549. *The Kinetics of Halogen Addition to Unsaturated Compounds. Part XX. αβ-Unsaturated Sulphones.*

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The strong electron-attracting power ($-I$) of the $SO_2{\cdot}CH_3$ and SO_2Cl groups is shown by the sequence of relative rates of electrophilic chlorine addition in acetic acid, *viz.*, $CH_2{:}CH{\cdot}CO_2Et > CH_2{:}CH{\cdot}SO_2Me$ and $CHPh{:}CH{\cdot}COCl > CHPh{:}CH{\cdot}NO_2 > CHPh{:}CH{\cdot}SO_2Cl$. Bromine addition to $CH_2{:}CH{\cdot}SO_2Me$ and to $CH_2{:}CH{\cdot}SO_2Bu$ is more rapid than chlorine addition, and is catalysed considerably by lithium chloride, and more so by lithium bromide. These reactions with bromine differ from the corresponding reactions of *αβ*-unsaturated aldehydes and similar compounds, in that the former are little catalysed by acids, hydrogen bromide being less effective as a catalyst than lithium bromide. The kinetics of halogenation of $CH_2{:}CH{\cdot}SO_3H$, $CH_2{:}CH{\cdot}SO_3Na$, and $CHPh{:}CH{\cdot}SO_3Na$ are complicated by the ionisation of these compounds in acetic acid.

There do not appear to have been any previous rate measurements of halogen addition to the αβ-unsaturated sulphones, or related compounds containing a sulphonyl group. In connection with the general development of the theory of halogen addition, it was demonstrated by Ingold and Smith (*J.*, 1931, 2749) that in the action of iodine chloride on ethylenesulphonic acid, the electrophilic attack was on the α-carbon atom of the ethylene system, the product being the compound $CH_2{:}CI{\cdot}SO_3H$. Similarly, ethylenesulphonic acid on bromination in water forms the α-bromo-derivative (cf. Suter, "Organic Chemistry of Sulphur," p. 171). The occurrence of substitution in preference to addition when the attack is on a negative ion was also found by Bardwell and Rondestvedt (*J. Amer. Chem. Soc.*, 1948, **70**, 2429) for the action of bromine on the salt $CHPh{:}CH{\cdot}SO_3Na$ in aqueous solution; on the other hand, they noted addition of bromine to the un-ionised compounds, $CHPh{:}CH{\cdot}SO_3Et$ and $CHPh{:}CH{\cdot}SO_2NH_2$, in non-aqueous solvents.

Rates of reaction of chlorine and of bromine in acetic acid at 25° with various sulphones and sulphonyl derivatives have been measured, and are recorded as bimolecular coefficients (k_2, l. g.-mol.$^{-1}$ min^{-1}.).

Electrophilic Chlorine Addition.—The following rates of chlorine disappearance, whether due to addition or to substitution, are for electrophilic reactions, as is shown by the effect of structure on reactivity :

	$CH_2{:}CH{\cdot}CO_2Et$	$CH_2{:}CH{\cdot}SO_2Me$	$CH_2{:}CH{\cdot}SO_3H$	$CH_2{:}CH{\cdot}SO_3Na$
k_2	0·056	0·0001	0·11	0·73
	$CHPh{:}CH{\cdot}COCl$	$CHPh{:}CH{\cdot}NO_2$	$CHPh{:}CH{\cdot}SO_2Cl$	
k_2	5·7	0·020	0·006	

Because of the great electron attraction of the SO_2 group, the neutral compound methyl vinyl sulphone is extremely unreactive by this mechanism, reacting with chlorine more slowly than ethyl acrylate by a factor of about 600. The relatively high rate for ethylenesulphonic acid is due to the fact that this compound is ionised in acetic acid, having a conductivity between those of sulphuric and perchloric acid. The reaction is, therefore, substantially that of the anion, and the high electrophilic reactivity of unsaturated anions, previously demonstrated in aqueous solution (*J.*, 1937, 335), is now shown for acetic acid as solvent. The salt sodium ethylenesulphonate, which, owing to its conductivity being higher than that of the acid, is expected to be more dissociated, correspondingly has a higher electrophilic rate of chlorination. The SO_2Cl group is even more powerfully deactivating than SO_2Me, being considerably greater in its effect on the rate than COCl, and even more than NO_2.

Bromine Addition.—The reactions of methyl vinyl sulphone (I) and of *n*-butyl vinyl sulphone (II) have been studied in some detail, since they give a clear indication of the incursion of a new mechanism, which has not previously been demonstrable with certainty. The following table summarises the effect of catalysts (M/20) on the rate of reaction (k_2) between bromine (M/40) and the two sulphones :

	No catalyst.	H_2SO_4.	NaOAc.	LiCl.	HBr.	LiBr.	LiBr + NaOAc.
(I)	0·0011	—	—	0·023	0·045	0·091	—
(II)	0·0008	0·0015	0·0052 *	0·018	—	0·071	0·060

* Rising coefficients, due to elimination of the HBr from the reaction product.

These compounds react with bromine by a second-order mechanism (*e.g.*, for vinyl *n*-butyl sulphone: reactants M/40, $k_2 = 0{\cdot}0008$; reactants M/20, $k_2 = 0{\cdot}0008$). Lithium bromide is a powerful catalyst for the reaction, and sodium acetate slightly reduces the rate of the lithium bromide-catalysed reaction. Both lithium chloride and hydrobromic acid also catalyse the reaction, but less powerfully than lithium bromide. Sodium acetate has some catalytic power, but sulphuric acid is relatively ineffective as a catalyst.

Olefinic compounds reacting by the electrophilic mechanism show with bromine in the concentration region M/40 a third-order reaction, which is considerably (usually some 300 times) slower than the corresponding reaction with chlorine. In the present case, a different type of reaction is clearly under observation, since the reaction is of the second order, and is some ten times faster than the corresponding chlorination. Previous results (*J.*, 1949, 297) were held to suggest that for olefinic compounds of the type $CH_2{:}CHX$, where X is a group with powerful electron-withdrawing characteristics, *e.g.*, CHO, NO_2, CN, bromine addition might proceed by a nucleophilic mechanism, in which the active reagent is the trihalide ion. The present results confirm these conclusions, and, in the authors' opinion, require the intervention in the catalysed reactions, of the ions Br_3^-, Br_2Cl^-, Br_2OAc^-, of diminishing stability, as shown by the diminishing effectiveness as catalysts of lithium bromide, lithium chloride, and sodium acetate.

It is to be emphasised that the reactions at present under consideration differ from those which in previous papers we have described as acid-catalysed additions, *e.g.*, to αβ-unsaturated acids, aldehydes, ketones, nitriles, and nitro-compounds. For these compounds, in contrast with the results given in the table above, sodium acetate reduces very considerably the rate of uncatalysed bromine addition, and sulphuric acid is an efficient catalyst. A proton-transfer to a basic group in the unsaturated compound is then a fundamental stage of such reactions, as illustrated by acid-catalysis of addition to crotonaldehyde [$k_2(H_2SO_4) = ca.\ 400$; $k_3(NaOAc) = 0{\cdot}22$]. Similarly, Nozaki and Ogg (*J. Amer. Chem. Soc.*, 1942, **64**, 697, 704, 709) found for bromine addition to maleic and fumaric acids that hydrogen bromide was a much more efficient catalyst than lithium bromide.

The mechanism of the reaction described in this paper also seems to differ from those anion-catalysed reactions described by Swedlund and Robertson (*J.*, 1945, 141; 1947, 630) and by Nozaki and Ogg (*loc. cit.*) for addition to allyl chloride, vinyl bromide, and related substances. Bromine addition, under the conditions specified, appears, for the latter compounds, to be catalysed to a greater extent by lithium chloride than by lithium bromide, and this characteristic is maintained for compounds of widely different reactivity. The problem will be discussed in more detail in a following paper.

Our finding, that bromine addition to αβ-unsaturated sulphones is little catalysed by acids, suggests that the sulphone group (unlike the carbonyl, cyano-, and nitro-groups) is conjugated inefficiently with the double link, as also seems to be indicated for the ground state of the molecule (though not for excited states), both from theoretical considerations and from studies of the infra-red spectra of these compounds (Koch, *J.*, 1949, 409; Barnard, Fabian, and Koch, *ibid.*, p. 2442). The absence of conjugation between the sulphone group and the double link may also explain the fact that these compounds show little tendency to polymerise, whereas the related αβ-unsaturated aldehydes, acids, nitriles, and nitro-compounds, in which an electron-withdrawing group is certainly conjugated with the double link, readily polymerise. Nucleophilic addition of bromine to the αβ-unsaturated sulphones, therefore, appears to be caused solely by the strong inductive effect ($-I$) of the sulphonyl group, and this represents the simplest type of nucleophilic reaction which has been observed. The reaction with the bromine molecule alone is excessively slow, and in acetic acid solution may be due in part to the intervention of acetate ions. In general, all nucleophilic anions act as catalysts, according to the formulation :

$$X^-\ Br\text{-}Br \rightleftharpoons [X\text{-}Br\text{-}Br]^-;\ [X\text{-}Br\text{-}Br]^-\ CH_2{:}CH\cdot SO_2Me \longrightarrow CH_2Br\cdot CHBr\cdot SO_2Me + X^-$$

EXPERIMENTAL.

The following compounds were used in this investigation : ethylenesulphonic acid, b. p. 120°/0·8 mm., d_4^{20} 1·405, n_D^{20} 1·451, neutralisation equiv., 110 (Calc. : 108); sodium ethylenesulphonate, from the acid and an equivalent amount of sodium acetate, in acetic acid solution; phenylethanesulphonyl chloride, m. p. 78·5°; sodium phenylethylenesulphonate, recrystallised before use (for these two compounds we are indebted to Professor F. G. Bordwell, North Western University, Illinois); methyl vinyl sulphone, b. p. 115—117°/19 mm.; *n*-butyl vinyl sulphone, b. p. 135°/15 mm. (for these two compounds we are indebted to Dr. G. D. Buckley, I.C.I., Northwich, Cheshire); the methyl compound was not further purified, but the butyl compound was redistilled before use, and the previously recorded b. p. was confirmed.

All measurements were made in duplicate or triplicate, specially ground and tested stoppered bottles being used protected from light. Volatility corrections were applied to all chlorine reactions as previously described. Herewith are details of a typical rate determination :

M/40-$CH_2{:}CH{\cdot}SO_2Me$ + M/40-Br_2 + M/20-LiBr, in HOAc at 25°;
1-ml. samples titrated with N/80-$Na_2S_2O_3$.

Time (mins.)	0	50	160	230 ;	0	110	275	350
Titre (ml.)	4·02	3·58	2·93	2·63 ;	4·00	3·22	2·45	2·20

From the separate curves, $x = 20$, $t = 108$; $x = 20$, $t = 111$.

Additional results are expressed as times (minutes) for x% halogen absorption at 25° in acetic acid, unless otherwise stated :

M/40-$CH_2{:}CH{\cdot}SO_2Me$ + M/40-Br_2, $x = 10$, $t = 4050$; +M/10-H_2SO_4, $x = 10$, $t = 1580$; +M/20-LiCl, $x = 20$, $t = 435$; +M/5-LiBr, $x = 20$, $t = 123$; +M/10-LiBr, $x = 20$, $t = 110$; +M/20-LiBr, $x = 20$, $t = 110$; +M/40-LiBr, $x = 20$, $t = 129$; +M/80-LiBr, $x = 20$, $t = 173$; +M/160-LiBr, $x = 20$, $t = 276$; +M/20-LiBr + M/20-NaOAc, $x = 20$, t = 130; +M/20-HBr, $x = 20$, $t = 221$.

M/40-$CH_2{:}CH{\cdot}SO_2Bu$ + M/40-Br_2, $x = 10$, $t = 5710$; +M/20-H_2SO_4, $x = 20$, $t = 6220$; +M/20-NaOAc, $x = 20$, $t = 1920$; +M/20-LiCl, $x = 20$, $t = 555$; +M/20-LiBr, $x = 20$, $t = 141$. M/10-$CH_2{:}CH{\cdot}SO_2Bu$ + M/20-Cl_2, $x = 10$, t = 11,600; +M/20-NaOAc, $x = 10$, $t = 11{,}900$. M/20-$CH_2{:}CH{\cdot}SO_2Bu$ + M/20-Br_2, $x = 10$, $t = 2830$. From this last result and the value for reactants at M/40, $n = 2{\cdot}0$.

M/10-$CHPh{:}CH{\cdot}SO_2Cl$ + M/20-Cl_2, $x = 20$, $t = 560$.

In addition to these neutral compounds, certain compounds ionised in acetic acid solution have also been examined :

M/80-$CH_2{:}CH{\cdot}SO_3H$ + M/80-Cl_2, $x = 20$, $t = 175$; M/10-$CH_2{:}CH{\cdot}SO_3H$ + M/80-Br_2, $x = 20$, $t = 1235$; +M/20-LiCl, $x = 20$, $t = 265$; M/80-$CH_2{:}CH{\cdot}SO_3Na$ + M/80-Cl_2 + M/80-NaOAc, $x = 20$, $t = 27{\cdot}5$; M/80-$CHPh{:}CH{\cdot}SO_3Na$ + M/80-Cl_2, $x = 50$, $t = 0{\cdot}80$; M/80-$CHPh{:}CH{\cdot}SO_3Na$ + M/80-Br_2, $x = 20$, $t = 12$; +M/20-LiCl, $x = 20$, $t = 8{\cdot}75$.

The rates of bromine addition to $CH_2{:}CH{\cdot}SO_3H$ ($k_2 = 0{\cdot}002$) and the more ionised $CH_2{:}CH{\cdot}SO_3Na$ ($k_2 = 0{\cdot}006$), in comparison with the values for $CH_2{:}CH{\cdot}SO_2Me$, and the fact that the bromine rates are now slower than the chlorine rates, indicate that the nucleophilic reactions are in part obscured by electrophilic addition to the anions.

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