Characteristics and Spectra of Phenyl Vinyl Sulfide and Sulfone

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The unusual conjugation in diphenyl sulfone, indicated by its strong absorption at 235 mμ, is present to a lesser extent in phenyl vinyl sulfone, λ_{max} 225 mμ. For the latter sulfone (as for diphenyl sulfone), there is but very little shift of the characteristic sulfur–oxygen infrared bands at 7.6 and 8.7 μ. The vinyl double bond absorptions at 6.1, 10.1 and 10.9μ are all very considerably affected in both phenyl vinyl sulfide and sulfone. The copolymerization characteristics of phenyl vinyl sulfide ($Q = 0.32$, $e = -1.4$) and sulfone ($Q = 0.07$, $e = 1.0$) are very nearly identical to those for methyl vinyl sulfide and sulfone. An explanation has been suggested for the lack of added conjugation when a phenyl sulfide group is attached to a vinyl or phenyl group, whereas there is a marked increase in conjugation when a vinyl sulfide group is attached to a vinyl group.

Koch[2] has suggested that the strong ultraviolet absorption in diaryl sulfones (*e.g.*, for diphenyl sulfone, λ_{max} 235 mμ, log ε 4.2) involves resonance interaction between the two benzene rings, facilitated by a vacant 3d-orbital on the sulfur atom. This has prompted the investigation reported herein, designed to determine whether this type of conjugation might influence the spectral and copolymerization characteristics of phenyl vinyl sulfone.

Experimental

β-Chloroethyl Phenyl Sulfide.—Thiophenol (b.p. 166–167°, prepared in 82.4% yield[3]) was converted to β-hydroxyethyl phenyl sulfide (99%) by the procedure of Kirner and Richter.[4]

Crude β-hydroxyethyl phenyl sulfide in pyridine was treated with freshly-redistilled thionyl chloride to obtain β-chloroethyl phenyl sulfide (84.2%), b.p. 114–115° (9 mm.) (lit.[4] b.p. 117° (12 mm.)).

β-Chloroethyl phenyl sulfone was prepared by oxidation of the sulfide with hydrogen peroxide in glacial acetic acid.[5] After one crystallization from Skellysolve (b.p. 90–110°), a 76% yield of colorless crystals, m.p. 47–49°, was obtained. A second recrystallization from fresh Skellysolve gave m.p. 50–51° (lit.[5] m.p. 52°).

Phenyl Vinyl Sulfone.—A solution of 20 g. (0.1 mole) of β-chloroethyl phenyl sulfone in 120 ml. of dry ether and 30 ml. of dry benzene was added dropwise over a period of 25 minutes to a solution of 10 g. (0.1 mole) of triethylamine in 60 ml. of dry ether. When this addition was completed, the mixture was stirred for an additional 2.5 hours and left overnight.

The resulting amine salt was separated from the solvents by decantation, washed several times with ether, and the combined ether–solvent mixture washed with one-fifth its volume of water. After drying over anhydrous calcium chloride and removing the solvent at room temperature at reduced pressure, a white crystalline solid was obtained. Recrystallization from Skellysolve E gave 14.6 g. (89%), m.p. 65–67°. A second crystallization gave m.p. 66.5–67.5° (lit.[6] m.p. 68.5°).

Anal. Calcd. for $C_9H_8SO_2$: C, 57.08; H, 4.81; S, 19.06. Found: C, 57.24; H, 5.04; S, 18.97.

In another trial, using one-mole quantities, after removal of the solvents, the solid residue was redissolved in warm dry benzene and the vinyl sulfone reprecipitated by the addition of an equal volume of cold ligroin. The yield from this precipitation and that recovered from the mother liquors amounted to 136.0 g. (82.8%), m.p. 66–67°. Sodium fusion of this product followed by 5% silver nitrate solution gave a negative test for halogen.

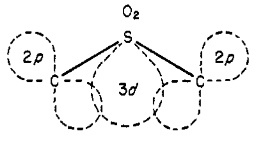

Fig. 1.

Phenyl vinyl sulfide was prepared by treatment of phenyl β-chloroethyl sulfide with sodium amylate in amyl alcohol according to Brown and Moggridge[7]: yield 53%, b.p. 84.5–85° (15 mm.), 94–94.5° (25 mm.), 102° (45 mm.), 106° (48 mm.), 198° (745 mm.), $n^{25}\mathrm{D}$ 1.5878, d^{20}_4 1.0386, *MR*D calcd. 43.88,[8] found 44.12 (lit.[7] b.p. 200–201°).

The vinyl sulfide, obtained as a colorless liquid, was found to darken noticeably when left at room temperature for a few days. It was found advisable therefore to store the liquid in tightly-sealed cooled containers out of contact with air and in the dark. For subsequent use, redistillation was necessary.

Purification of Monomers.—The liquid monomers were redistilled through a 40-cm. glass helices-packed column with a total condensation-partial take-off head, the middle fraction being collected as the pure compound. The fractions were taken at the indicated boiling point: styrene (Dow), 32.5° (10 mm.); vinyl acetate (Niacet), 71.5–72.0°; methyl acrylate (Rohm and Hass), 79.0°; and phenyl vinyl sulfide, 90.5° (22 mm.).

All the liquid samples were stored in the cold and in the absence of light. Phenyl vinyl sulfide was freshly redistilled for each copolymerization experiment.

Phenyl vinyl sulfone was recrystallized by dissolving the solid in benzene or ether and then reprecipitated by the addition of cold ligroin. The solid was dried *in vacuo* before use.

Copolymerization Procedure.—The method described by Price and Zomlefer[9] was adopted. Pairs of monomer mixtures containing a total of 0.08 mole of monomers and 0.2% of recrystallized benzoyl peroxide were prepared over the entire composition range in seven equally spaced intervals. The copolymerizations were carried out in 25 × 150-mm. rimless Pyrex test-tubes necked down for easy sealing. The reactants, as well as the solvents, where used, were weighed to the nearest milligram. The reaction tubes when filled were cooled in an ice-bath then flushed for one minute with a stream of nitrogen, the latter being purified through Fieser's solution. The tubes were then sealed off with an oxygen hand torch and immersed in a constant temperature bath kept at 60.0 ± 0.1°.

The extent to which the copolymerization was allowed to proceed was judged, as far as possible, by the viscosity of the solution so that conversions would not exceed 10%. The copolymers were isolated by pouring the reactants into 250 ml. of cold filtered absolute methanol. After allowing the precipitate to settle for a few hours, the major portion of the solvent was decanted and the copolymer filtered through a fritted Pyrex glass Gooch funnel. The solid was redissolved in benzene, then poured into 200 ml. of ice-cold,

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(1) Abstracted from the Ph.D. dissertation of Hirokazu Morita, June, 1952.

(2) H. P. Koch, *J. Chem. Soc.*, 408 (1949); H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

(3) R. Adams and C. S. Marvel, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 504.

(4) W. R. Kirner and G. H. Richter, THIS JOURNAL, **51**, 3409 (1929).

(5) G. D. Buckley, J. L. Charlish and J. D. Rose, *J. Chem. Soc.*, 1515 (1947).

(6) A. H. Ford-Moore, R. A. Peters and R. W. Wakelin, *ibid.*, 1754 (1949).

(7) R. Brown and R. C. G. Moggridge, *ibid.*, 816 (1946).

(8) A. I. Vogel, *ibid.*, 1842 (1948); A. I. Vogel, W. T. Cresswell, G. H. Jeffrey and J. Leicester, *ibid.*, 514 (1952).

(9) C. C. Price and J. Zomlefer, THIS JOURNAL, **72**, 14 (1950).

filtered absolute methanol. The precipitate was again allowed to settle, then filtered on to a fritted-glass Gooch filter funnel, and dried at room temperature overnight at 1 mm.

In the case of styrene–phenyl vinyl sulfone, the reactions were carried out in thiophene-free redistilled benzene. The amount of benzene used was twice the combined weight of the two monomers, weighed to the nearest centigram.

The copolymerization of methyl acrylate–phenyl vinyl sulfide was performed in 50% by weight thiophene-free benzene. In the case of 0.125 mole sulfide copolymerization, the copolymer precipitated. As this constituted a heterogeneous reaction, the isolated copolymer was discarded. The copolymers obtained in this system formed sticky gum-like solids when reprecipitated from benzene in the usual way. Although other solvents such as acetone, ether, chloroform and *n*-hexane were tried without success, a 30:10 mixture of chloroform and dry ether was found appropriate. The copolymer was dissolved in 30 ml. of the mixed solvent, filtered through a fluted filter paper and the clear filtrate cooled in ice–water mixture. When cold the solution was added dropwise to 150 ml. of ice-cold methanol with vigorous stirring. The addition was interrupted frequently to ensure proper stirring. The precipitate so obtained was filtered through a fritted-glass Gooch funnel and washed repeatedly with ice-cold methanol in such a manner that the copolymer was never allowed to become dry until it had been washed several times with methanol. The use of benzene as a solvent was, as in the previous case, found to be convenient in order to increase the solubility of the monomers as well as the copolymer product.

Tables I to IV give the data for the copolymerizations. The *Q* and *e* values as well as the experimentally found r_1 and r_2 values are summarized in Table IX. For these calculations, the composition of copolymer calculated by sulfur analysis was taken as the more reliable.

Softening Points of Copolymers.—These were determined by the use of a calibrated melting point block and the results are shown in Tables V and VI.

Infrared Absorption Measurements.—These were obtained through the generous coöperation of Prof. C. L. Wilson of the Ohio State University, Columbus, Ohio. The measurements were carried out in a Baird Infrared Spectrophotometer with a sodium chloride prism. In the case of solids, chloroform was used as the solvent. The pertinent data are summarized in Table VII.

TABLE I

COPOLYMERIZATION OF STYRENE (M_1) WITH PHENYL VINYL SULFONE (M_2)

$M_2{}^a$	Time, hr.	Conversion, %	Percentages S	Percentages C	Percentages H	$dM_2{}^b$	$dM_2{}^c$
0.125	3.0	8.22	2.91	86.20	7.46	0.093	0.067
.250	2.0	3.55	5.00	81.85	6.85	.149	.120
.375	2.0	5.72	6.36	78.95	6.84	.183	.160
.500	2.0	4.38	7.53	76.84	6.64	.209	.196
.625	2.0	4.17	8.53	75.71	6.52	.231	.265
.750	8.0	..[d]	..				

[a] Mole fraction of sulfone in original monomer mixture. [b] Mole fraction of sulfone in copolymer, calculated from sulfur analysis. [c] Mole fraction of sulfone in copolymer, calculated from carbon analysis. [d] Yield too small for analysis.

TABLE II

COPOLYMERIZATION OF VINYL ACETATE (M_1) WITH PHENYL VINYL SULFONE (M_2)

$M_2{}^a$	Time, hr.	Conversion, %	Percentages S	Percentages C	Percentages H	$dM_2{}^b$
0.125	22.36	0.42	9.58	57.74	5.76	0.315
.250	49.30	4.13	11.29	57.86	5.67	.352
.375	49.08	5.50	12.01	57.34	5.57	.366
.500	49.00	4.88	13.09	57.23	5.54	.388
.625	50.00	..	...[c]			

[a] Mole fraction of sulfone in original monomer mixture. [b] Mole fraction of sulfone in copolymer, calculated from the sulfur analysis. [c] Yield too small for analysis.

TABLE III

COPOLYMERIZATION OF STYRENE (M_1) WITH PHENYL VINYL SULFIDE (M_2)

$M_2{}^a$	Time, hr.	Conversion, %	Percentages S	Percentages C	Percentages H	$dM_2{}^b$	$dM_2{}^c$
0.125	11.00	12.27	1.22	90.22	7.72	0.043	0.036
.125	11.00	10.02	2.44	89.00	7.61	.079	.070
.375	11.00	9.56	4.20	87.78	7.68	.129	.116
.500	12.41	6.22	6.27	85.78	7.03	.183	.177
.625	10.00	5.60	10.10	82.78	7.19	.262	.286
.750	13.33	4.86	12.43	79.65	6.78	.304	.402
.875	14.66	3.18	16.87	76.08	6.50	.372	.425

[a] Mole fraction of sulfide in original monomer mixture. [b] Mole fraction of sulfide in copolymer, calculated from sulfur analysis. [c] Mole fraction of sulfide in copolymer, calculated from carbon analysis.

TABLE IV

COPOLYMERIZATION OF METHYL ACRYLATE (M_1) WITH PHENYL VINYL SULFIDE (M_2)

$M_2{}^a$	Time, min.	Conversion, %	Percentages S	Percentages C	Percentages H	$dM_2{}^b$	$dM_2{}^c$
0.125	7	11.70	...[d]				
.250	15	7.02	10.96	61.95	6.45	0.346	0.261
.375	25	2.45	12.48	62.94	6.44	.375	.291
.500	35	4.41	14.50	65.03	6.36	.412	.381
.625	45	5.70	14.75	69.97	6.44	.419	.526

[a] Mole fraction of sulfide in original monomer mixture. [b] Mole fraction of sulfide in copolymer, calculated from sulfur analysis. [c] Mole fraction of sulfide in copolymer, calculated from carbon analysis. [d] Copolymer precipitated, analysis not attempted.

TABLE V

SOFTENING POINTS OF PHENYL VINYL SULFONE COPOLYMERS

With styrene		With vinyl acetate	
S, %	Softening point, °C.	S, %	Softening point, °C.
2.91	133–136	11.29	123–129
6.36	145–152	12.01	131–136
8.53	154–160	13.09	139–145

TABLE VI

SOFTENING POINTS OF PHENYL VINYL SULFIDE COPOLYMERS

With styrene		With methyl acrylate	
S, %	Softening point, °C.	S, %	Softening point, °C.
2.44	124–131	10.96	59–65
4.20	129–135	12.48	64–69
10.10	98–103	14.50	45–49
16.87	83–88	14.75	52–57

Ultraviolet Spectra.—The measurements were made with a Beckman quartz spectrophotometer, the samples being dissolved in 95% ethanol. The concentration *c* represented in the molar extinction coefficient equation ($e = D/c$) was in all cases 3×10^{-5} *M*.

Discussion

The ultraviolet spectra data are summarized in Table VIII.

Comparison of the ultraviolet spectra in Table VIII for the three sulfones indicates that the pronounced shift of the intense, low wave length band to 235 mμ in diphenyl sulfone is present to a lesser extent (λ_{max} 225 mμ) in phenyl vinyl sulfone. Phenyl β-chloroethyl sulfone shows the normal

TABLE VII

INFRARED ABSORPTION BANDS FOR PHENYL VINYL SULFIDE, β-CHLOROETHYL PHENYL SULFONE AND PHENYL VINYL SULFONE (5–15μ)

Phenyl vinyl sulfide		β-Chloroethyl phenyl sulfone		Phenyl vinyl sulfone	
λ, μ	Intensity	λ, μ	Intensity	λ, μ	Intensity
5.80	Med.	6.25	Weak	6.15	V. weak
6.25	V. strong	6.72	Weak	6.25	Weak
6.75	Strong	6.88	Med.	6.74	Weak
6.94	Strong	7.05	Weak	6.87	Med.
7.25	Med.	7.15	Weak	7.20	Med.
7.86	Med.	7.52	V. strong	7.55	V. strong
9.10	Strong	7.62	Med.	7.70	Med.
9.30	Med.	7.90	Weak	7.97	Weak
9.75	Strong	8.13	Med.	8.12	Weak
9.98	Weak	8.65	V. strong	8.67	V. strong
10.55	Strong	8.80	Weak	9.15	Strong
11.25	V. strong	9.15	Strong	9.74	Weak
13.45	V. strong	9.30	Weak	9.97	Weak
14.55	Strong	9.70	Med.	10.25	Strong
		9.97	Weak	10.52	Med.
		10.30	Med.	14.35	Strong
		11.38	Med.	14.67	Med.
		12.50	Strong	15.60	Med.
		14.62	Strong		

TABLE VIII

ULTRAVIOLET ABSORPTION CHARACTERISTICS

Compound	λ_{max}, mμ	log ϵ	λ_{min}, mμ	log ϵ
Phenyl β-chloroethyl sulfone	263	3.0	235	1.7
	210	4.0		
Phenyl vinyl sulfone	267	3.02	247	2.3
	225	4.1		
Diphenyl sulfone[2,f]	270	3.3	260	3.0
	235	4.2		
Phenyl vinyl sulfide	266	4.0	255	3.95
	247	4.02	230	3.75
Diphenyl sulfide[a,c]	278	3.6	270	3.5
	250	4.1	240	3.8
Divinyl sulfide[b]	275	3.7	260	3.6
	255	3.75	220	3.3
Thioanisole[c]	280[d]	3.3	235	3.9
	255	4.1		
1,3,5-Hexatriene[e]	268	4.8		
	258	4.9		
	248	4.7		
Methyl vinyl sulfide[9]	240[d]	4.0		
	225	4.2		
Butadiene[e]	217	4.3		

[a] H. P. Koch, *J. Chem. Soc.*, 387 (1949). [b] H. Mohler and J. Sorge, *Helv. Chim. Acta*, **23**, 1200 (1940). [c] E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 84 (1949); C. C. Price and J. J. Hydock, *ibid.*, **74**, 1943 (1952). [d] This represents a shoulder, not a clear maximum. [e] F. A. Miller in H. Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 166; W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (*London*), **A185**, 182 (1946). [f] E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 231 (1949).

position for this band in phenyl alkyl sulfones (*ca.* 210 mμ). This is in accord with the explanation offered by Koch, illustrated in Fig. 1. Note that the geometry for such conjugation requires that the axes of the two 2p- and the 3d-orbitals involved be in a single plane. The two benzene rings would then, of necessity, be perpendicular to this plane. This geometry is facilitated by the steric interference of the ortho-hydrogens in the two phenyl groups (see Fig. 3). This geometry required for conjugation would be less favorably assisted by steric factors in the phenyl vinyl sulfone, perhaps in part accounting for the shift to shorter wave length.

In the case of the sulfides, there appears to be much less difference in ultraviolet spectra between monophenyl (thioanisole) and diphenyl compounds, although the position and intensity of the absorption indicates much more effective conjugation in both cases with a sulfide group than with a sulfone group. This is in agreement with the much greater conjugation found in vinyl sulfides as compared to vinyl sulfones.[9]

The general similarity between the ultraviolet spectra of divinyl sulfide and 1,3,5-hexatriene offers another example of the similar conjugative properties of the sulfide group and double bond.[9] As in the case of butadiene and methyl vinyl sulfide, the unsaturated sulfide has its absorption at somewhat longer wave length than the corresponding polyene.

The marked similarity between thioanisole and diphenyl sulfide, as contrasted to the big difference between methyl vinyl sulfide and divinyl sulfide, is of considerable interest. We would like to suggest that the large increment in conjugation observed on flanking a sulfide with a second vinyl group, as contrasted in the lack of added conjugation when a sulfide is flanked with a second phenyl group may be explained by steric restriction of resonance in the latter case.

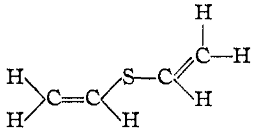

Fig. 2.

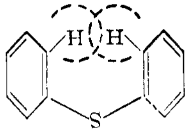

Fig. 3.

In contrast to the resonance interaction with the sulfone group, schematically represented in Fig. 1, which involves a vacant 3d-orbital,[2] it has been suggested[9] that resonance with the sulfide group undoubtedly involves the unshared electrons in 3p-orbitals, with resulting contributions from a 2p (C)–3p (S) double bond. Presumably the geometry of this double bond, like the better-known 2p–2p double bond, will require coplanarity of the atoms directly bonded to it.[10] Thus, for a continuous hybrid orbital involving the sulfur and both double bonds of divinyl sulfide, the entire molecule should be planar. This is possible for divinyl sulfide in the conformation schematically represented by Fig. 2. There will therefore be a much more extended conjugative system in divinyl sulfide than in methyl vinyl sulfide.

In the case of diphenyl sulfide, however, the necessary coplanarity of the sulfur and both benzene rings is sterically hindered because of the overlap of the two hydrogen atoms indicated in Fig. 3.

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(10) The observation of Fehnel and Carmack (THIS JOURNAL, **71**, 84, 2889 (1949)), that there is a steady decrease in absorption in the phenyl alkyl sulfides as the alkyl group is changed from methyl to ethyl to isopropyl to *t*-butyl is an indication of the sensitivity of sulfide conjugation to steric factors.

Thus, resonance can occur with but one ring at a time, accounting for the very close similarity of the spectra of thioanisole and diphenyl sulfide.

The significance of the infrared data, summarized in Table VII, will be discussed in the following paper.[11] It is, however, appropriate to point out that, although the SO bands of the sulfone are unaffected by whatever conjugation occurs, the C—C bands at 6.2, 10.55 and 11.2 μ have all been considerably displaced, presumably by resonance of the type indicated by the ultraviolet data.

The general conclusion we draw from this ultraviolet and infrared spectral data is that there can be significant resonance interactions between carbon unsaturation and either sulfide or sulfone groups. In both cases this may involve expansion of the sulfur octet. The data support the conclusion that the geometrical requirements for the sulfide and for the sulfone resonance are quite different, in accord with the postulate that in the sulfone conjugation involves overlap of 2p- and 3d-orbitals, while in the sulfide it involves overlap of 2p- with 3p-orbitals.

The data on copolymerization in Tables I through IV are summarized in Table IX in terms of the copolymerization ratios, r_1 and r_2,[12] and the monomer constants, Q and e.[13] The values of Q and e used for the monomers M_1 were those previously reported.[13b]

TABLE IX

M_1	M_2	r_1	r_2	Q_2	e_2
Styrene	Sulfone	3.3	0.01 ± 0.01	0.07	1.0
Vinyl acetate	Sulfone	0.28	.35	.07	1.2
Styrene	Sulfide	4.5	.15	.35	−1.4
Methyl acrylate	Sulfide	0.40	.05 ± 0.02	.29	−1.4

In view of the considerable uncertainties in the values for r_2 for the styrene–sulfone and methyl acrylate–sulfide pairs, Q and e were also calculated from the equations

$$r_1 = (Q_1/Q_2)e^{-e_1(e_1 - e_2)}$$
$$r_1' = (Q_1'/Q_2)e^{-e_1'(e_1' - e_2)}$$

Making suitable substitutions, values of $Q = 0.07$ and $e = 1.0$ were obtained for the sulfone and $Q = 0.30$ and $e = -1.2$ for the sulfide.

Thus the average values for the resonance (Q) and the electrical (e) factors for phenyl vinyl sulfone, $Q = 0.07$ and $e = 1.1$, are very nearly the same as those for methyl vinyl sulfone, $Q = 0.09 \pm 0.02$ and $e = 1.2$.[7] In the same way, these factors for phenyl vinyl sulfide, $Q = 0.32$ and $e = -1.3$, are very nearly the same as for methyl vinyl sulfide, $Q = 0.35$ and $e = -1.5$.[8]

The lack of evidence for added resonance stabilization (Q) for the phenyl sulfone as compared to the methyl sulfone leads us to suggest that the excitation involved in the intense, short wave length band for aromatic compounds, the one which is so profoundly shifted by flanking a phenyl sulfone with a second unsaturated group (phenyl or vinyl), is due to a transition to an excited state largely ionic in character,[14] rather than one resembling a diradical.[9]

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[11] C. C. Price and R. G. Gillis, THIS JOURNAL, **75**, 4750 (1953).

[12] See F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 190 (1950).

[13] (a) T. Alfrey and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947); (b) C. C. Price, *ibid.*, **3**, 772 (1948).

[14] See, *e.g.*, L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947); **71**, 2414 (1949).

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Spectra and Molecular Refraction for Some Unsaturated Sulfides, Sulfoxides and Sulfones

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The molecular refractions of several sulfoxides and sulfones support the recent report by Vogel[2] that the sulfur–oxygen bond in such compounds has an abnormally low contribution to the molecular refraction, confirming the formulation of this bond as a semipolar single covalent bond. Additional evidence for this view is the lack of influence of a vinyl group on the characteristic infrared frequencies for the sulfur–oxygen bond in sulfoxides and sulfones. The sulfide, and to a lesser extent the sulfoxide and sulfone groups, do however influence the characteristic infrared absorption of the carbon–carbon double bond.

The purpose of the present investigation was to obtain additional evidence on the conjugative properties of sulfide, sulfoxide and sulfone groups, seeking confirmation for the earlier conclusions from copolymerization[3-5] and ultraviolet absorption[6] that the sulfur–oxygen bond in such compounds is indeed a semipolar single covalent bond rather than a covalent double bond. For this purpose we have measured the infrared spectrum and the molecular refraction for methyl vinyl, methyl allyl and methyl propyl sulfide, sulfoxide and sulfone.

Experimental[7]

Methyl 2-hydroxyethyl sulfide[8] had the following properties: b.p. 62–65° (13–14 mm.), $n^{20}\text{D}$ 1.4900, d^{20}_4 1.0581, $R^{20}\text{D}$ 25.18[9] (lit.[10] b.p. 80.5–81° (30 mm.), $n^{30}\text{D}$ 1.4867, d^{20}_{20} 1.0640).

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[1] Abstracted from the Ph.D. dissertation of Richard G. Gillis, January, 1953.

[2] A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, *J. Chem. Soc.*, 514 (1952).

[3] C. C. Price and J. Zomlefer, THIS JOURNAL, **72**, 14 (1950).

[4] C. C. Price and R. D. Gilbert, *ibid.*, **74**, 2073 (1952).

[5] C. C. Price and H. Morita, *ibid.*, **75**, 4747 (1953).

[6] C. C. Price and J. J. Hydock, *ibid.*, **74**, 1943 (1952).

[7] All melting points are uncorrected. Analyses by Micro Tech Laboratories, Skokie, Ill.

[8] W. Windus and P. R. Shildneck, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 345.

[9] We will follow Vogel[2] and use RD to represent the molecular refraction.

[10] W. R. Kirner, THIS JOURNAL, **50**, 2441 (1928).