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THE KINETICS OF BROMINATION OF SUBSTITUTED STYRENES. THE BROMONIUM ION MECHANISM.

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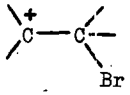
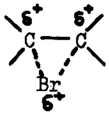
Cyclic bromonium ions were first postulated (1) as reaction intermediates to account for the highly stereospecific nature of bromination of maleic and fumaric acids (2). Subsequent attempts to obtain evidence for such intermediates in olefin additions have either been based on product stereochemistry or on studies of solvolysis reactions rather than additions. However, there is at least one case where stereospecificity of bromine addition decreases markedly with increased solvent polarity (3) and a number of others where the actual degree of stereospecificity has not been investigated. It has been pointed out (4) that few other mechanisms have been so widely accepted on the basis of such limited evidence. There are three reasonable intermediates which are consistent with the evidence from addition reactions: 1. a bromocarbonium ion I, whose rate of internal rotation is comparable with the rate of attack by external nucleophiles; 2. a cyclic bromonium ion II, in which bromine is bonded strongly to each carbon; 3. an unsymmetrical bromonium ion III, in which bromine is strongly bonded to only one carbon and the charge is shared essentially by bromine and the other carbon. Stereochemical evidence has recently (5) been obtained for an iodonium ion similar



I



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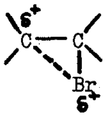


III

to III in the addition of iodine isocyanate to styrene.

We have attempted to obtain evidence of a non-stereochemical nature which would help decide between these alternatives by studying the effects of substitution on the rate of bromination of styrenes in anhydrous acetic acid. The reactions were followed by the change in bromine absorption at 450 mμ and at the concentrations necessary for spectrophotometric measurements the rate was given by

$$v = k_2\,[\text{styrene}]\,[Br_2] + k_3\,[\text{styrene}]\,[Br_2]^2$$

By means of a non-linear least squares treatment requiring the use of a computer, the separated rate constants k_2 and k_3 were obtained from each kinetic run, using equal initial reactant concentrations. As a check, these rate constants were then combined with other sets of kinetic data obtained at several different unequal initial concentrations. Using the appropriate functions from the integrated form of the above rate equation, good linear plots were obtained in every case. The rate constants k_2 for the simple bimolecular processes are listed in Table I (6).

Since the reactions are fairly rapid, only styrenes containing electron withdrawing groups were studied, styrene itself being slightly too reactive to permit accurate rate measurements by the present method. Nonetheless a plot of log k_2 against sigma for these substituents gives a very satisfactory linear free energy relationship ($r = 0.991$, $s = 0.15$) with a rho-value of -2.23. The negative sign is as expected for an electrophilic addition, but rho is much smaller numerically than the value of -4.01 observed for the analogous chlorination of cinnamic acids (7), also in acetic acid at 24°C. This is the only other available quantitative study of substituent effects on halogen addition which can be compared directly with the present case (8). The lower sensitivity of the bromine additions to substituents in the phenyl ring indicates that charge delocalization in the side chain is also important, and the rho value of -2.23 is more consistent with bromonium ion intermediates of types II or III than with a classical bromocarbonium ion. Typical rho-values for solvolysis reactions which involve carbonium ion intermediates similar to I are all in the range -4.0 to -4.7 (9). The fact that chlorination of cinnamic acids also has a rho-value in this range is more consistent with a classical chlorocarbonium ion of type I in which the importance of

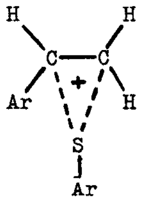
TABLE I

Second Order Rate Constants for the Bromination of Substituted Styrenes

Substituent	Temp. °C.	$10^2\ k_2$ $(\mathrm{l.mole.}^{-1}\mathrm{sec.}^{-1})$
3-fluoro-	25.4	45.5
3-chloro-	25.4	29.2
3-bromo-	25.4	27.8
3,4-dichloro-	25.4	12.3
3-nitro-	18.0	3.8
	25.4	6.6
	35.3	12.1
	44.8	19.2
4-nitro-	18.0	2.1
	25.4	3.7
	35.3	7.1
	44.8	11.8

charge delocalization into the ring is enhanced, partly because chlorine is not an effective neighbouring group and partly because of the electron-withdrawing β-carboxyl group.

Kharasch and Orr (10) have made a similar study of substituent effects on the addition of 2,4-dinitrobenzenesulfenyl chloride to styrenes, also in dry acetic acid at 25°C. Their rho-value of -2.41 is very similar to that for bromine addition. Since the addition of arylsulfenyl chlorides is believed to involve a cyclic sulfonium ion the



close similarity in sensitivity to substituent effects for the analogous bromine addition supports the idea of a cyclic bromonium ion intermediate. Further support comes from the activation parameters for these two reactions. We have measured the rates of bromination of the two nitrostyrenes at several temperatures and obtained the values of ΔH^{*} and ΔS^{*} given in Table II. Also included are the corresponding values obtained by Kharasch and Orr (10) for p-nitrostyrene.

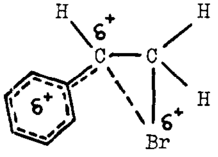
TABLE II

Activation Parameters for Nitrostyrenes

Reaction	ΔH^{*} (kcal.)	ΔS^{*} (e.u.)
m-$NO_2C_6H_4CH{=}CH_2$ + Br_2	10.5	-28.0
p-$NO_2C_6H_4CH{=}CH_2$ + Br_2	11.3	-27.0
p-$NO_2C_6H_4CH{=}CH_2$ + 2,4$(NO_2)_2C_6H_5SCl$	16.9	-26.5

The enthalpy terms are only of the same order of magnitude since the bond energies of the reactants are different, but the entropy terms are strikingly similar, suggesting comparable charge separation and solvent restriction in the two types of transition state.

Of the two cyclic intermediates, type III seems more reasonable for bromination of an unsymmetrical olefin like styrene, since part of the charge could be more effectively delocalized by the ring than by the β-carbon.



We are presently investigating the products of reaction of styrene and bromine in the presence of added nucleophile to determine the extent of attack on the α- and β-carbons.

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