Properties of Some Disulphones: Acidities, Rates of Ionization and Bromination, and Hydrogen Isotope Effects

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Measurements are reported of the rates of bromination and acid dissociation constants of the disulphones $(EtSO_2)_2$-CHMe, $(MeSO_2)_2CH_2$, $(EtSO_2)_2CH_2$, $(EtSO_2)_2CHPh$, and $(EtSO_2)_2CHBr$. For $(EtSO_2)_2CHMe$ the order with respect to bromine is between zero and unity, and it was possible to derive both rates of ionization (and of the reaction of the anions with acids) and velocity constants for the reaction between anion and bromine or tribromide ion. For the remaining disulphones only the latter were obtained.

THE catalysed halogenation of compounds of the type $R^1R^2CH{\cdot}COR^3$ is well known to proceed through the enol or the enolate ion. Under most conditions these reactions are of zero order with respect to halogen, so that the rate-limiting process is enolization or ionization, but by making measurements at extremely low halogen concentrations it has proved possible to make the halogenation step rate-limiting and to determine velocity constants for the reaction of enols and enolate ions with halogen molecules and trihalide ions.[1-6] Much less is known about halogenation of CH-groups activated by groups other than carbonyl, for example the sulphones. For these compounds the situation should be simpler than for ketones, since no analogue of the enol form is known to exist, and the carbanion is likely to be the only reactive species.

Previous work on sulphones suggests that both ionization and halogenation rates should be derivable from a kinetic study of halogenation under suitable conditions. Ramberg and his co-workers found that the bromination of some optically active monosulphones was of zero order in halogen and close to the rates of racemization;[7,8] on the other hand, for disulphones it was found that rates were proportional to bromine concentration and inversely proportional to hydrogen ion concentration, corresponding to the reaction of bromine with anions in equilibrium with the undissociated disulphone.[9] However, the last measurements were made in strongly acid solutions, which favours the addition of a proton to the anion before it has time to react with bromine, and it seemed likely that under less acid conditions zero-order bromination would be observable.

The present paper shows that both ionization and bromination rates can be determined for the disulphone $(EtSO_2)_2CHMe$, and reports ionization rates in the presence of a number of bases. The rate of proton exchange of this substance in *m*-nitrophenolate buffers has previously been determined directly from n.m.r. line broadening.[10] Velocity constants were also determined for the reactions of Br_2 and Br_3^- with the anions of five disulphones, which involved the measurement of their p*K*-values.

EXPERIMENTAL

Materials.—Following Cronyn[11] the disulphones $(R^2SO_2)_2CHR^1$ were prepared by the reactions $2R^2SH + R^1CHO \rightarrow (R^2S)_2CHR^1 + H_2O$ and $(R^2S)_2SHR^1$ ($+ H_2O_2$ in glacial acetic acid) $\rightarrow (R^2SO_2)_2CHR^1$. In the final oxidation the product was separated by pouring into water and was recrystallized from ethanol. The m.p.s (in agreement with literature values) were: $(EtSO_2)_2CHMe$ 75—76 °C, $(EtSO_2)_2CH_2$ 103—104 °C, $(EtSO_2)_2CHPh$ 133—134 °C, and $(MeSO_2)_2CH_2$ 148—150 °C. The last substance was kindly supplied by Dr. D. T. Gibson.

$(EtSO_2)_2CHBr$ was prepared by adding a slight excess of bromine in 1·5M-acetic acid to a solution of $(EtSO_2)_2CH_2$ in aqueous 1M-sodium hydroxide followed by the addition of

[1] R. P. Bell and M. Spiro, *J. Chem. Soc.*, 1953, 429.
[2] R. P. Bell and P. Engel, *J. Chem. Soc.*, 1957, 247.
[3] R. P. Bell and D. C. Vogelsong, *J. Chem. Soc.*, 1958, 243.
[4] R. P. Bell and D. J. Rawlinson, *J. Chem. Soc.*, 1961, 726.
[5] R. P. Bell and K. Yates *J. Chem. Soc.*, 1962, 1927, 2285.
[6] R. P. Bell and G. G. Davis, *J. Chem. Soc.*, 1964, 902.
[7] L. Ramberg and A. Mellander, *Arkiv Kemi, Min., Geol.*, 1934, **11**, *B*, No. 31.
[8] L. Ramberg and I. Hedlund, *Arkiv Kemi, Min., Geol.*, 1934, **11**, *B*, No. 41.
[9] L. Ramberg and E. Samen, *Arkiv Kemi, Min., Geol.* 1934, **11**, *B*, No. 35; 1936, **12**, *A*, No. 8.
[10] B. G. Cox, F. G. Riddell, and D. A. R. Williams, *J. Chem. Soc.* (*B*), 1970, 859.
[11] M. W. Cronyn, *J. Amer. Chem. Soc.*, 1952, **74**, 1225.

sodium thiosulphate to remove the excess of bromine. The solid which separated was shown by n.m.r. spectroscopy to consist of about 80% $(EtSO_2)_2CHBr$, together with 10% each of $(EtSO_2)_2CH_2$ and $(EtSO_2)_2Br_2$. Attempts at further purification were not successful, but because of the large differences in reactivity and pK between the three components, the unpurified material could be used directly.

$(EtSO_2)_2CDMe$ was prepared by dissolving $(EtSO_2)_2CHMe$ in hot deuterium oxide containing sodium acetate to catalyse the exchange. The deuteriated material crystallized on cooling, and the procedure was repeated to ensure complete deuteration. The n.m.r. spectrum showed the isotopic purity of the final product to be at least 97%.

Inorganic materials were of AnalaR grade, and water was redistilled from alkaline permanganate.

Kinetic Measurements.—The kinetic scheme envisaged is shown in reactions (A), (B), and (C) where SH is the disulphone and A–B any acid–base pair. For reaction in a simple buffer solution kinetic analysis gives the relation (1) where k_2, K, and k_1 are given by equations (2a), (2b), and (3) and $[Br_2^*] = [Br_2] + [Br_3^-]$. When $[H^+]$ is low and $[Br_2^*]$ fairly high (10^{-3} to 10^{-2}M) both terms of equation (1) are found to be significant. Provided that $[Br_2^*]$ does not vary greatly during a reaction, and $[H^+]$ and $[Br^-]$ are also constant, equation (1) can be written as (4) where k_{obs} is the observed first-order velocity constant and $[Br_2^*]_{av}$ is an average value. K'_{SH} is the dissociation constant at the ionic strength of the experiment, rather than the thermodynamic value.

$$\mathrm{SH} + \Sigma\mathrm{B} \overset{k_1}{\rightleftharpoons} \mathrm{S}^- + \Sigma\mathrm{A} \qquad \text{(A)}$$

$$\mathrm{S}^- + \mathrm{Br}_2 \xrightarrow{k_2'} \mathrm{SBr} + \mathrm{Br}^- \qquad \text{(B)}$$

$$\mathrm{S}^- + \mathrm{Br}_3^- \xrightarrow{k_2''} \mathrm{SBr} + 2\mathrm{Br}^- \qquad \text{(C)}$$

$$[\mathrm{SH}]/\mathrm{d}[\mathrm{SH}]/\mathrm{d}t = ([\mathrm{H}^+]/k_2K'_{\mathrm{SH}}[\mathrm{Br}_2^*]) + 1/k_1 \qquad (1)$$

$$k_2 = (k_2' + k_2''K[\mathrm{Br}^-])/(1 + K[\mathrm{Br}^-]) \qquad \text{(2a)}$$

$$K = [\mathrm{Br}_3^-]/[\mathrm{Br}_2][\mathrm{Br}^-],\ K'_{\mathrm{SH}} = [\mathrm{H}^+][\mathrm{S}^-]/[\mathrm{SH}] \qquad \text{(2b)}$$

$$k_1 = k_0 + k_{\mathrm{B}}[\mathrm{B}] + k_{\mathrm{OH}}[\mathrm{OH}^-] \qquad (3)$$

$$1/k_{\mathrm{obs}} = ([\mathrm{H}^+]/k_2K'_{\mathrm{SH}}[\mathrm{Br}_2^*]_{\mathrm{av}}) + 1/k_1 \qquad (4)$$

If, on the other hand, $[H^+]$ is fairly high and $[Br_2^*]$ very low (10^{-5}—10^{-6}M) it was found that the second term of equation (1) is negligible, and since [SH] is now effectively constant the observed first-order constant for the disappearance of bromine is given by equation (5).

$$k_{\mathrm{obs}} = k_2K'_{\mathrm{SH}}[\mathrm{SH}]/[\mathrm{H}^+] \qquad (5)$$

The bromination of $(EtSO_2)_2CHMe$ at high bromine concentrations was followed at 398 nm with a Unicam SP500 or SP700 spectrophotometer. The initial concentration of bromine was about 20% greater than that of the disulphone, and the apparent first-order velocity constants were obtained from plots of lg $(A_\infty - A_t)$ against time, where A is the absorbance. For each value of $[Br_2^*]_{av}$ the corresponding value of k_{obs} was obtained from the slope of this plot over the range $[Br_2^*]_{av}$ + 10% to $[Br_2^*]_{av}$ − 10%: thus several values were obtained from each complete kinetic curve. The concentration of bromide ion was throughout 0·02M, and all measurements were made at 25 °C.

For $(EtSO_2)_2CHMe$ the reaction at low bromine concentrations (*ca.* 10^{-4}M) was also followed spectrophotometrically; since the disulphone was in large excess (0·05M) the reaction was of the first order in bromine [cf. equation (5)]. For the remaining disulphones initial bromine concentrations of *ca.* 10^{-5}M were used, and the reaction followed by observing the redox potential at a platinum electrode, as previously described.[12–14] There exists a possibility of dibromination for $(EtSO_2)_2CH_2$ and $(MeSO_2)_2CH_2$: however, its effect should be inappreciable, since the disulphone is present in about 1000-fold excess, and our measurements show that under the same conditions $(EtSO_2)_2CHBr$ reacts with bromine only about 20 times as fast as $(EtSO_2)_2CH_2$. This conclusion is confirmed by the fact that the reactions followed a strictly first-order course for at least five half-lives. These experiments were carried out over a range of bromide ion concentrations in order to determine the separate reactivities of Br_2 and Br_3^-.

Measurements of pK.—The anions of the disulphones exhibit strong u.v. absorption, and the equilibrium constant for the reaction $SH + OH^- \rightleftharpoons S^- + H_2O$ could be determined spectrophotometrically. This equilibrium constant is equal to K_w/K_{SH}, where K_{SH} is the acid dissociation constant of SH. For solutions of moderate ionic strength we can assume that $f_{OH}/f_S = 1$, and K_w/K_{SH} is equal to the ratio of the thermodynamic constants. It is easily shown that $\varepsilon = \varepsilon_S - \varepsilon K_w/K_{SH}[OH^-]$, where ε is the apparent extinction coefficient and ε_S the extinction coefficient of the anion. A plot of ε against $\varepsilon/[OH^-]$ therefore gives a straight line of slope $-K_w/K_{SH}$ and intercept ε_S. The hydroxide ion concentration is slightly decreased by the conversion of SH into S^-, and the values of $[OH^-]$ given in Table 4 have been corrected for this.

$(EtSO_2)_2CHBr$ is a relatively strong acid (pK 10·7), and measurements were therefore made both in dilute sodium hydroxide solutions and in carbonate buffers with $[HCO_3^-]/[CO_3^{2-}]$ between 0·05 and 2·0. The buffer ratios were corrected for displacement by the formation of S^-, and values of $[OH^-]$ were calculated from the measured pH on the assumption that $f_\pm = 0·71$.

The compound $(EtSO_2)_2CHMe$ is such a weak acid (pK 14·6) that it was necessary to use sodium hydroxide solutions between 0·1M and 4M in order to obtain appreciable degrees of ionization. It was therefore no longer adequate to express equilibrium constants in terms of $[OH^-]$, and the function h_- has been used instead, the values in the Table being those compiled by Bowden.[15] It follows from the definition of h_- that $\varepsilon = \varepsilon h_-/K_{SH}$, and K_{SH} was therefore derived from a plot of ε against h_-.

RESULTS

Rates of Ionization of $(EtSO_2)_2CHMe$.—Measurements were first made in three acetate buffer solutions of ratios $r = [HOAc]/[AcO^-] = 2$, 1, and 0·5, $[AcO^-]$ being kept constant at 0·1M throughout. In each of these series $[Br_2^*]_{av}$ was varied in the range 10^{-3}M to 10^{-2}M, and the results are in Table 1. Since these results were used mainly to derive the rates of ionization from the observed rates of bromination in a series of buffer solutions, it is convenient

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[12] R. P. Bell and R. R. Robinson, *Proc. Roy. Soc.*, 1962, *A*, **270**, 411.

[13] J. R. Atkinson and R. P. Bell, *J. Chem. Soc.*, 1963, 3260.

[14] R. P. Bell and P. de Maria, *J. Chem. Soc.* (*B*), 1969, 1057.

[15] K. Bowden, *Chem. Rev.*, 1966, **66**, 119.

TABLE 1

Bromination of $(EtSO_2)_2CHMe$ in acetate buffers at 25 °C; effect of bromine concentration; k_{obs} in s^{-1}; $[Br^-] = 0{\cdot}02$; $I = 0{\cdot}25$ ($NaClO_4$); $[AcO^-] = 0{\cdot}10$

$r = 2$

$10^5[Br_2^*]_{av}$	147	185	215	274	422	575	835	1190
10^6k_{obs}	106	132	157	190	242	298	371	427

$r = 1$

$10^5[Br_2^*]_{av}$	159	181	208	260	268	304	400	497
10^6k_{obs}	227	258	280	324	314	379	406	430
$10^5[Br_2^*]_{av}$	565	680	1080					
10^6k_{obs}	497	505	605					

$r = 0{\cdot}5$

$10^5[Br_2^*]_{av}$	146	169	198	261	394	549	800	1130
10^6k_{obs}	377	420	476	560	695	850	964	1010

to re-write equation (4) in terms of buffer ratios. For a buffer A–B of ratio r, it becomes (6), where K_A and K_{SH} are

$$1/rk_{\text{obs}} = (K_A/k_2K_{SH}[Br_2^*]_{av}) + 1/rk_1 \qquad (6)$$

thermodynamic constants, the ionic activity coefficients having cancelled. A plot of $1/rk_{\text{obs}}$ against $1/[Br_2^*]_{av}$ should therefore give a straight line of slope K_A/k_2K_{SH}, and Figure 1 shows that parallel straight lines are in fact obtained for the two extreme buffer ratios investigated: the points for the intermediate ratio fall between these two lines and are omitted for clarity. The measured slope can then be used to calculate k_1 from k_{obs} for any buffer solution by means of equation (6) and the appropriate values of K_A and r.*

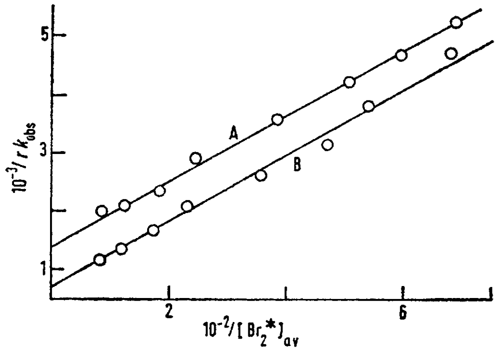

FIGURE 1 Rate of bromination of $(EtSO_2)_2CHMe$ as a function of bromine concentration; A, $r = 0{\cdot}5$; B, $r = 2$

Rates of ionization were measured in buffer solutions of β-chloropropionate, acetate, and trimethylacetate, k_1 being obtained from k_{obs} by the procedure just described. The results are in Table 2. The velocity constant for proton abstraction by the basic component of the buffer [(k_B in equation (3)] was obtained from the slope of plots of k_1 against [B] at constant buffer ratio, which was found to be independent of buffer ratio.

According to equation (3), the intercepts of the plots of k_1 against [B] at constant r should give the value of $k_0 + k_{OH}[OH^-]$. These values are collected in Table 3, together with the values of $[OH^-]$ calculated from the thermodynamic dissociation constants of the buffer acids and K_W, since the ionic activity coefficients cancel. Table 3 also contains intercepts for four acetate buffer solutions not included in Table 2 (r = 1·00, 2·22, 3·85, and 9·09). For these solutions the difference between k_1 and k_{obs} is large, and the values of k_1 therefore less reliable. We have therefore not used these results in determining k_B, but it is found that the intercepts of the k_1–[B] plots are insensitive to the value taken for the correction term in equation (4): in fact, almost identical values were obtained for the intercepts if k_{obs} is plotted instead of k_1. The calculated rates in the last column of Table 3 are derived from the velocity constants given at the head of the Table.

TABLE 2

Rate of ionization of $(EtSO_2)_2CHMe$ in buffer solutions at 25 °C; k_{obs} and k_1 in s^{-1}; k_B in l mol^{-1} s^{-1}; $[Br^-] = 0{\cdot}02$; $I = 0{\cdot}25$ ($NaClO_4$)

β-Chloropropionate, $k_B = 3{\cdot}23 \times 10^{-3}$

	r = 1·11			r = 0·175			
$10^3[B]$	20	70	100	100	140	160	200
10^6k_{obs}	98	155	208	512	570	604	670
10^6k_1	133	278	456	650	747	815	959

r = 0·137

$10^3[B]$	100	120	140	160	200
10^6k_{obs}	586	609	630	667	730
10^6k_1	700	785	827	910	1070

r = 0·095

$10^3[B]$	120	140	160	180	200
10^6k_{obs}	816	860	900	940	975
10^6k_1	1030	1100	1160	1250	1300

Acetate, $k_B = 9{\cdot}0 \times 10^{-3}$

r = 0·526

$10^3[B]$	40	60	80	120	160	200
10^5k_{obs}	71	77	86	103	125	139
10^5k_1	88	97	117	160	195	230

r = 0·325

$10^3[B]$	60	80	120	160	200
10^5k_{obs}	111	119	141	161	182
10^5k_1	139	152	192	228	276

r = 0·208

$10^3[B]$	60	80	100	120	160	200
10^5k_{obs}	145	159	170	182	202	230
10^5k_1	173	193	215	230	265	315

Trimethylacetate, $k_B = 1{\cdot}58 \times 10^{-2}$

r = 0·99

$10^3[B]$	40	60	80	100	120	140
10^5k_{obs}	82	101	105	117	125	143
10^5k_1	110	140	160	197	222	257

r = 0·650

$10^3[B]$	40	60	80	100	120	140
10^5k_{obs}	108	125	140	157	177	192
10^5k_1	143	177	197	235	277	315

r = 0·480

$10^3[B]$	60	80	100	120	140
10^5k_{obs}	158	170	202	213	240
10^5k_1	210	240	282	308	350

The rates of bromination of $(EtSO_2)_2CH_2$, $(EtSO_2)_2CHBr$, and $(EtSO_2)_2CHPh$ were also investigated in acetate buffers, but it was not found possible to approach zero-order conditions with respect to bromine, and no rate of ionization was derived.

Values of K_{SH}.—The spectrophotometric results are

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* In practice these calculations were carried out in terms of the average absorbance rather than $[Br_2^*]_{av}$: since the concentration of bromide ion was 0·02M throughout, these two quantities are proportional to one another. The values of $[Br_2^*]_{av}$ in Table 1 and Figure 1 were calculated from a measured extinction coefficient of 270 at 398 nm, though this figure did not in fact enter our calculations.

TABLE 3

Rate of ionization of $(EtSO_2)_2CHMe$ in presence of water and hydroxide ions; $k_0 = 3{\cdot}5 \times 10^{-5}$ s^{-1}, $k_{OH} = 4{\cdot}3 \times 10^5$ l mol^{-1} s^{-1}

Buffer	r	$10^{10}[OH^-]$	$10^5(k_0 + k_{OH})[OH^-]$ obs.	$10^5(k_0 + k_{OH})[OH^-]$ calc.
b	9·1	0·63	7	6
a	1·11	1·10	7	8
b	3·85	1·48	9	10
b	2·22	2·57	15	15
b	1·00	5·71	26	28
a	0·175	7·05	31	34
a	0·128	7·72	37	37
b	0·525	10·8	42	50
c	0·99	11·3	51	52
a	0·095	13·0	63	60
c	0·650	15·9	77	72
b	0·325	17·6	77	79
c	0·477	21·6	110	97
b	0·208	27·4	115	121

a = β-chloropropionate. *b* = acetate. *c* = trimethylacetate.

collected in Table 4, and the values of K_{SH} derived from plots of ε against ε/[OH⁻] are in Table 6.

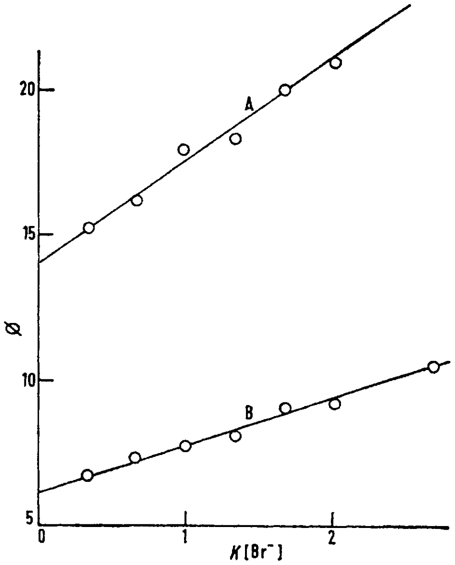

FIGURE 2 Effect of bromide concentration on bromination rate.
A, $(EtSO_2)_2CH_2$, $\phi = 10^4 k_{II}[H^+](1 + K[Br^-])$
B, $(EtSO_2)_2CHMe$ $\phi = 10^6 k_{II}[H^+](1 + K[Br^-])$

Rates of Bromination of Disulphone Anions.—The results obtained for reaction with low concentrations of bromine (*ca.* 10^{-5}M) are given in Table 5. The tabulated constant k_{II} is $k_{obs}/[SH]$, where k_{obs} is the observed first-order velocity constant, and is shown by equation (5) to be equal to $k_2K'_{SH}/[H^+]$. It follows from equation (2) that a plot of $k_{II}[H^+](1 + K[Br^-])$ against $K[Br^-]$ should give a straight line of slope $K'_{SH}k_2''$ and intercept $K'_{SH}k_2'$. The value of K has been taken as 16·8.[16] Examples of these plots are shown in Figure 2. In deriving the values of k_2'' and k_2' from the slopes and intercepts we have assumed that $K'_{SH} = K_{SH}/0{\cdot}50$, where K_{SH} is the thermodynamic value as given in Table 4, and 0·50 is the value assumed for f_Hf_S at an ionic strength of $I = 0{\cdot}2$ on the basis of the expression $-\lg f_z = 0{\cdot}51z^2I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$, where z is the ionic

TABLE 4

Spectrophotometric measurements of K_{SH} at 25 °C

$(EtSO_2)_2CHMe$, $K_{SH} = 2{\cdot}74 \times 10^{-15}$

$[OH^-]$	0·10	0·25	0·50	1·00	1·50
$10^{14}h_-$	9·77	3·89	1·95	0·977	0·603
ε (250 nm)	15·0	35·0	63·4	117	172
$[OH^-]$	2·00	2·50	3·00	4·00	
$10^{14}h_-$	0·398	0·288	0·219	0·135	
ε (250 nm)	220	266	296	376	

$(MeSO_2)_2CH_2$, $K_{SH} = 2{\cdot}43 \times 10^{-13}$, $I = 0{\cdot}2$ $(NaClO_4)$

$[OH^-]$	0·0060	0·0097	0·0196	0·0396	0·0800	0·120	0·200
ε (240 nm)	36·0	52·5	90·0	138	186	222	245

$[EtSO_2)_2CH_2$, $K_{SH} = 6{\cdot}26 \times 10^{-13}$, $I = 0{\cdot}2$ $(NaClO_4)$

$[OH^-]$	0·00389	0·00782	0·0118	0·0157	0·0197
ε (290 nm)	58·7	99·4	125	145	159
$[OH^-]$	0·0396	0·0796	0·120	0·200	
ε (290 nm)	201	240	256	264	

$(EtSO_2)_2CHPh$, $K_{SH} = 7{\cdot}53 \times 10^{-13}$, $I = 0{\cdot}2$ $(NaClO_4)$

$[OH^-]$	0·00486	0·0098	0·0197	0·0496	0·200
ε (290 nm)	545	848	1200	1540	1860

$(EtSO_2)_2CHBr$, $K_{SH} = 1{\cdot}95 \times 10^{-11}$
Sodium hydroxide solutions, $I = 0{\cdot}25$ $(NaClO_4)$

$[OH^-]$	0·00110	0·00343	0·00864	0·0786	0·200
ε (300 nm)	95	123	133	139	140

Carbonate buffers, $I = 0{\cdot}2$

$[HCO_3^-]/[CO_3^{2-}]$	2·04	1·01	0·515	0·218	0·116	0·067
$10^6[OH^-]$	57	113	217	487	865	1120
ε (300 nm)	14·6	25·3	41·9	67·5	88·1	101

TABLE 5

Bromination rates at different bromide ion concentrations; $k_{II} = k_{obs}/[SH]$; $I = 0{\cdot}20$ $(NaClO_4)$; perchloric acid solutions, unless stated otherwise

$(EtSO_2)_2CHMe$, [SH] = *ca.* 0·05, $[H^+] = 0{\cdot}01$, $[Br_2^*]_0$ = *ca.* 5×10^{-4}

$[Br^-]$	0·02	0·04	0·06	0·08	0·10	0·12	0·16
10^6k_{II}	506	437	386	348	335	306	285

$(MeSO_2)_2CH_2$, [SH] = *ca.* 0·01, $[H^+] = 2{\cdot}5 \times 10^{-3}$, $[Br_2^*]_0$ = *ca.* 10^{-5}

$[Br^-]$	0·02	0·04	0·06	0·08	0·10	0·12	0·16	0·20
10^3k_{II}	192	172	153	142	142	133	127	125

$(EtSO_2)_2CH_2$, [SH] = *ca.* 0·008, $[H^+]$ = (*a*) $2{\cdot}0 \times 10^{-3}$, (*b*) $3{\cdot}0 \times 10^{-3}$, $[Br_2^*]_0$ = *ca.* 10^{-5}

$[Br^-]$	0·01	0·02	0·04	0·06	0·08	0·12	0·16
10^3k_{II}	620(*a*)	380(*b*)	325(*b*)	438(*a*)	263(*b*)	234(*b*)	327(*a*)

$(EtSO_2)_2CHPh$, [SH] = *ca.* 5×10^{-4}, acetate buffer, $r = 1$, $[Br_2^*]_0$ = *ca.* $5 = 10^{-6}$

$[Br^-]$	0·02	0·04	0·06	0·08	0·10
k_{II}	160	138	119	110	101

$(EtSO_2)_2CHBr$, [SH] = *ca.* 0·002, $[H^+] = 0{\cdot}0099$, $[Br_2^*]_0$ = *ca.* 3×10^{-5}

$[Br^-]$	0·01	0·02	0·04	0·08	0·10	0·12	0·16
k_{II}	3·46	3·10	2·65	2·18	2·10	1·95	1·83

TABLE 6

Velocity constants for reactions of anions with bromine and tribromide ion; k_2' refers to $S^- + Br_2$; $(k_2'')_0$, extrapolated to $I = 0$, refers to $S^- + Br_3^-$

Anion	K_{SH}	$10^{-9}k_2'$	$10^{-9}(k_2'')_0$	$k_2'/(k_2'')_0$
$[(EtSO_2)_2CMe]^-$	$2{\cdot}74 \times 10^{-15}$	1·14	0·13	8·7
$[(MeSO_2)_2CH]^-$	$2{\cdot}43 \times 10^{-13}$	1·15	0·23	5·1
$[(EtSO_2)_2CH]^-$	$6{\cdot}26 \times 10^{-13}$	1·55	0·19	8·3
$[(EtSO_2)_2CPh]^-$	$7{\cdot}53 \times 10^{-13}$	0·34	0·035	9·8
$[(EtSO_2)_2CBr]^-$	$1{\cdot}95 \times 10^{-11}$	0·95	0·14	6·8

[16] D. B. Scaife and H. J. V. Tyrrell, *J. Chem. Soc.*, 1958, 386.

charge. The velocity constants for the various disulphone anions are in Table 6. Since k'_2 refers to a reaction between an anion and an uncharged species it should vary little with ionic strength. On the other hand, k_2'' refers to a reaction between two singly charged anions at $I = 0{\cdot}2$, and is related to $(k_2'')_0$, the value at zero ionic strength, by $k_2''f_2/f_1^2 = (k_2'')_0$. In deriving the values of $(k_2'')_0$ in Table 6 we have assumed that $f_2/f_1^2 = 0{\cdot}50$: this is consistent with the expression used for $f_{\mathrm{H}}f_{\mathrm{S}}$.

For the substance $(EtSO_2)_2CHMe$ a check on the velocity constants in Table 6 can be obtained from the slope of the plots in Figure 1. According to equation (6) this slope is $K_{\mathrm{A}}/k_2K_{\mathrm{SH}}$: the measured slope is 5·6 mol l^{-1} s, and insertion of the thermodynamic value of K_{A} gives $K_{\mathrm{SH}}k_2 = 3{\cdot}1 \times 10^{-6}$ s^{-1}. Another value for $K_{\mathrm{SH}}k_2$ can be obtained from equation (2). K_{SH} and k_2' are taken directly from Table 6, and k_2'' at $I = 0{\cdot}25$ is given by $k_2'' = (k_2'')_0f_1^2/f_2$ with $-\log f_z = 0{\cdot}51z^2I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$. This gives $K_{\mathrm{SH}}k_2 = 2{\cdot}6 \times 10^{-6}$ s^{-1}. The difference between the two values probably does not exceed the uncertainties in the assumptions about activity coefficients.

DISCUSSION

The rate constants for the ionization of $(EtSO_2)_2CHMe$ given in Tables 2 and 3 can be combined with the values of K_{SH} and K_{A} to give forward and reverse velocity constants for the reactions $\mathrm{SH} + \mathrm{B} \rightleftharpoons \mathrm{S}^- + \mathrm{A}$. These values are collected in Table 7, which includes a value for *m*-nitrophenolate previously derived from n.m.r. line broadening,[10] decreased by 9% to convert it from 26 °C to 25 °C. This correction is based upon an assumed activation energy of 15 kcal mol^{-1}. The value of $k_{\mathrm{OH}} = 4{\cdot}3 \times 10^5$ l mol^{-1} s^{-1} in Table 7 is derived from Table 3. Another estimate can be made from the n.m.r. observations in *m*-nitrophenolate buffers, but the value previously given[10] ($7{\cdot}1 \times 10^5$ l mol^{-1} s^{-1}) needs modification. In the first place it refers to 26 °C, and should be reduced by *ca.* 8% for comparison at 25 °C. In the second place, the values of $[\mathrm{OH}^-]$ on which it is based were derived from measured pH-values at 26 °C by the formula $\lg[\mathrm{OH}^-] = \mathrm{pH} - 14{\cdot}00$. A better approximation at 26 °C is $\lg[\mathrm{OH}^-] = \mathrm{pH} - 13{\cdot}933 - \lg f_{\pm}$, where $f_{\pm}$ relates to $I = 0{\cdot}1$ and has been taken as 0·76. The revised value is $k_{\mathrm{OH}} = 4{\cdot}6 \times 10^5$ l mol^{-1} s^{-1}, in reasonable agreement with the value found in the present investigation.

TABLE 7

Rates of proton-transfer reactions involving $(EtSO_2)_2CHMe$

$$\mathrm{SH} + \mathrm{B} \underset{k_{\mathrm{A}}}{\overset{k_{\mathrm{B}}}{\rightleftharpoons}} \mathrm{S}^- + \mathrm{A},\ k_{\mathrm{B}}/k_{\mathrm{A}} = K_{\mathrm{SH}}/K_{\mathrm{A}}$$

A	K_{A}	k_{B}	K_{A}
H_3O^+	55·5	$3{\cdot}5 \times 10^{-5}/55{\cdot}5$	$1{\cdot}3 \times 10^{10}$
$CH_2Cl{\cdot}CH_2{\cdot}CO_2H$	$8{\cdot}0 \times 10^{-5}$	$3{\cdot}23 \times 10^{-3}$	$9{\cdot}4 \times 10^{7}$
AcOH	$1{\cdot}75 \times 10^{-5}$	$9{\cdot}0 \times 10^{-3}$	$5{\cdot}7 \times 10^{7}$
Bu^nCO_2H	$9{\cdot}3 \times 10^{-6}$	$1{\cdot}58 \times 10^{-2}$	$5{\cdot}4 \times 10^{7}$
m-$C_6H_4(OH)NO_2$	$4{\cdot}4 \times 10^{-9}$	$6{\cdot}5 \times 10^{1}$	$1{\cdot}0 \times 10^{8}$
H_2O	$1{\cdot}8 \times 10^{-16}$	$4{\cdot}3 \times 10^{5}$	$2{\cdot}8 \times 10^{4}$

The values of k_{B} in Table 7 show the usual type of dependence upon K_{A}, and the plot of lg k_{B} against pK_{A} has an average slope of *ca.* $\beta = 0{\cdot}8$. Correspondingly, the values of k_{A} vary more slowly with K_{A}: in both series the value for *m*-nitrophenol is somewhat anomalous. The reaction between hydrogen ions and the disulphone anion appears to be diffusion-controlled. This would of course correspond to a direct proportionality between k_{B} and $1/K_{\mathrm{A}}$ in this region, but there are not enough experimental data to detect any curvature in the plot of log k_{B} against pK_{A}. Comparison of the values of k_{A} with the rate constants for reaction of the anion with bromine (Table 6) shows that incomplete scavenging of the anion by halogen should be observed, as is in fact the case.

It was hoped to study primary deuterium isotope effects for ionization by measuring the rate of bromination of $(EtSO_2)_2CDMe$ in H_2O. However, because of the incomplete scavenging of the anion by halogen, the deuterium in the unchanged disulphone becomes gradually replaced by protium, and the kinetics become complicated. Although it is possible in principle to derive ionization rates for the deuterium compound from the observed rates of bromination, this involves a laborious trial-and-error procedure and a low final accuracy. We have therefore instead derived isotope effects by comparing our present results with those previously obtained[10] for the rate of de-deuteriation of $(EtSO_2)_2CDMe$ in acetate buffers.* The results are $k_0^{\mathrm{H}}/k_0^{\mathrm{D}} = 1{\cdot}8$, $k_{\mathrm{OAc}}^{\mathrm{H}}/k_{\mathrm{OAc}}^{\mathrm{D}} = 2{\cdot}1$, $k_{\mathrm{OH}}^{\mathrm{H}}/k_{\mathrm{OH}}^{\mathrm{D}} = 3{\cdot}8$, showing the expected trend with basic strength for a substrate having a p*K* of *ca.* 15.[17] Since the activation energy for the reaction between the anion and the hydronium ion is close to zero (*cf.* Table 7) the value $k_0^{\mathrm{H}}/k_0^{\mathrm{D}} = 1{\cdot}8$ must be close to $3K_{\mathrm{e}}$, where K_{e} is the equilibrium constant for the reaction $\mathrm{SH} + \mathrm{DH_2O^+} \rightleftharpoons \mathrm{SD} + \mathrm{H_3O^+}$: the factor 3 arises from the statistical difference between DH_2O^+ and H_3O^+.

As expected, the disulphones are all considerably more acidic than the monosulphones, which are estimated[18] to have p*K*-values in the range 22—30. Our results show the expected electron-donating and -withdrawing effects of the substituents Me and Br on the acidity of the disulphones.

Table 6 shows that the disulphone anions resemble enolate anions[19] in reacting with bromine at close to the diffusion-controlled rate. $[(EtSO_2)_2CPh]^-$ shows a somewhat lower velocity constant, perhaps because the negative charge is partly delocalised into the phenyl group. The tribromide ion is throughout less reactive than molecular bromine, the average k_2'/k_2'' being 8.

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* The values given in ref. 10 for k_0^{D} have been miscalculated: the correct values are $k_0^{\mathrm{D}} = 1{\cdot}97 \times 10^{-5}$, $1{\cdot}91 \times 10^{-5}$, average $1{\cdot}94 \times 10^{-5}$ l mol^{-1} s^{-1}.

[17] D. J. Barnes and R. P. Bell, *Proc. Roy. Soc.*, 1970, *A*, **318**, 421.

[18] F. G. Bordwell, R. H. Innes, and E. C. Steiner, *J. Amer. Chem. Soc.*, 1967, **89**, 5069.

[19] R. P. Bell and K. Yates, *J. Chem. Soc.*, 1962, 2285, and earlier papers.