TABLE V

pK' VALUES IN WATER AND IN 50% METHANOL AT 25°
BENZYLIDENEPYRUVIC ACIDS,[a] $XC_6H_4CH{=}CHCOCOOH$

X	Water Moles/l. × 10^2	Water *pK'*	50% aqueous methanol–0.2 *M* LiCl Moles/l. × 10^2	50% aqueous methanol–0.2 *M* LiCl *pK'*[c] (relative)
H	3.54	1.97	6.71–8.87	2.49
3-OCH_3	3.60–6.54	1.97		
4-OCH_3	2.68–3.89	1.96	6.53–6.75	2.57
4-Br	1.81–2.30	1.99	6.60–6.75	2.48
4-CH_3	3.33–6.20	1.96	5.24–6.78	2.52
Reference acids[a,b]				
Benzoic	5.30–11.60	4.15	7.18	5.03
Cinnamic	1.49–3.23	4.47	7.30	5.10

[a] Average deviation of *pK'* values in *pK'* units: benzylidenepyruvic acids in water, 0.05; in 50% methanol, 0.02; reference acids in water, 0.02; in 50% methanol, 0.01. [b] J. F. J. Dippy, ref. 1a, p. 206, lists the following values at 25°: benzoic acid in water, $K' = 6.27–6.527 \times 10^{-5}$ (*pK'* 4.185–4.20); *trans*-cinnamic acid in water, $K' = 3.65 \times 10^{-5}$ (*pK'* 4.43). Dippy's values were determined by conductivity measurements and include activity corrections of about +0.02 *pK* unit. [c] The *pK'* values in methanol were obtained by substituting *p*H values as given by the glass electrode, and have only relative validity.

TABLE VI

HYDROLYSIS RATE CONSTANTS IN 50% DIOXANE
BENZYLIDENEPYRUVIC ESTERS $XC_6H_4CH{=}CHCOCOOCH_3$

X	Temp.,[a] °C.	HCl,[b] moles/l. × 10^2	Ester, moles/l. × 10^3	$k' \times 10^3$ hr.$^{-1}$[c]
H	25.0	10.37	20.00	14.3
H	25.0	4.28	8.00	6.0
H	44.9	4.28	8.00	29.6[d]
4-OCH_3	25.2	4.28	8.00	5.9
4-Br	25.2	4.28	6.40	6.1
4-CH_3	25.0	4.28	8.00	5.6
Reference ester: ethyl acetate				
	25.2	4.28	22.76–24.44	12.6

[a] ±0.2°. [b] Determined by titration at zero time. [c] Calculated probable error ± 1%. [d] The activation energy E for methyl benzylidenepyruvate calculated from $d \ln k/dt = E/RT^2$, is about 15 kcal./mole.

alyst were found to have the expected first-order kinetics with respect to the concentration of ester and of hydrochloric acid. The activation energy for the hydrolysis of benzylidenepyruvic acid calculated from rates at 25° and at 45° was found to be about 15 kcal./mole. Timm and Hinshelwood[4] report a value of 18.24 kcal./mole for the activation energy of methyl benzoate in 60% methanol and 16.20 kcal./mole for ethyl acetate in 60% ethanol.

The effect of substituent groups on the rate of acid-catalyzed hydrolysis of methyl benzylidenepyruvate is slight ($k' = 5.6$ to 6.1×10^{-3} hr.$^{-1}$) and is of the order of magnitude of these effects in the benzoic acid series. The actual rate of hydrolysis of the methyl benzylidenepyruvates, however, is about 90 times as fast as that of the methyl benzoates. In the benzoates, steric hindrance by the phenyl group inhibits the addition of water to the carbon atom of the carboxyl group as postulated in the Ingold mechanism.[14] Ethyl acetate was hydrolyzed as a reference substance with a rate at 25° of 12.6×10^{-3} hr.$^{-1}$, or twice as fast as the methyl benzylidenepyruvates. Methyl pyruvate in water solution hydrolyzes 1.2 times as fast as methyl acetate[15] and ethyl cinnamate has a rate 0.22 times that of ethyl acetate.[4] In ethyl cinnamate and methyl benzylidenepyruvate the phenyl group is farther away from the carboxyl group so that it exerts little steric effect, and as a result the rates are higher than that of methyl benzoate.

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[14] S. C. Datta, J. N. E. Day and C. K. Ingold, *J. Chem. Soc.*, 838 (1939).

[15] A. Skrabal, F. Pfaff and H. Airoldi, *Monatsh.*, **45**, 148 (1924).

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The Cryoscopic Behavior of Organic Compounds in Sulfuric Acid. III. Diaryl Sulfones

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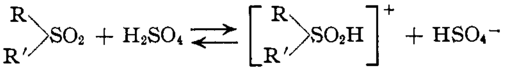
Additional cryoscopic data of substituted diaryl sulfones in sulfuric acid are reported. The effect of the substituents on the basicity of the sulfone group is interpreted in terms of changes in the electronic structure of the latter.

In a recent publication[1] from this Laboratory it was shown that sulfones are weak bases in sulfuric acid, and that substituents present on the two aryl groups affect equilibrium (1) so that the observed "*i*" factor can vary between the values of 1 and 2. In view of the fact that di-(*p*-nitrophenyl) sulfone gave an "*i*" factor of 2 while di-(*p*-nitrobenzyl) sulfone gave an "*i*" factor of 1, it was concluded that the site of the protonation is the sulfone (rather than nitro) group. Since the cryoscopic study of the sulfones in sulfuric acid seemed to offer an opportunity to compare the basicity of the sulfone group as a function of the electronic effects caused by the substituents R and R', we have extended this work so that a total of eleven diaryl sulfones has now been investigated.



$$\begin{matrix}R\\R'\end{matrix}\!\!>SO_2 + H_2SO_4 \rightleftharpoons \left[\begin{matrix}R\\R'\end{matrix}\!\!>SO_2H\right]^+ + HSO_4^- \quad (1)$$

Experimental

Di-(*p*-chlorophenyl) sulfone, di-(*p*-aminophenyl) sulfone, and bis-(3-nitro-4-chlorophenyl) sulfone were obtained from the Monsanto Chemical Co. and were carefully purified and dried before use. Di-(*m*-nitrophenyl) sulfone[2] was prepared by the nitration of phenyl sulfone, while 2,4-dinitrophenyl phenyl sulfone[3] and 2,4-dinitrophenyl 4-chlorophenyl sul-

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[1] H. H. Szmant and G. A. Brost, THIS JOURNAL, **73**, 4175 (1951).

[2] C. A. Buehler and J. C. Masters, *J. Org. Chem.*, **4**, 262 (1939).

[3] Ullmann and Pasdermadjian, *Ber.*, **34**, 1151 (1901).

fone[4] were prepared by the Friedel–Crafts reaction of 2,4-dinitrophenylsulfenyl chloride with benzene and chlorobenzene, respectively, followed by the oxidation of the sulfides. *o*-Nitrophenylphenyl sulfone[3] was prepared by the oxidation of the sulfide obtained from the reaction of thiophenol and *o*-chloronitrobenzene.

The apparatus and experimental technique was the same as previously described.[5] Representative cryoscopic measurements are listed in Table I.

Table I

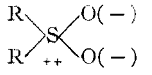
Freezing Point Depression Measurements

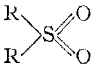
	Δm	Time, hr.	F.p., °C. (initial)	ΔT	"i"
Di-(*m*-nitrophenyl)	0.04013	2	10.040	0.305	1.28
sulfone	0.04186	5.5	9.725	0.355	1.31
Bis-(3-nitro-4-chloro-	0.03288	17.5	9.947	0.245	1.20
phenyl) sulfone	0.03318	8.5	10.130	0.248	1.22
Di-(*p*-chlorophenyl)	0.03073	78.5	9.863	0.188	0.96
sulfone	0.03521	23.75	9.675	0.218	1.06
o-Nitrophenyl phenyl	0.04088	19	9.990	0.285	1.13
sulfone	0.04253	24	9.705	0.297	1.14
2,4-Dinitrophenyl	0.03798	3	9.715	0.317	1.36
phenyl sulfone	0.03586	25	9.922	0.297	1.35
2,4-Dinitrophenyl 4-	0.03671	22.5	9.774	0.307	1.36
chlorophenyl sulfone	0.03917	8	9.902	0.324	1.35
Di-(*p*-aminophenyl)	0.01484	68	9.873	0.327	3.59
sulfone	0.01407	2 weeks	9.546	0.305	3.52
p-Nitrophenyl	0.02748	3	9.951	0.226	1.33
p-tolyl sulfone	0.02914	5	9.755	0.248	1.39

All of the compounds studied here could be recovered in nearly quantitative fashion by pouring the sulfuric acid solution on ice. In the case of the amino sulfone the resulting solution was neutralized with soda ash and the precipitated sulfone was filtered, washed, dried and recrystallized from hot water.

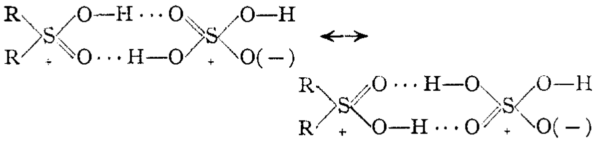
Discussion

The nature of the sulfur–oxygen bonds in sulfones (and sulfoxides) has been under frequent discussion in recent years.[6] It is, of course, more than likely that the single- or double-bond character of the sulfur–oxygen bonds depends on the remainder of the sulfone molecule, and in that case it is of interest to know what structural factors control the relative contributions of the extreme electron distributions I and II.


I


II

The initial results of the behavior of sulfones in sulfuric acid[1] and the results reported here seem to offer a method of differentiating sulfones in their ground states with respect to their ability to be protonated. In the previous paper on this subject it was postulated that the basicity of the sulfone increases proportionally with the resonance stabilization of the protonated complex and thus with the double-bond character of the sulfur–oxygen bonds. This working hypothesis was found to be applicable to the results reported here, and an improved representation of the protonated sulfone complex is shown in III


III

The arguments used in arriving at the abovementioned hypothesis were based mainly on the effect of the para-nitro substituents on the i factor of phenyl sulfone. For this reason it was of utmost interest to investigate the effect of meta-nitro groups and it was found that two meta-nitro groups caused essentially no increase in the i value of phenyl sulfone. This result indicates again that the high basicity of di-(*p*-nitrophenyl) sulfone is not due to a cumulative partial protonation of the three oxygen-containing groups.

A nitro group in the ortho position was found to depress the protonation of phenyl sulfone. Thus *o*-nitrophenyl phenyl sulfone has a lower i factor than phenyl sulfone (*ca.* 1.1 and 1.3, respectively), and 2,4-dinitrophenyl phenyl sulfone is less protonated than *p*-nitrophenyl phenyl sulfone (*ca.* 1.35 and 1.5, respectively). This marked lowering of the i factor by an ortho-nitro group fits in well with the picture of the protonated and solvated sulfone complex (III) since steric effects should be very pronounced under these circumstances.

In line with the working hypothesis employed in this study the substituents which are capable of donating electrons to the sulfone group should decrease the latter's basicity. An attempt to verify this prediction by means of di-(*p*-methoxyphenyl) sulfone failed because the compound was rapidly sulfonated. The result obtained with di-(*p*-chlorophenyl) sulfone did, however, agree with this prediction since this compound gave an i value of 1.0 as compared with 1.3 obtained with phenyl sulfone. Of the potential $-$I and $+$E effects of a chloro substituent the latter effect seems to predominate when the halogen is conjugated with a strongly electron-withdrawing sulfone group. The same effect of para-chloro substituents was noticed with di-(3-nitro-4-chlorophenyl) sulfone which gave a lower i value than m,m'-dinitrophenyl sulfone (*ca.* 1.2 and 1.3, respectively). The lowering of the i factor was also caused by the para-methyl substituent when one compares *p*-nitrophenyl *p*-tolyl sulfone and *p*-nitrophenyl phenyl sulfone (*ca.* 1.35 and 1.5, respectively).

The formation of the disulfate would account for an i factor of 3.0 in the case of p,p'-diaminophenyl sulfone. The observed value of 3.5 implies that additional protonation is possible at the sulfone function but the magnitude of the effect of the two para-substituents acting by an $-$I effect is about half as large as the effect caused by two para-nitro groups (acting by an $-$E effect). The fact that the two ammonium substituents cause a larger basicity increase in the sulfone function than two meta-nitro groups is not surprising since we are comparing positively charged with neutral substituents.

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[4] C. H. Buess and N. Kharasch, This Journal, **72**, 3532 (1950).

[5] H. H. Szmant, O. M. Devlin and G. Brost, *ibid.*, **73**, 3059 (1951).

[6] See for example the recent papers by Koch (*J. Chem. Soc.*, 408 (1949)); Fehnel and Carmack, This Journal, **71**, 231 (1949); Amstutz, *et al.*, *ibid.*, **73**, 1220 (1951).