TABLE II (*Continued*)

Extinction	Elongation	$2V$[a]	Optic sign	Dispersion	Refractive indices[b] α	β	γ
Symmetrical	Parallel to *c*	21°[d]	+	None	1.559	1.564	1.727
$Y\parallel b$, $Z\wedge c = 35°$	Parallel to *b* (±)	76°	+	Axial, r>*v*	1.596	1.675	1.830
$Y\parallel b$, $Z\wedge c = 17°$	Parallel to *b* (±)	86° ?	+	Axial, *r*>*v*	1.586	1.649[f]	1.731
Parallel	(±)	58°	−	Very strong, rhombic, *r*>*v*[h]	1.568	1.657	1.687
$Y\parallel b$, $Z\wedge c = 39°$	(±)	88°	+	Very strong axial, *r*>*v*	1.670	1.736	1.813
$Y\parallel b$, $X\wedge c = 23°$[k]	Parallel to *b* (±)	52°	−	Inclined, *r*>*v*	1.598	1.741	1.780
Parallel	Parallel to *c* (±)	Very large	+	Rhombic, *r*>*v*	1.507	1.682	>1.86
$Y\parallel c$, $Z\wedge a = 40°$ (?)	(±)	Large	+	Axial, *r*>*v*	1.563	1.695	>1.86
$Y\parallel b$, $Z\wedge c = 58°$	(±)	Small	+	Slight axial, *r*>*v*	1.577	1.614	>1.86
Variable (?)	(−)	Large	+	Anomalous, *r*>*v*	1.548	1.669	>1.86
Maximum = 21°.[m]	(+)	Very large	−	None	1.542	1.750	>1.86
Parallel	Parallel to *c*	Very large	+	Rhombic *r*>*v*	1.632	1.734	>1.86
Maximum = 12°.[m]	(±)	Very large	+	Very great axial, *r*>*v*	1.491	1.689	>1.86
$Y\parallel b$, $Z\wedge c = 38°$[k]	Parallel to *b* (±)	Large	+	Slight axial *r*>*v*	1.573	1.686	>1.86
Parallel	(±)	Large	+	None	1.561	1.668	>1.86
$Y\parallel b$, max. = 22°[m]	(+)	Large	+	Slight axial *r*>*v*	1.553	1.679	>1.86
$Z\parallel b$, $X\wedge c = 43°$	(±)	Large	+	Axial, *r*>*v*	1.619	1.750	>1.86
$Y\parallel b$, $Z\wedge c = 31°$	Parallel to *b* (±)	Large	+	Axial, *r*>*v*	1.601	1.735	>1.86
$X\parallel b$, max. = 40° (?)	(±)	51°	−	Very strong crossed, *v*>*r*	1.561	1.724	1.769
(?)	(?)	Large	−	Slight axial, *v*>*r*	1.399?	1.659	1.754?
(?)	(?)	Variable[n]	−	Very strong crossed, *v*>*r*	?	1.714	?
Variable oblique	(+)	87°	+	Axial, *r*>*v*	1.572	1.688	1.854
Parallel	Parallel to *c* (−)	40°	−	Rhombic, *v*>*r*	1.506	1.720	1.755
$Y\parallel b$(?), $X\wedge c = 26°$	(±)	24°	−	Axial, *r*>*v*	1.542	1.785	1.799[o]
Maximum = 10° (?)	(−)	63°	−	Strong axial, *v*>*r*	1.565	1.716	1.785

[a] Calcd. from α, β and γ. [b] The values of the refractive indices are accurate to ±0.002 unless otherwise noted. [c] The crystals show only the pyramid faces. [d] The calculated value appears to be too high since the isogyres scarcely separate on rotation. [e] Wilkerson[6] has published the following data: $\alpha = 1.680$, $\beta = 1.695$, $\gamma = 1.788$, $2V = 45\text{–}46°$, $Z\wedge c = 20°$?. [f] Dispersion of the β index of refraction. [g] Equant from hot water, skeleton crystals from butanol-1, and tabular from ethanol. [h] The interference figure shows characteristic purple color fringes. [i] For the details of the optical properties of sulfapyridine, Phase I–V see ref. 8. [j] Grove and Keenan[3] reported the following: $\alpha = 1.605$, $\beta = 1.733$, $\gamma > 1.733$, and parallel extinction. [k] Common orientation shows parallel extinction. [l] The absorption formula was not readily determinable. [m] The relationship of the ellipsoidal axes to the crystallographic axes was not readily determinable, thus a maximum extinction angle is reported. [n] $2V$ varies from 15 to 60° (estimated). The value for β is constant regardless of $2V$. γ varies greatly depending upon $2V$. The reason for this variation in optic axis is not understood. [o] Accuracy probably not greater than ±0.008.

BOULDER, COLORADO

RECEIVED APRIL 27, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Ultraviolet Absorption Spectra of Organic Sulfur Compounds. II. Compounds Containing the Sulfone Function[1]

BY EDWARD A. FEHNEL[2] AND MARVIN CARMACK

In a continuation of the work described in the preceding paper in this series,[3] we have determined the ultraviolet absorption spectra of a number of mono- and polysulfones, ketosulfones and carbalkoxysulfones in both neutral and alkaline solutions. As was anticipated on the basis of the limited spectroscopic data previously available for several simple aromatic sulfones,[4] no characteristic absorption bands attributable to the isolated sulfone function were observed in ethanol solutions in the near-ultraviolet region of the spectrum, and interaction between the sulfur-containing function and adjacent chromophores was found to be of a much lower order than in the corresponding sulfides. Strong conjugative effects were ap-

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[1] Presented in part before the Division of Organic Chemistry of the American Chemical Society at the Washington meeting, August, 1948.

[2] American Chemical Society Postdoctoral Fellow, 1946–1948. Present address: Department of Chemistry, Swarthmore College, Swarthmore, Pa.

[3] Fehnel and Carmack, THIS JOURNAL, **71**, 84 (1949).

[4] (a) Chaix, *Bull. soc. chim.*, [4] **53**, 700 (1933); (b) Gibson, Graham and Reid, *J. Chem. Soc.*, **123**, 874 (1923); (c) Böhme and Wagner, *Ber.*, **75**, 606 (1942).

parent, however, in the spectra of the anions formed by the methylene disulfones, β-ketosulfones, and α-carbalkoxysulfones in alkaline solutions. These observations are of interest from the theoretical point of view because of their bearing on the question of the ability of the sulfonyl sulfur atom to accommodate more than eight electrons in its valence shell.

Monosulfones.—Solutions of the simple alkyl sulfones, such as ethyl sulfone, in ethanol and in ethanolic sodium ethoxide are completely transparent throughout the range of the Beckman quartz spectrophotometer (down to *ca.* 210 mμ). Ethanol solutions of the α,β-unsaturated sulfone, vinyl ethyl sulfone, however, begin to absorb strongly at about 240 mμ and appear to have a maximum in the neighborhood of 208–212 mμ[5] (Fig. 1). This represents a marked bathochromic displacement (*ca.* 15–20 mμ) of the absorption characteristic of the isolated vinyl group, as observed, for example, in the spectra of the simple alkenes, which exhibit maxima below 200 mμ.[6]

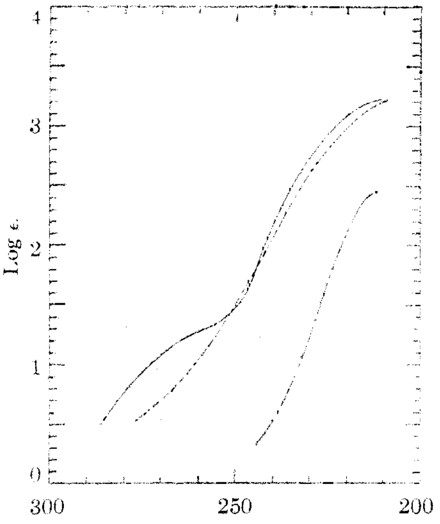
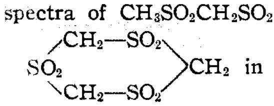


Fig. 1.—Absorption spectra of $CH_3SO_2CH_2SO_2CH_3$ in 0.01 *N* NaOEt, —;  $SO_2\langle{}^{CH_2-SO_2}_{CH_2-SO_2}\rangle CH_2$ in 0.01 *N* NaOEt, - - - -; $CH_2{=}CHSO_2C_2H_5$ in EtOH, —·—.

The aralkyl sulfones, benzyl ethyl sulfone (Fig. 2), benzyl sulfone (Fig. 3) and phenethyl sulfone (Fig. 3), give absorption curves which are essentially the same as those of the analogous benzenoid hydrocarbons.[7] When the sulfone function is attached directly to a benzene ring, as in phenyl sulfone (Fig. 3) and the phenyl alkyl sulfones (Fig. 2), bathochromic and hyperchromic displacements of the benzenoid absorption are observed which are very similar to the effects produced by the carboxyl group in benzoic acid. The absorp-

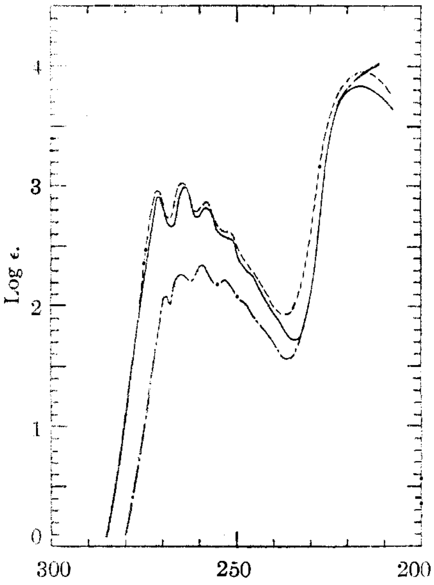


Fig. 2.—Absorption spectra of $C_6H_5SO_2CH_3$, —; $C_6H_5SO_2C(CH_3)_3$, - - - -; $C_6H_5CH_2SO_2C_2H_5$, —·—; (in EtOH).

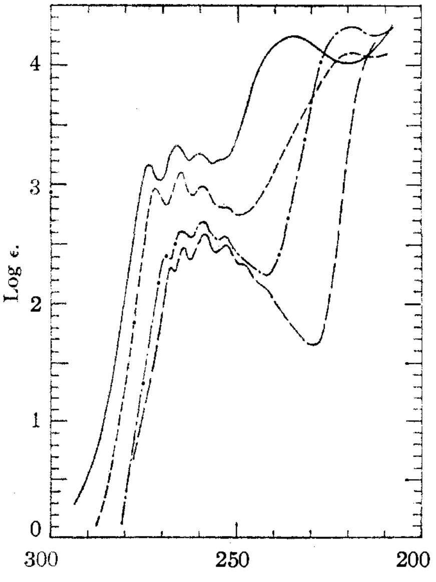


Fig. 3.—Absorption spectra of $(C_6H_5)_2SO_2$, —; $C_6H_5SO_2CH_2C_6H_5$, - - - -; $(C_6H_5CH_2)_2SO_2$, —·—; $(C_6H_5CH_2CH_2)_2SO_2$, — — —; (in EtOH).

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(5) The uncertainties involved in making readings close to the lower limit of observation (below *ca.* 215 mμ with the ethanol used in the present work) do not permit an accurate description of this portion of the curve.

(6) Absorption spectra of most of the comparison compounds mentioned in this paper may be found in the "International Critical Tables," Vol. V, McGraw-Hill Book Co., New York, N. Y., 1929, p. 359 ff.

(7) Compare, for example, benzyl ethyl sulfone with the alkylbenzenes (*e. g.*, toluene) and the symmetrical aralkyl sulfones with the diphenylalkanes (*e. g.*, diphenylmethane).

tion spectra of these aromatic monosulfones remain unchanged in ethanolic sodium ethoxide.

Polysulfones.—Like the corresponding monosulfones, the simple aliphatic methylene disulfones, *e. g.*, bis-(methylsulfonyl)-methane, are transparent in ethanol solution throughout the range of the Beckman spectrophotometer, and aromatic methylene disulfones, *e. g.*, bis-(phenylsulfonyl)-methane (Fig. 4), exhibit spectra characteristic of the phenylsulfonyl portions of the molecule. On formation of the sulfone anions by solution of these compounds in ethanolic sodium ethoxide, the optical properties are greatly modified. Under these conditions bis-(methylsulfonyl)-methane and trimethylene trisulfone begin to absorb strongly in the near-ultraviolet region of the spectrum and appear to have an intense absorption band with a maximum somewhat below 210 mμ (Fig. 1).[8] In alkaline solutions of bis-(phenylsulfonyl)-methane the benzenoid fine structure is replaced by a single broad absorption band of much higher intensity (Fig. 4). When the central carbon atom of a methylene disulfone is completely alkylated so that no anion can be formed in alkaline solution, the spectra in neutral and alkaline media are identical (Table I).

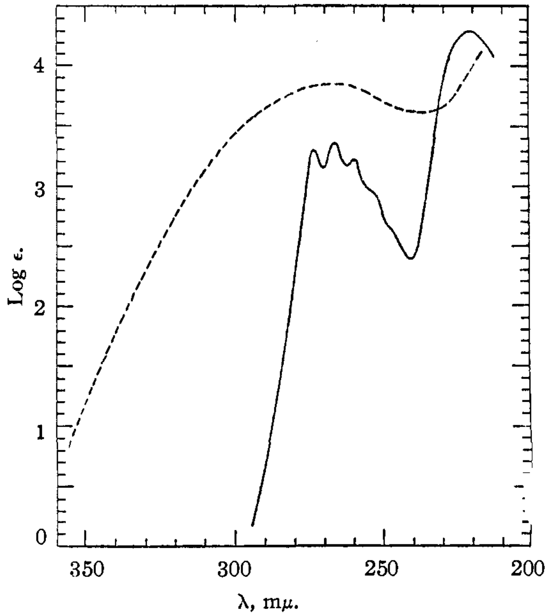


Fig. 4.—Absorption spectra of $C_6H_5SO_2CH_2SO_2C_6H_5$ in EtOH, —; in 0.01 N NaOEt, - - - -.

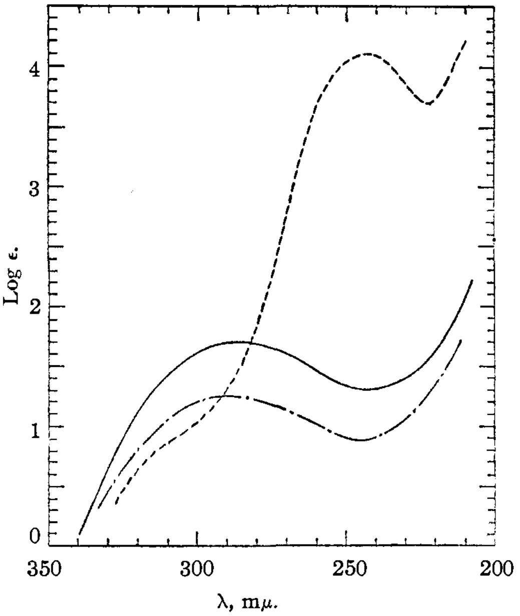
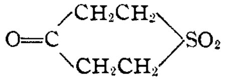


Fig. 5.—Absorption spectra of n-$C_4H_9SO_2CH_2COCH_3$ in EtOH, —; in 0.01 N NaOEt, - - - -; in EtOH, –·–·–.



$$O{=}C\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}SO_2$$

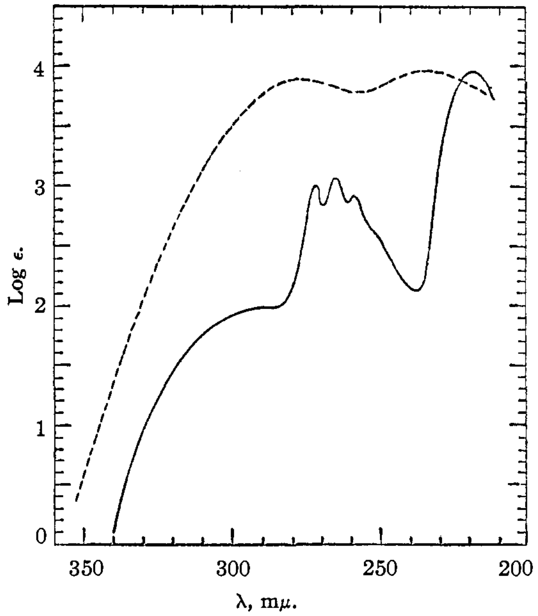


Fig. 6.—Absorption spectra of $C_6H_5SO_2CH_2COCH_3$ in EtOH, —; in 0.01 N NaOEt, - - - -.

Ketosulfones and Carbalkoxysulfones.—As in the case of the methylene disulfones described above, the spectra of the β-ketosulfones, RSO_2CH_2COR, and α-carbalkoxysulfones, $RSO_2CH_2CO_2R$, are greatly modified in the presence of strong alkali. The effect is illustrated by the absorption curves for n-butylsulfonylacetone (Fig. 5), phenylsulfonylacetone (Fig. 6), and ethyl phenylsulfonylacetate (Fig. 7). In ethanol the spectra of these compounds are approximately summations of the spectra of the component chromophores, while in ethanolic sodium ethoxide marked changes in the form, intensity and location of the absorption bands are observed. The spectrum of α-phenylsulfonylisopropyl methyl

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[8] *Cf.* ref. 4c.

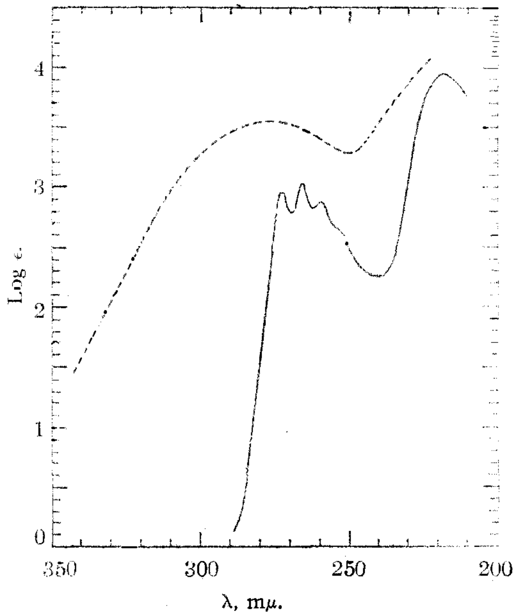


Fig. 7.—Absorption spectra of $C_6H_5SO_2CH_2CO_2C_2H_5$ in EtOH, —; in 0.01 *N* NaOEt, - - - -.

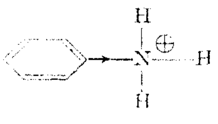
ketone (Table I), which is incapable of forming a stable anion in ethanolic alkali, shows no change in alkaline solution.

Discussion

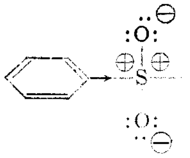
Although the question of the ability of the sulfur atom in the sulfone function to undergo an expansion of the valence shell has stimulated many interesting investigations, no general agreement seems to have been reached on the interpretation of the results.[9] A large body of chemical evidence[10] has accumulated which reveals an extensive similarity in the activating influence of the sulfonyl, carbonyl and nitro functions on adjacent methylene groups and olefinic bonds. These observations seem to favor the interpretation that the sulfonyl group, like the carbonyl and nitro groups, promotes an electromeric withdrawal of electrons from the adjacent carbon atoms. The application of such a resonance mechanism to the sulfones, however, requires that the sulfonyl sulfur atom be capable of accommodating, at least temporarily, more than eight electrons in its valence shell. Several investigators[11] have concluded on the basis of the chemical evidence that this is quite probably the case.

Others[9c,12] have preferred to attribute the activating influence of the sulfone function to the inductive effect produced by the net positive charge on the sulfur atom in the static system  $\overset{\ominus}{:}\ddot{O}\!-\!\!-\overset{\oplus|\oplus}{\underset{|}{S}}\!-\!\!-\ddot{O}\overset{\ominus}{:}$; the assumption of an expanded valence shell is rejected on the grounds that it violates the classical "octet rule" and that there is no evidence for sulfur–oxygen double bonds in the sulfone group. As G. N. Lewis has clearly pointed out, however, it is entirely possible that under certain conditions the sulfur atom (and other atoms beyond the first period of the periodic table) may exceed a covalence of four.[13] In support of this view, recent physical evidence based on X-ray[14] and electron-diffraction[15] studies, dipole moment measurements,[16] and thermochemical data[16] has indicated that the sulfur–oxygen link in sulfones possesses considerable double-bond character. In addition, evidence for the conjugative interaction of the sulfone function with an attached benzene ring has been obtained in studies of the dipole moments of aryl sulfones[17] and sulfonamides[18] and in a study of the ultraviolet absorption spectra of several benzenesulfonamides.[19]

An expansion of the sulfur valence shell also appears to provide the only satisfactory basis on which to account for the spectroscopic data obtained in the present investigation. Like the spectrum of the anilinium cation[20] (I), the spectrum of a phenyl alkyl sulfone would be expected to be very nearly identical with that of benzene, if the sulfonyl sulfur atom bears a fixed positive charge and exerts only a coulombic displacement effect on the electrons of the benzene ring (structure II).[19,21] The observed shift of the absorption



I



II

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(9) See, for example, (a) Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 658–660, 740; (b) Connor, Gilman's "Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 879–885; (c) Shriner, Adams and Marvel, *ibid.*, pp. 393–396; (d) Johnson, *ibid.*, p. 1839; (e) Gibson, *Chem. Revs.*, **14**, 431 (1934); (f) Price, "Mechanisms of Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, New York, N. Y., 1946, pp. 7, 12, 32.

(10) This evidence is summarized in refs. 9a and 9b.

(11) (a) Kohler and Potter, THIS JOURNAL, **57**, 1316 (1935); (b) Connor, Fleming and Clayton, *ibid.*, **58**, 1386 (1936); (c) Rothstein, *J. Chem. Soc.*, 309 (1937). *Cf.* also ref. 9a, p. 740; ref. 9b, p. 885.

(12) (a) Shriner, Struck and Jorison, THIS JOURNAL, **52**, 2060 (1930); (b) Arndt and Martius, *Ann.*, **499**, 228 (1932); (c) Arndt and Eistert, *Ber.*, **74B**, 423 (1941); (d) Eistert, *Z. Elektrochem.*, **47**, 35 (1941).

(13) Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, N. Y., 1923, pp. 97, 101–103. *Cf.* also Sidgwick, "The Electronic Theory of Valency," Oxford University Press, London, 1927, pp. 62–63, 152, 284; Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 289 ff.

(14) Toussaint, *Bull. soc. chim. Belg.*, **54**, 319 (1945); *C. A.*, **41**, 2297 (1947).

(15) Lister and Sutton, *Trans. Faraday Soc.*, **35**, 495 (1939).

(16) Phillips, Hunter and Sutton, *J. Chem. Soc.*, 146 (1945).

(17) Leonard and Sutton, THIS JOURNAL, **70**, 1564 (1948).

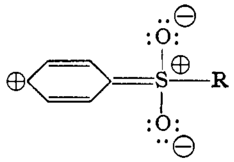
(18) Kumler and Halverstadt, *ibid.*, **63**, 2182 (1941).

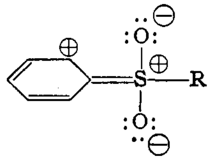
(19) Kumler and Strait, *ibid.*, **65**, 2349 (1943).

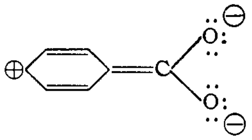
(20) Flexser, Hammett and Dingwall, *ibid.*, **57**, 2103 (1935); *cf.* also ref. 19.

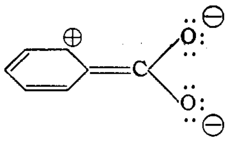
(21) The usefulness of ultraviolet absorption spectra as a means of detecting mesomeric interactions between unsaturated groups has been discussed by Price, ref. 9f, pp. 9–12; *cf.* also Doub and Vandenbelt, THIS JOURNAL, **69**, 2714 (1947).

curves of the phenyl alkyl sulfones toward longer wave lengths and higher intensities, as compared with benzene, can be readily accounted for, however, if structures such as IIIa and IIIb may be considered to make significant contributions to the resonance in these molecules. The close resemblance between the spectra of the phenyl alkyl sulfones and the spectrum of the benzoate anion[19,22] is consistent with this interpretation, since the displacement of the benzenoid absorption by the substituent carboxylate function is attributed to resonance involving structures IVa and IVb.


IIIa

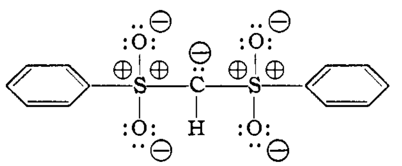

IIIb

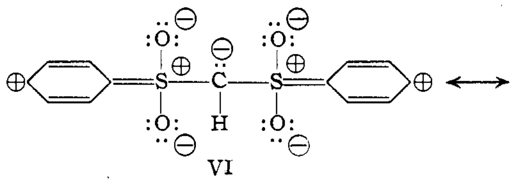

IVa

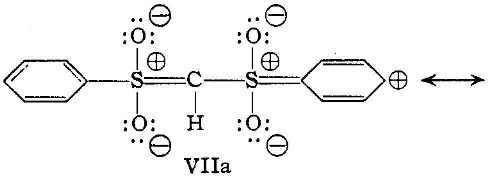

IVb

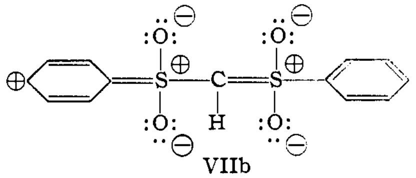
Similar considerations lead to the conclusion that the observed bathochromic displacement of the ethylenic absorption in vinyl ethyl sulfone must result from the conjugative interaction between the sulfone function and the attached vinyl group.

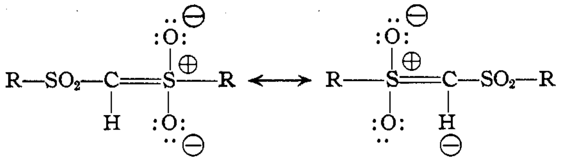
Resonance interactions between the sulfone functions in the methylene disulfone anions appear to provide the only satisfactory basis on which to account for the profound differences in the optical properties of neutral and alkaline solutions of these polysulfones. Thus, for example, a static charge distribution such as that represented in structure V should have little or no effect on the absorption by the benzenoid portions of the carbanion derived from bis-(phenylsulfonyl-methane). The fact that the anion exhibits greatly increased absorption at longer wave lengths, while the spectrum of the undissociated molecule is essentially that of phenyl methyl sulfone at twice the molar concentration, clearly suggests a conjugative redistribution of charge involving the unshared pair of electrons on the central carbon atom, as in structures VI, VIIa and VIIb. In the case of the bis-(alkylsulfonyl)-methane anions, similar considerations lead to structures VIIIa and VIIIb,


V


VI


VIIa


VIIb


VIIIa VIIIb

which are identical with those previously proposed by Rothstein[11c] to account for the chemical properties of these compounds.

The application of these concepts to the interpretation of the spectra of the analogous keto- and carbalkoxysulfones might, of course, be questioned on the ground that enolization in the $-\underset{|}{\mathrm{C}}\mathrm{H}-\underset{|}{\mathrm{C}}{=}\mathrm{O}$ system could, by itself, give rise to the observed effects.[23] It seems reasonable to assume, however, that if the sulfonyl sulfur atom is capable of expanding its valence shell in the bis-sulfonylmethane anions, it is capable of doing so in the anions of the β-ketosulfones and α-carbalkoxysulfones. Our observations on the spectra of these compounds are consistent with this interpretation. It does not seem possible, for example, to account for the intense absorption of the anions of phenylsulfonylacetone or ethyl phenylsulfonylacetate in terms of isolated enolic and benzenoid chromophores. Displacement of the benzenoid absorption toward longer wave lengths and higher intensities and loss of fine structure are features which are characteristic of benzene derivatives having unsaturated substituents conjugated with the aromatic nucleus.[24] The striking similarity of the absorption spectra of the β-keto- and α-carbalkoxysulfone anions and the spectra of benzalacetone ($\lambda_{\max.}$ 286, 220.5 mμ; log ϵ 4.37, 4.08, resp.[24a]) and cinnamic acid ($\lambda_{\max.}$ 282, 222 mμ; log ϵ 4.30, 4.16, resp.[24b]) clearly suggests a conjugative interaction, *through the sulfone function*, of

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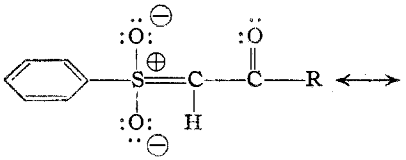
(22) Doub and Vandenbelt, ref. 21.

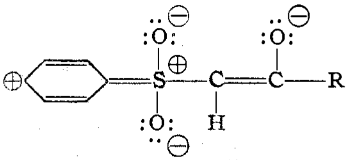
(23) Böhme and Wolff, *Chem. Ber.*, **80**, 193 (1947); *C. A.*, **42**, 864 (1948).

(24) (a) Wilds, Beck, Close, Djerassi, Johnson, Johnson and Shunk, THIS JOURNAL, **69**, 1985 (1947); (b) Campbell, Linden, Godshalk and Young, *ibid.*, **69**, 880 (1947).

the carbonyl group with the benzene ring, as in structures IXa and IXb.

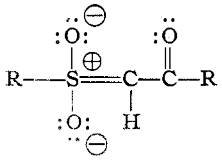


IXa

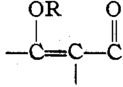


IXb

In the case of the aliphatic β-ketosulfone anions, significant contributions from structures such as X are indicated by the close resemblance between



X

the spectrum of the *n*-butylsulfonylacetone anion and the spectra of aliphatic compounds containing the grouping  $-\overset{\text{OR}}{\overset{|}{\text{C}}}=\underset{|}{\text{C}}-\overset{\text{O}}{\overset{\|}{\text{C}}}-$ (*e. g.*, γ-pyrone, $\lambda_{\text{infl.}}$ 278 mμ, log ε 1.73; $\lambda_{\text{max.}}$ 246 mμ, log ε 4.09[25]).

Experimental[26]

The ultraviolet absorption measurements were made as described in the preceding paper in this series.[3] The wave lengths and logarithms of the molar extinction coefficients at the absorption maxima and at prominent points of inflection are listed in Table I.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF SULFONES

Compound	Source[a]	Solvent[b]	Maxima[c] λ (mμ)	Log ε
Ethyl sulfone	1	EtOH	Transparent[d]	
Ethyl sulfone	1	NaOEt	Transparent	
Vinyl ethyl sulfone	2	EtOH	~210?[e]	2.45
bis-(Methylsulfonyl)-methane	3	EtOH	Transparent	
bis-(Methylsulfonyl)-methane	3	NaOEt	(256)	1.33
			<210	>3.20
2,2-bis-(Methylsulfonyl)-propane	4	EtOH	Transparent	
2,2-bis-(Methylsulfonyl)-propane	4	NaOEt	Transparent	
Trimethylene trisulfone	5	NaOEt	<210	>3.20
Phenyl methyl sulfone[f]	6	EtOH	271	2.91
			264	2.99
			258	2.82
			(253)	2.58
			217	3.83
Phenyl *t*-butyl sulfone	7	EtOH	271	2.95
			265	3.02
			258	2.87
			(253)	2.62
			216	3.94
Benzyl ethyl sulfone	8	EtOH	269	2.08
			265	2.26
			259	2.34
			253	2.21
Benzyl phenyl sulfone	9	EtOH	272	2.97
			265	3.09
			259	2.98
			(253)	2.81
			219	4.10
Benzyl phenyl sulfone	9	NaOEt	272	2.96
			265	3.08
			259	2.97
			(253)	2.80
			219	4.10
Benzyl sulfone[f]	10	EtOH	269	2.41
			265	2.61
			259	2.68
			253	2.56
			219	4.32
Phenethyl sulfone	11	EtOH	268	2.29
			264	2.47
			259	2.58
			253	2.50
			(249)	2.34
Phenyl sulfone[f,g]	12	EtOH	274	3.16
			266	3.33
			260	3.25
			(254)	3.21
			235	4.24
bis-(Phenylsulfonyl)-methane	13	EtOH	274	3.28
			267	3.35
			260	3.20
			(254)	2.96
			221	4.29
bis-(Phenylsulfonyl)-methane	13	NaOEt	~267	3.85
2,2-bis-(Phenylsulfonyl)-propane	14	EtOH	274	3.29
			267	3.38
			261	3.22
			(255)	3.00
			222	4.34
2,2-bis-(Phenylsulfonyl)-propane	14	NaOEt	274	3.29
			267	3.37
			261	3.21
			(255)	3.00
			222	4.32
n-Butylsulfonylacetone	2	EtOH	287	1.71
n-Butylsulfonylacetone	2	NaOEt	(306)	0.93
			243	4.11

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[25] Baer, Cavalieri and Carmack, unpublished work. An interesting study of the relation between absorption spectra and constitution of keto-enols has been made by Morton, Hassan and Calloway, *J. Chem. Soc.*, 883 (1934).

[26] Microanalyses were performed by Mrs. Sarah M. Woods.

TABLE I (*Continued*)

Compound	Source[a]	Solvent[b]	Maxima[c] λ (mμ)	Log ε
Phenylsulfonylacetone	15	EtOH	289	1.98
			272	3.00
			265	3.05
			259	2.90
			219	3.94
Phenylsulfonylacetone	15	NaOEt	278	3.88
			236	3.96
α-Phenylsulfonylisopropyl methyl ketone	2	EtOH	294	2.08
			273	3.00
			266	3.06
			260	2.90
			218	4.00
α-Phenylsulfonylisopropyl methyl ketone	2	NaOEt	294	2.10
			273	3.00
			266	3.05
			260	2.90
			218	4.01
Tetrahydro-1,4-thiapyrone 1-dioxide	16	EtOH	290	1.25
Ethyl phenylsulfonylacetate	17	EtOH	272	2.95
			266	3.02
			259	2.87
			(254)	2.65
			218	3.94
Ethyl phenylsulfonylacetate	17	NaOEt	275	3.55

[a] Source references: (1) Pummerer, *Ber.*, **43**, 1407 (1910); (2) see section on "Preparation of Compounds"; (3) Böhme and Marx, *Ber.*, **74B**, 1667 (1941); (4) Baumann, *ibid.*, **23**, 1875 (1890); (5) Camps, *ibid.*, **25**, 233 (1892); (6) oxidation of phenyl methyl sulfide with 30% hydrogen peroxide in acetic acid; (7) Ipatieff, Pines and Friedman, THIS JOURNAL, **60**, 2731 (1938); (8) Böhme, *Ber.*, **69B**, 1610 (1936); (9) Knoevenagel, *ibid.*, **21**, 1344 (1888); (10) Smythe, *J. Chem. Soc.*, **101**, 2079 (1912); (11) Bermejo and Herrera, *IX Congr. intern. quim. pura aplicada*, 4, 238 (1934) [*C. A.*, **30**, 3418 (1936)]; (12) Hinsberg, *Ber.*, **43**, 289 (1910); (13) Kohler and Tishler, THIS JOURNAL, **57**, 217 (1935); (14) Fromm, *Ann.*, **253**, 135 (1889); (15) Otto and Otto, *J. prakt. Chem.*, [2] **36**, 401 (1887); (16) Fehnel and Carmack, THIS JOURNAL, **70**, 1813 (1948); (17) Michael and Comey, *Am. Chem. J.*, **5**, 116 (1883). [b] EtOH designates absolute ethanol; NaOEt designates 0.01 *N* sodium ethoxide prepared by dissolving sodium in absolute ethanol. [c] The wave lengths in parentheses refer to inflection points. [d] A 0.1 *M* solution in a 1-cm. cell gave transmission readings above 90% at all wave lengths down to limit of observation (*ca.* 208 mμ). [e] See footnote 5. [f] *Cf.* Gibson, Graham and Reid, ref. 4b. [g] *Cf.* Chaix, ref. 4a.

Preparation of Compounds.—Most of the previously known compounds were prepared by procedures described in the literature, and were purified by two or more recrystallizations[27] immediately before determination of the spectra. Source references are given in Table I.

Vinyl ethyl sulfone[28] was obtained by treating a solution of 52.8 g. (0.26 mole) of ethyl β-bromoethyl sulfone in 600 ml. of benzene with 55.5 g. (0.55 mole) of triethylamine and allowing the mixture to stand for thirty minutes. The precipitate of triethylamine hydrobromide was filtered off, the solvent and excess amine were removed on the steam-bath, and the residual oil was distilled under diminished pressure to yield 24.8 g. (79%) of almost colorless oil, b. p. 103–107° at 8 mm. Redistillation of this product offered a colorless oil, b. p. 105–106° at 8 mm.

Anal. Calcd. for $C_4H_8O_2S$: C, 39.94; H, 6.71. Found: C, 39.85; H, 6.63.

***n*-Butylsulfonylacetone** was prepared by refluxing a mixture of 13.9 g. (0.15 mole) of chloroacetone, 21.6 g. (0.15 mole) of sodium butanesulfinate, and 100 ml. of ethanol for one hour. At the end of this time, most of the solvent was removed by distillation and the residue was diluted with several times its volume of water. The layers were separated and the aqueous layer was extracted several times with ether. The combined oil layer and ether extracts were dried over anhydrous magnesium sulfate and distilled under diminished pressure to yield 16.5 g. (62%) of a yellow oil, b. p. 147–150° at 7 mm. Redistillation of this material gave the pure product as a viscous, colorless oil, b. p. 136–137° at 4 mm.

Anal. Calcd. for $C_7H_{14}O_3S$: C, 47.18; H, 7.92. Found: C, 47.32; H, 7.73.

α-Phenylsulfonylisopropyl methyl ketone was prepared in a similar manner by treating 16.5 g. (0.10 mole) of α-bromoisopropyl methyl ketone with 20.0 g. (0.10 mole) of sodium benzenesulfinate dihydrate in refluxing ethanol. The oily product slowly crystallized on standing; yield, 10.8 g. (48%) of colorless crystals, m. p. (cor.) 42–46°. Recrystallization from aqueous ethanol afforded colorless leaflets melting at 47–48° (cor.).

Anal. Calcd. for $C_{11}H_{14}O_3S$: C, 58.38; H, 6.24. Found: C, 58.24, 58.47; H, 6.13, 6.10.

Summary

The ultraviolet absorption spectra of a number of mono- and polysulfones, ketosulfones and carbalkoxysulfones have been determined in both neutral and alkaline solutions. The preparation of vinyl ethyl sulfone and two new ketosulfones is described.

No characteristic absorption bands attributable to the isolated sulfone function are observed in ethanol solutions in the near-ultraviolet region of the spectrum, although the attachment of a sulfonyl group to benzene shifts and intensifies the benzenoid peaks in a manner similar to the carboxyl group in benzoic acid. Strong conjugative effects are observed in the anions formed by the methylene disulfones, β-ketosulfones and α-carbalkoxysulfones in alkaline solutions. When the central carbon atom in the latter compounds is completely alkylated so that no anion can be formed, the spectra in neutral and alkaline solutions are identical.

These effects are interpreted as evidence for the conjugative interaction of the sulfone function with attached aromatic nuclei in aryl sulfones and with the unshared pair of electrons on the central carbon atom in sulfone anions. Resonance forms involving pentacovalent sulfur are discussed.

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[27] Trimethylene trisulfone was purified by recrystallization of the potassium salt from aqueous potassium hydroxide, followed by reprecipitation with hydrochloric acid.

[28] *Cf.* Ramberg and Bäcklund, *Arkiv. Kemi. Mineral. Geol.*, **13A**, No. 27 (1940); *C. A.*, **34**, 4725 (1940).