Kinetics of Bromine Addition to Unsaturated Sulphones

Part 2*.-Effect of Conjugation

By Sp. Shanmuganathan and V. Subramanian

Dept. of Chemistry, Pachaiyappa's College, Madras-30, India

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The rates of bromine addition to several α,β - and β,γ -unsaturated sulphones in glacial acetic acid at 30° follow second-order kinetics. β,γ -unsaturated sulphones add bromine at a slightly faster rate than the corresponding α,β -unsaturated sulphones, indicating that the electrophilic mechanism of addition is operating. The absence of significant decrease in the rate of bromine addition to an α,β -, as compared to the corresponding β,γ -unsaturated sulphone, indicates the absence of significant conjugation of the sulphonyl group with the ethylenic link in the ground state of α,β -unsaturated sulphones.

A systematic study of the addition of bromine to α,β - and β,γ -unsaturated sulphones in carbon tetrachloride was made by Baliah and Shanmuganathan.¹ The addition followed second-order kinetics, and the kinetic data were interpreted on the basis of the inductive effect of the sulphonyl group. Robertson *et al.*² have studied the kinetics of bromine addition to methyl vinyl sulphone and n-butyl vinyl sulphone and observed the effect of an anion-catalyzed nucleophilic addition, following secondorder kinetics, thus substantiating the prediction of Ingold and Ingold ³ that if the ethylenic link were polarized by a sufficiently strong electron-attracting group, an addition involving nucleophilic attack by halogen molecule might follow. Apart from the above work, no kinetic investigation of the influence of structure, solvent and catalysts on the rate and mechanism of bromine addition to unsaturated sulphones seems to have been made. Hence it was thought that such a study was necessary to understand the mechanism of bromine addition to unsaturated sulphones under varying conditions. In this paper we report the results obtained with glacial acetic acid as solvent.

EXPERIMENTAL

MATERIALS

Methyl vinyl sulphone was prepared by the method of Buckley, Charlish and Rose ⁴; allyl methyl sulphone was obtained by the method of Price and Gillis ⁵; the procedure of Smith and Davis ⁶ was employed for the preparation of phenyl vinyl sulphone and p-tolyl vinyl sulphone. Allyl phenyl sulphone and allyl p-tolyl sulphone were prepared by the method of Otto.⁷ Phenyl styryl sulphone and styryl p-tolyl sulphone were obtained by the method of Balasubramanian and Baliah.⁸ Cinnamyl phenyl sulphone, cinnamyl p-tolyl sulphone and cinnamyl methyl sulphone were prepared by the method of Balasubramanian, Baliah and Rangarajan.¹⁰ However, the methylsulphonylacetic acid used for this purpose was obtained more conveniently by oxidizing methylthioacetic acid with hydrogen peroxide in acetic acid solution.

* part 1: V. Baliah and Sp. Shanmuganathan, J. Physic. Chem., 1959, 63, 2016.

BROMINE ADDITION TO UNSATURATED SULPHONES

p-Chlorophenyl styryl sulphone was prepared from p-chlorophenylsulphonylacetic acid by the method employed for the preparation of styryl p-tolyl sulphone. p-Chlorophenylsulphonylacetic acid was prepared by the method of Gabriel¹¹ from sodium p-chlorobenzenesulphinate (obtained by reduction of p-chlorobenzenesulphonyl chloride ¹² by the method of Vogel¹³ for the preparation of sodium p-toluenesulphinate dihydrate). p-Chlorophenyl styryl sulphone was recrystallized from ethanol. Fine colourless needles melting at 83-84° were obtained. (Anal: calc. for $C_{14}H_{11}ClO_2S: C, 60.34$; H, 3.98; S, 11.5. Found: C, 60.20; H, 4.15; S, 11.31 %.)

p-Chlorophenyl cinnamyl sulphone was prepared from sodium p-chlorobenzenesulphinate by the method described by Baliah and Shanmuganathan ⁹ for the preparation of cinnamyl phenyl sulphone. Recrystallization of the product from 96 % ethanol gave colourless flakes melting at 103-104°. (Anal: calc. for C₁₅H₁₃ClO₂S: C, 61.53; H, 4.47; S, 10.95. Found: C, 61.56; H, 4.36; S, 10.78 %.) The solid sulphones were purified by repeated recrystallization and dried in vacuo. The liquid sulphones were purified by distillation under reduced pressure.

Glacial acetic acid, free from water, was used as the solvent. Bromine and acetic acid were purified in the usual manner. The kinetics of bromine addition to the unsaturated sulphones was studied at 30° at a total concentration of about M/120, and second-order rate constants were obtained.

RESULTS

The bimolecular rate constants and the $k_2(\beta,\gamma)/k_2(\alpha,\beta)$ ratios are given in table 1.

sulphone	$k_2 \times 10^2$ (mole/l.) ⁻¹ min ⁻¹	$k_2(\beta,\gamma)/k_2(\alpha,\beta)$
C ₆ H ₅ SO ₂ CH=CH ₂	3.872	5.45
C ₆ H ₅ SO ₂ CH ₂ CH=CH ₂	21.09	
C ₆ H ₅ SO ₂ CH=CHC ₆ H ₅ *	10-42	21.0
C ₆ H ₅ SO ₂ CH ₂ CH==CHC ₆ H ₅ *	219-1	
p-CH ₃ C ₆ H ₄ SO ₂ CH=CH ₂	4.143	5.12
p-CH ₃ C ₆ H ₄ SO ₂ CH ₂ CH=CH ₂	21.20	
p-CH ₃ C ₆ H ₄ SO ₂ CH==CHC ₆ H ₅ *	12.96	17.6
p-CH ₃ C ₆ H ₄ SO ₂ CH ₂ CH=CHC ₆ H ₅ *	227.5	
p-ClC ₆ H ₄ SO ₂ CH==CHC ₆ H ₅ †	31.99	5.78
p-ClC ₆ H ₄ SO ₂ CH ₂ CH=CHC ₆ H ₅ [†]	184.8	
$CH_3SO_2CH = CH_2 \ddagger$	2.360	9.66
CH ₃ SO ₂ CH ₂ CH=CH ₂	22.80	
CH ₃ SO ₂ CH=CHC ₆ H ₅ *	13.20	19.6
CH ₃ SO ₂ CH ₂ CH=CHC ₆ H ₅ *	258.2	

TABLE 1.-RATE CONSTANTS FOR THE BIMOLECULAR ADDITION OF BROMINE IN ACETIC ACID AT 30°

* trans isomer 14; † trans isomer 15

‡ Robertson et al.² report $k_2 \times 10^2 = 0.11$ l. mole⁻¹ min⁻¹ using M/40 solutions of sulphone and bromine in acetic acid at 25°. The rate constant varies considerably with initial concentrations of sulphone and bromine (cf. Robertson, Rev. Pure Appl. Chem., 1957, 7, 155). In the present investigation the concentration was ca. M/120 and it is therefore is not possible to compare the rate constants.

DISCUSSION

The rate constant for the addition of bromine to an α,β -unsaturated sulphone does not differ markedly from that for the corresponding β_{y} -unsaturated sulphone, though the former is consistently lower than the latter, whereas for unsaturated acids, β ,y-unsaturated acids add bromine about 10⁴-10⁶ times faster than the corresponding α,β -unsaturated acids.¹⁶ This indicates the absence of efficient conjugation between

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the sulphone group and the ethylenic link in the ground state of α - β -unsaturated sulphones. A similar conclusion was drawn earlier.^{2, 17-19} However, ultra-violet spectral studies ^{18, 20} show the existence of efficient conjugation between the sulphone group and the ethylenic bond in the excited state of α , β -unsaturated sulphones. The study of the conjugative effect of CH₃SO₂-group by Bordwell *et al.*^{21, 22} by determining the σ -constants for m- and p-CH₃SO₂-groups from the acid dissociation constants of benzoic acid, phenol, thiophenol and anilinium ion indicates that conjugative effects are appreciable in sulphones even in the ground state.

Infra-red ⁵, ²³ and ultra-violet ²⁴ spectra of some saturated and unsaturated sulphones indicate that the S—O bond in sulphoxides and sulphones is a semi-polar bond. Szmant and his co-workers,²⁵ from the cryoscopic behaviour of a number of sulphones in sulphuric acid, proposed that the electronic structures of the SO₂ group range from those in which both sulphur-oxygen bonds are doubly covalent to those in which both bonds are semipolar (structures I and III).



The actual structure of the sulphones is considered to be a resonance hybrid of structures I-III, the relative contribution of the individual structures depending on the structural features of a given molecule. In sulphones in which nitro groups are conjugated with the sulphone function, the negative electromeric effect of the nitro group causes an electron deficiency near the sulphone group resulting in increased contributions of structures I and II to the ground state of the molecule, whereas sulphones containing electron-donating substituents are best represented by resonance structures such as IV.



In order to interpret the rates of bromine addition to unsaturated sulphones, it is necessary to assess the relative contribution of the different resonating structures. The experimental results indicate the absence of any appreciable conjugation of the sulphonyl group with the ethylenic bond, in α,β -unsaturated sulphones. Hence it may be inferred that in these compounds contributions of structures I and II are of minor importance, though we cannot rule out the possibility of their contributions to sulphones in which a nitro group is conjugated with the sulphonyl group.

The lower rate of addition of bromine to α,β -compared to β,γ -unsaturated sulphones, is attributed to the decreased electron density at the double bond caused by the strong inductive effect (-I) of the sulphone group, superimposed on its insignificant mesomeric effect (-M). The slightly higher rate of bromine addition to β,γ -unsaturated sulphones is attributed to the weakening of the inductive effect due to the intervening methylene group. These data indicate that electron concentration at the ethylenic bond is the dominant factor controlling the addition of bromine to these sulphones.

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