

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY]

Some Properties of β -Ketosulfones and β -DisulfonesE. H. HOLST¹ AND W. CONARD FERNELIUS

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Compounds of the general formula $\text{RSO}_2\text{CH}_2\text{SO}_2\text{R}'$ are weaker acids than the corresponding β -diketones and compounds of the general formula $\text{RCOCH}_2\text{SO}_2\text{R}'$ are acids of the same strength as the corresponding β -diketones. Neither the β -disulfones nor the β -ketosulfones possess any chelating power toward metal ions in contrast to the behavior of β -diketones. These facts are interpreted as indicating that there is no tautomerism involving enolic forms in the sulfur compounds. This interpretation is supported by the lack of any indication of hydrogen bonding in the infrared spectra of the sulfones.

Because of the outstanding ability of β -diketone anions to coordinate with metal ions,^{2,3} it seemed worth-while to determine whether or not compounds with the groupings $-\text{COCH}_2\text{SO}_2-$ and $-\text{SO}_2\text{CH}_2\text{SO}_2-$ possess a similar ability. In the course of this study the dissociation constants and infrared spectra of some β -carbonylsulfones and β -disulfones were measured.

Formation constants could not be determined because of precipitation of the metal hydroxides. Titration of $\text{C}_6\text{H}_5\text{-COCH}_2\text{SO}_2\text{C}_6\text{H}_5$ in the presence of Be^{++} , Ni^{++} and Zn^{++} resulted in almost immediate precipitation. The systems $(\text{CH}_3\text{SO}_2)_2\text{CH}_2$ with Ni^{++} and UO_2^{++} behaved similarly. With Cu^{++} and the latter compound, precipitation was not detected until the titration was half completed.

The infrared spectra of the sulfones were measured in benzene solution. The absorption bands pertinent to the present study are recorded in Table 2.

EXPERIMENTAL

Synthetic. The sulfones used were prepared by literature methods: $(\text{CH}_3\text{SO}_2)_2\text{CH}_2$, m.p. 145°;⁴ $(\text{C}_6\text{H}_5\text{SO}_2)_2\text{CH}_2$, m.p. 188°;⁵ $\text{CH}_3\text{COCH}_2\text{SO}_2\text{C}_6\text{H}_5$, m.p. 57–8°;⁶ $\text{CH}_3\text{SO}_2\text{CH}_2\text{COC}_6\text{H}_5$, 110°;⁷ $\text{C}_6\text{H}_5\text{COCH}_2\text{SO}_2\text{C}_6\text{H}_5$, m.p. 96°.⁸ Dissociation constants in mixtures of dioxane and water were determined by a method previously described,⁹ and are listed in Table I.

TABLE I

pK_D VALUES FOR VARIOUS SULFONYL AND CARBONYL COMPOUND IN 50% ($N_2 = 0.171$) AND 75% ($N_2 = 0.380$) DIOXANE AT 30°.

	pK_D	
	50% Dioxane	75% Dioxane
$\text{CH}_3\text{COCH}_2\text{SO}_2\text{C}_6\text{H}_5$	10.9	
$\text{CH}_3\text{SO}_2\text{CH}_2\text{COC}_6\text{H}_5$	10.7	12.9
$\text{C}_6\text{H}_5\text{COCH}_2\text{SO}_2\text{C}_6\text{H}_5$		12.9
$\text{CH}_3\text{SO}_2\text{CH}_2\text{SO}_2\text{CH}_3$		13.4, 13.1
$\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_5$	Too weak to be measured	
$\text{CH}_3\text{COCH}_2\text{COCH}_3^a$	10.4	12.7
$\text{CH}_3\text{COCH}_2\text{COC}_6\text{H}_5^a$	10.5	12.8
$\text{C}_6\text{H}_5\text{COCH}_2\text{COC}_6\text{H}_5^a$	11.2	13.8

^a Values for the compounds marked (a) are taken from L. G. Van Uitert *et al.*²

(1) Present address: Research Department, The Texas Company, Port Arthur, Tex.

(2) L. G. Van Uitert, C. G. Haas, Jr., W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 455, (1953); L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 457, 2736, 2739, 3577, 3862 (1953); L. G. Van Uitert and W. C. Fernelius, *J. Am. Chem. Soc.*, **76**, 5887 (1954).

(3) R. M. Izatt, C. G. Haas, Jr., B. P. Block, and W. C. Fernelius, *J. Phys. Chem.*, **58**, 1133 (1954); R. M. Izatt, W. C. Fernelius, and B. P. Block, *J. Phys. Chem.*, **59**, 80, 235 (1955); R. M. Izatt, W. C. Fernelius, C. G. Haas, Jr., and B. P. Block, *J. Phys. Chem.*, **59**, 170 (1955).

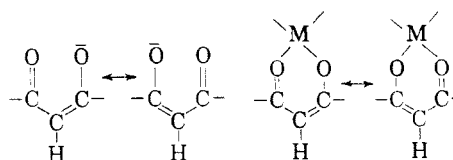
(4) H. Bohme and R. Max, *Ber.*, **74B**, 1667–75 (1941).

(5) R. L. Shriner, H. C. Struck, and W. J. Jorison, *J. Am. Chem. Soc.*, **52**, 2060–9 (1930).

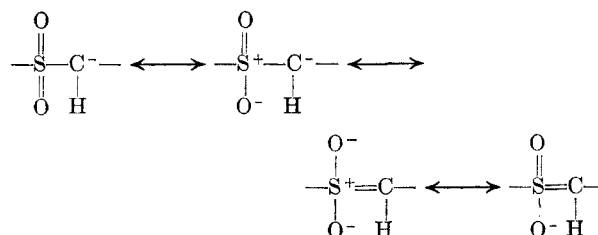
(6) R. Otto and W. Otto, *J. prakt. Chim.*, (2) **36**, 403 (1887).

DISCUSSION

The anions of β -diketones as well as the metal coordination compounds of β -diketones presumably are stabilized by resonance.¹⁰ If similar effects hold



for the sulfone group, they should be evident in the acid strength of compounds containing the groupings $-\text{COCH}_2\text{SO}_2-$ and $(-\text{SO}_2)_2\text{CH}_2$, in the coordinating ability of such compounds, and in their infrared spectra (enol form with hydrogen bonding). That enolization of these sulfones would necessitate an expansion of the valence shell of sulfur to 10 or 12 electrons need not deter one



(7) H. Bohme and H. Fischer, *Ber.*, **76B**, 99 (1943).

(8) J. Tröger and O. Beck, *J. prakt. Chim.*, (2) **87**, 295 (1912).

(9) L. G. Van Uitert and C. G. Haas, Jr., *J. Am. Chem. Soc.*, **75**, 451–5 (1953); L. G. Van Uitert and W. C. Fernelius, *J. Am. Chem. Soc.*, **76**, 5887–8 (1954).

(10) M. Calvin and K. W. Wilson [*J. Am. Chem. Soc.* **67**, 2003–7 (1945)] are of the opinion that resonance extends through the metal also.

TABLE II
 INFRARED ABSORPTION PEAKS IN CM.⁻¹ FOR SULFONES AND RELATED COMPOUNDS

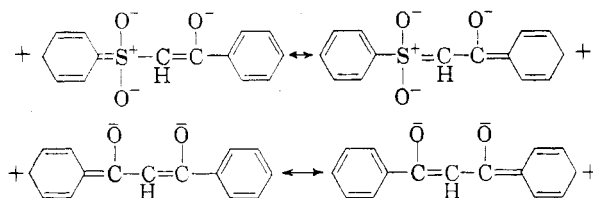
Compound	—SO ₂ —	—SO ₂ —	—CO—	Chelation
CH ₃ SO ₂ CH ₃	1153	1320		
C ₆ H ₅ SO ₂ CH ₃ ^a	1160	1334		
C ₆ H ₅ SO ₂ C ₆ H ₅ ^{a,b}	1155	1325		
		1337 _s		
(CH ₃ SO ₂) ₂ CH ₂	1137	1314 _w		
C ₆ H ₅ SO ₂ CH ₂ COCH ₃	1160	1329	1723	
CH ₃ SO ₂ CH ₂ COC ₆ H ₅	1157	1330	1683	
C ₆ H ₅ SO ₂ CH ₂ COC ₆ H ₅	1160	1330	1683	
CH ₃ COCH ₃ ^c			1718–1728	
C ₆ H ₅ COCH ₃ ^c			1686	
CH ₃ COCH ₂ COCH ₃ ^d			1707, 1727	1616
C ₆ H ₅ COCH ₂ COCH ₃				1572, 1600
C ₆ H ₅ COCH ₂ COC ₆ H ₅				1548, 1597

^a D. Barnard, J. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, 2442(1949). ^b K. C. Schreiber, *Anal. Chem.*, 21, 1168 (1949).
^c L. G. Bellamy, Ref. 15, p. 116. ^d R. Mecke and E. Funck, Ref. 18.

from considering this possibility because this situation seems to exist in the sulfate ion.¹¹

There is some evidence already available bearing on this matter. In contrast to the β -diketones, no *O*-methyl derivative of the —SO₂CH₂— group has ever been obtained by methylation¹² which indicates true carbon-hydrogen acidity with no enolization.

Dissociation constants. The pK_D values listed in Table 1 show that (CH₃SO₂)₂CH₂ is a weaker acid than (CH₃CO)₂CH₂ and that (C₆H₅SO₂)₂CH₂ is weaker than (C₆H₅CO)₂CH₂ or that the influence of the sulfonyl group on adjacent groups is less than that of the carbonyl group. If the cases were strictly comparable one would expect the more electronegative element, sulfur, to produce the stronger acid. If resonance in the enol form is operative as is



indicated for dibenzoylmethane,¹³ then there should be a difference in the pK_D values for C₆H₅COCH₂SO₂CH₃ and C₆H₅COCH₂SO₂CH₃. However, no such difference is found which indicates that the effect is purely inductive.

Metal derivatives. A copper derivative of C₆H₅COCH₂SO₂CH₃ has been reported¹⁴ but its preparation could not be repeated. The behavior of a mixture of copper ion and C₆H₅COCH₂SO₂CH₃ on titration with base indicates the possible existence

(11) L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.* 59, 13 (1937).

(12) F. Arndt, *Problems in Theoretical Organic Chemistry*, Twenty-eighth Annual Priestley Lectures, The Pennsylvania State University, University Park, Pennsylvania, 1954, p. 26.

(13) G. E. K. Branch and M. Calvin, *Theory of Organic Chemistry*, Prentice-Hall, 1941, pp. 239, 294.

(14) H. Bohme and H. Fischer, *Ber.*, 76B, 99 (1943).

in solution of a very weak complex. However, the coordination tendency of the disulfones and the carbonyl-sulfones is very weak indeed and in sharp contrast to that for the β -diketones. It seems reasonable to attribute this difference to the inability of the sulfonyl group to enolize.

Infrared spectra. The infrared spectra of a number of hydrogen-bonded compounds containing keto and hydroxy groups show that hydrogen bonding (chelation) results in marked shifts in the characteristic absorption peaks due to both the keto and hydroxy groups.^{15–17} This effect is unusually pronounced in the β -diketones^{15,18,19} With acetylacetone, benzoylacetone, and dibenzoylmethane, a very broad band more than a hundred times as strong as the normal carbonyl vibration is observed in the range 1639–1538 cm.⁻¹ These compounds are known to exist largely in the enolic form^{10,20} and the absorption is attributed to a reduction of the double-bond character of the carbonyl group through resonance ("conjugate chelation").¹⁵

The data recorded in Table 2 show that the bands due to —SO₂— are practically the same in β -disulfones and β -ketosulfonyl compounds as in simple sulfones. Further, the carbonyl band in the latter is the same as that for simple ketones. Hence, the adjacent —CO— or —SO₂— group, just as the double bond in CH₂=CHSO₂CH₃,²¹ does not influence the characteristic frequencies of the sulfone group.

(15) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen and Co. Ltd., London, 1954, pp. 86, 90, 123, 135, 145, 157.

(16) H. Hoyer, *Chem. Ber.* 86, 1016 (1953).

(17) B. E. Bryant, J.-C. Pariaud, and W. C. Fernelius, *J. Org. Chem.* 19, 1889 (1954).

(18) R. Mecke and E. Funck, *Z. Elektrochem.* 60, 1124 (1956).

(19) R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nuclear Chem.* 2, 11 (1956).

(20) A. E. Gillam and E. S. Stern, *Electronic Absorption Spectroscopy*, Edward Arnold (Publishers) Ltd., London 1954, p. 223.

(21) C. C. Price and R. G. Gillis, *J. Am. Chem. Soc.* 75, 4750 (1953).

Once again the evidence indicates that the sulfonyl group is not capable of acting as a partner in conjugation.²²

(22) Cf., however, spectra of *o*-HOC₆H₄SO₂C₆H₅ and *o*-HOC₆H₄SOC₆H₅, E. D. Amstutz, I. M. Hunsberger, and J. J. Chessik, *J. Am. Chem. Soc.* **73**, 1220 (1951).

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[CONTRIBUTION FROM THE ST. LOUIS RESEARCH DEPARTMENT, ORGANIC CHEMICALS DIVISION, MONSANTO CHEMICAL CO.]

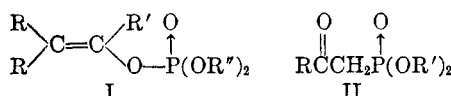
Reactions of Phosphorus Compounds. I. Diethyl Carbamoylmethylphosphonates

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2-Chloroacetamides were found to undergo the Arbuzov reaction with triethyl phosphite to give diethyl carbamoylmethylphosphonates. The infrared and nuclear magnetic resonance spectra of these compounds were compared with those of known phosphonates and vinyl phosphates derived from halo ketones and esters.

The reaction of triethyl phosphites with 2-halocarbonyl compounds has been shown to give vinyl phosphates (I) and/or phosphonates (II).

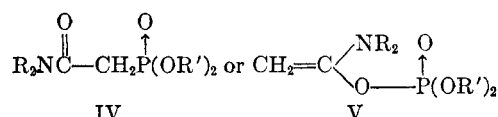
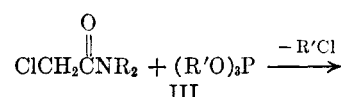


Mono-, di-, and trihaloaldehydes, di- and trihalo ketones, and trihaloesters gave the phosphate derivatives.¹⁻⁷ Monohaloesters⁸ afforded the phosphonate compounds whereas monohalo ketones gave phosphonates or phosphates depending on the halogen atom. Thus, chloroacetone^{2b,6,7,8b,9} gave predominantly the vinyl phosphate, bromoacetone^{7b,8b,9-11} gave a mixture of phosphate and

phosphonate, and iodoacetone^{6,7b} gave predominantly the phosphonate. 2-Haloacetoacetic esters and amides and 3-haloacetylacetone yielded phosphates.^{2b,7b,12}

It was of interest, therefore, to determine whether the reaction of 2-haloamides with trialkyl phosphites would give phosphonates (IV) (normal Arbuzov¹³ product) or phosphates (V) (Perkow rearrangement⁵).

In these laboratories, phosphonates (IV) rather than phosphates (V) were isolated from the reaction of trialkyl phosphites with 2-chloroacetamides.



- a R = R' = C₂H₅
b R = CH₂CH = CH₂; R' = C₂H₅
c R = *n*-C₃H₇; R' = C₂H₅

(1) W. F. Barthel, B. H. Alexander, P. A. Giang, and S. A. Hall, *J. Am. Chem. Soc.*, **77**, 2424(1955).

(2) (a) J. F. Allen, S. K. Reed, O. H. Johnson, and N. J. Brunsvold, *J. Am. Chem. Soc.*, **78**, 3715(1956); (b) J. F. Allen and O. H. Johnson, *J. Am. Chem. Soc.*, **77**, 2871(1955).

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(4) M. S. Kharasch and I. S. Bengelsdorf, *J. Org. Chem.*, **20**, 1356(1955).

(5) (a) W. Perkow, *Chem. Ber.*, **87**, 755(1954); (b) W. Perkow, W. Krockow, and K. Knoevenagel, *Chem. Ber.*, **88**, 662(1955).

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(8) (a) B. A. Arbuzov and V. S. Vinogradova, *Doklady Akad. Nauk S.S.S.R.*, **99**, 85(1954); (b) *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 54(1957); (c) A. E. Arbuzov and A. A. Dunin, *J. Russ. Phys. Chem. Soc.*, **46**, 295 (1914); (d) G. Kamai and E. Sh. Bastanos, *J. Gen. Chem. (U.S.S.R.)*, **21**, 2188, 2449(1951).

(9) (a) A. N. Pudovik and V. P. Aver'yanova, *J. Gen. Chem. (U.S.S.R.)*, **26**, 1426(1956). (b) A. N. Pudovik and N. M. Lebedeva, *Doklady Akad. Nauk S.S.S.R.*, **101**, 889 (1955).

(10) N. Kreutzkamp and H. Kayser, *Chem. Ber.*, **89**, 1614(1956).

(11) B. A. Arbuzov, V. S. Vinogradova, and N. P. Polezhaeva, *Doklady Akad. Nauk S.S.S.R.*, **111**, 107(1956).

(12) (a) A. N. Pudovik, *Zhur. Obshchei Khim.*, **26**, 2238 (1956); (b) A. R. Stiles, U. S. Patent 2,685,552; (c) R. R. Whetstone and A. R. Stiles, U. S. Patent 2,802,855.

(13) G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley and Son, Inc., N. Y., 1950, p. 121.