

MECHANISTIC STUDY OF DEBROMINATION OF SUBSTITUTED CINNAMIC ACID DIBROMIDES WITH IODIDE ION IN AQUEOUS ETHANOL

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Abstract. The debromination of erythrocinamic acid dibromide and its *p*-chloro, *p*-nitro, *m*-nitro and *p*-methoxy analogues with iodide ion in 80% aq. ethanol was studied. The debromination was found to obey the second order kinetic law, being first order in the concentration of each reactant. The observed rate for the debromination of *p*-chlorocinnamic acid dibromide was found to be nearly the same as that of erythrocinamic acid dibromide, the rate of *p*-nitro and *m*-nitrocinnamic acid dibromides was found to be nearly half of the erythrocinamic acid dibromide in each case and the rate of *p*-methoxycinnamic acid dibromide was about 450 times faster at 15°C than that of erythrocinamic acid dibromide at 30°C. The various changes in the rates of debromination of differently substituted cinnamic acid dibromides throw light on the mechanism of the reaction in connection with the existence of the synchronous and nonsynchronous transition state during the reaction. Activation parameters are reported.

The debromination of *vic*-dibromides with iodide ion has been extensively studied, as the method has been recommended for the preparation of pure olefins. The most suitable mechanism for the debromination of *vic*-dibromides with iodide ion was proposed by Winstein, Pressman and Young¹ and was supported by Trumbull and Ibne Rasa.² According to them this reaction proceeds by an E2 type mechanism. Hine and Brader³ proposed that ethylene and propylene dibromides react by different mechanisms. According to them, in the slow step of the reaction, the iodide ion performs an S_N2 attack on one of the carbon atoms displacing a bromide ion. The bromo-iodide thus formed then decomposes directly into an olefin. Since this mechanism predicts the wrong stereochemistry for the overall reaction, Hine and Brader³ suggested that in these dibromides where the nucleophilic attack of iodide ion on carbon is sterically hindered, the E2 type mechanism of Winstein, Pressman and Young¹ is operative. The stereochemistry of the debromination of erythro- and threocinnamic acid dibromides with iodide ion in 80% acetic acid, was studied by Trumbull and Ibne Rasa.² According to them the reaction follows second order kinetics, being first order in each reactant and is *trans*-stereospecific. The erythrocinamic acid dibromide reacts 85 times faster than its threo-isomer. They suggested that E2 type mechanism operates in these debrominations.

The aim of the present investigations was to study the debromination of differently substituted cinnamic acid dibromides with iodide ion in aq. ethanol and then to predict the exact nature of the E2 type transition state and to show which one of the two bromine atoms is attacked by the iodide ion. To achieve this, variously substituted cinnamic acid dibromides were synthesised and their rates of debromination with iodide ion in 80% ethanol aq. at different temperatures were measured by following the amount of iodine liberated. The observed rate constants and the activation parameters calculated

from this data, were used to predict the exact nature of the transition state in each case.

Experimental

Materials. Inorganic salts were of analytical grade and were used without further purification. Commercially available organic compounds were purified before use either by recrystallisation, if solid, or by distillation if liquid. Solvents were also purified before use. Distilled water was further distilled from an all-glass apparatus.

Preparations. Substituted cinnamic acids were prepared by the general method⁴⁻⁷ by treating the corresponding aldehydes with malonic acid using pyridine as a catalyst, and were recrystallised from alcohol to m.p. 240–2°C for *p*-chloro-, 284–5°C for *p*-nitro- and 201–2°C for *m*-nitrocinnamic acids. *p*-Methoxycinnamic acid was prepared according to Borsche and Walter⁸ and was recrystallised from chloroform to m.p. 172–3°C.

Substituted cinnamic acid dibromides were prepared^{9,10} by the treatment of the corresponding cinnamic acids with bromine in chloroform in the case of erythrocinamic acid dibromide, and in glacial acetic acid in the case of substituted cinnamic acid dibromides. Erythrocinamic acid dibromide was recrystallised from chloroform to m.p. 204–5°C and *p*-chloro-, *p*-nitro-, *m*-nitro- and *p*-methoxycinnamic acid dibromides were recrystallised from glacial acetic acid to m.p. 193–4°C, 213–5°C, 278–9°C and 155–6°C respectively.

The formation of the dibromides was checked by IR spectra and their purity was checked by the determination of neutralisation equivalents and by the estimation of total bromine iodometrically.

Kinetic Methods. To 160 ml of 0.03M solution of each dibromide in 80% ethanol was added 40 ml aq. solution (0.24M) of potassium iodide which were previously brought to the temperature of the bath. Zero time was taken when the potassium iodide solution was added.

Aliquots of 10 ml each were removed with the help of a pipette at recorded intervals and poured into a crushed ice-water mixture to quench the reaction. Liberated iodine was quickly titrated against standard sodium thiosulphate solution using starch as an indicator. A parallel blank run was taken and the volume of sodium thiosulphate was corrected from this blank reading.

For *p*-methoxycinnamic acid dibromide, low concentrations of the reactants were used at relatively low temperature (15°C) to find the rate constant. The solutions of *p*-methoxycinnamic acid dibromide (0.015M) and of KI (0.06M) in water were prepared separately. Then for each reading, 8 ml of acid dibromide solution and 2 ml of potassium iodide solution were mixed in a flask dipped in the bath. After the required time the reaction was quenched with crushed ice-water mixture and the liberated iodine was titrated against standard sodium thiosulphate solution as before.

Results

The kinetics of each dibromide were studied at three different temperatures and each run was repeated three times. *p*-Methoxycinnamic acid dibromide was studied only at 15°C because the reaction was too fast to study at higher temperature, with two different concentrations of KI and each run was repeated three times. The second order rate constant were calculated in all the cases by the application of the following equation:

$$k_2 = \frac{2.303}{t(3a-b)} \cdot \log\left(\frac{b(a-x)}{a(b-3x)}\right)$$

where, *a*, initial concentration of the dibromide in moles per litre; *b*, initial concentration of KI in moles per litre; and *x*, the number of moles per litre of the dibromide which have reacted at time *t*.

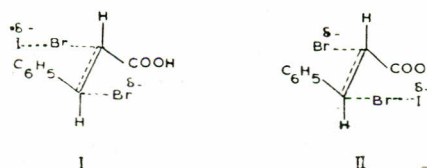
TABLE 1. SECOND ORDER RATE CONSTANTS FOR THE DEBROMINATION OF SUBSTITUTED CINNAMIC ACID DIBROMIDES WITH IODIDE ION IN 80% AQ. ETHANOL.

Dibromide	Temp (°C)	$k_2 \times 10^4$ (l/m. sec)
Erythrocinamic acid dibromide	30 ± 0.1	3.83
	40 ± 0.1	7.98
	50 ± 0.1	23.54
<i>p</i> -Chlorocinnamic acid dibromide	30 ± 0.1	4.01
	40 ± 0.1	9.64
	50 ± 0.1	24.06
<i>p</i> -Nitrocinnamic acid dibromide	40 ± 0.1	4.40
	50 ± 0.1	11.11
	60 ± 0.1	25.58
<i>m</i> -Nitrocinnamic acid dibromide	40 ± 0.1	4.60
	50 ± 0.1	10.87
	60 ± 0.1	27.20
<i>p</i> -Methoxycinnamic acid dibromide	15 ± 0.1	1785.00

$\log\left(\frac{b(a-x)}{a(b-3x)}\right)$ was plotted against time *t* and by using the slopes of the plots thus obtained, the second order rate constants were calculated for each dibromide at three different temperatures except for *p*-methoxycinnamic acid dibromide where runs were taken only at 15°C but at varying iodide ion concentrations. These rates are given in Table 1. The second order rate constants thus obtained were utilised in calculating activation parameters given in Table 2.

Discussion

As there are two bromine atoms in the cinnamic acid dibromide, either one of which may be attacked by the iodide ion, the two possible transition states are as follows:



Now the iodide ion may attack the outer bromine atom giving rise to the transition state (I) and the flow of electron density is in the same direction as in the transition state of the decarboxylative debromination of the anion of cinnamic acid dibromide.¹¹ The substituent effects in the reaction involving transition state (I) are, therefore, predicted to be similar to those expected for the decarboxylative elimination reaction. For the reaction passing through transition state (II), the flow of electron density would be in the same direction as observed in the dehydrobromination of 2-phenylethyl bromide.

The dehydrobromination reaction which involves the attack of base on a benzylic proton has been studied by other workers¹¹ and a value of +2.15 reported for ρ . In other words, the rate of dehydrobromination is greatly accelerated by electron withdrawing substituents, whereas the rate is retarded by electron donating groups. Since in the present reaction the observed substituent effects are in a direction opposite to that for dehydrobromination, the transition state (II) is ruled out for the present system.

Electron withdrawing substituents decrease the rate of the decarboxylative elimination of cinnamic acid dibromide whereas electron donating groups accelerate the rate of the reaction.¹¹ These effects seem to be identical to those observed during the present work for iodide ion induced debromination, suggesting close similarity between the two transition states. This may be taken as an evidence in support of the transition state (I).

Although the kinetic data has shown undoubtedly that the reaction is concerted, it is, however, not necessary that it may also be synchronous.^{12,13} In β -elimination reactions, the extent of bond making and bond breaking may not be the same in the transition state, as pointed out by Bunnett¹⁴ and experimentally shown by Saunders.¹⁵ Therefore,

TABLE 2. ACTIVATION PARAMETERS FOR THE DEBROMINATION OF SUBSTITUTED CINNAMIC ACID DIBROMIDES WITH IODIDE ION IN 80% AQ. ETHANOL.

Dibromides	E_a (kcal/mole)	ΔH^\ddagger (kcal/mole), ($^\circ\text{C}$)	ΔS^\ddagger (e.u.), ($^\circ\text{C}$)	ΔF^\ddagger (kcal/mole), ($^\circ\text{C}$)
Erythrocinamic acid dibromide	18.95	18.30 at 50	-15.3 at 50	23.12 at 50
<i>p</i> -Chlorocinnamic acid dibromide	18.29	17.64 at 50	-16.4 at 50	22.96 at 50
<i>p</i> -Nitrocinnamic acid dibromide	18.60	17.95 at 50	-16.9 at 50	23.42 at 50
<i>m</i> -Nitrocinnamic acid dibromide	17.28	16.63 at 50	-21.0 at 50	23.44 at 50
<i>p</i> -Methoxycinnamic acid dibromide	—	—	—	20.17 at 15

in the present system three different cases are conceivable.

The first case may involve the transition state in which the iodide ion abstracts the outer bromine atom nearly completely whereas the formation of the double bond and the departure of the benzylic bromine as Br^- is advanced to a relatively much smaller extent. Therefore, the α -carbon atom acquires a significant fraction of a unit negative charge. The electronic consequences of such a situation suggest that an electron donating substituent on the benzene ring should inductively decrease the rate of debromination by destabilising the incipient carbon ion whereas an electron withdrawing group should provide stabilisation of the incipient carbon ion and thus increase the rate of the reaction. These predictions are contrary to experimental observations made during the present investigations. It has been found that *p*-nitro-, *m*-nitro- and *p*-chloro substituents retard the rate of the reaction while the *p*-methoxy substituent accelerates the rate of debromination. Thus this transition state is rejected.

In the second case, a transition state can be considered in which the bond between the benzylic carbon and the leaving bromine atom breaks almost completely, although the double bond is developed only to a smaller extent and also the bond between α -carbon and the electrophilic bromine is broken to a relatively smaller extent. Therefore, the benzylic carbon bears a significant fraction of a unit positive charge. It would be expected that electron withdrawing groups strongly destabilise the transition state having a positive charge on the benzylic carbon whereas electron donating groups on the benzene ring would greatly stabilise such a transition state. As the *p*-nitro-, *m*-nitro- and *p*-chloro- substituents decrease the rate of the reaction only slightly, it appears that in these cases the debromination does not occur through this transition state. However, for *p*-methoxycinnamic acid dibromide, an acceleration in rate was observed relative to the unsubstituted cinnamic acid dibromide, which was much greater than that would be predicted on the basis of ρ value

as calculated from the rates of *p*-nitro-, *m*-nitro- and *p*-chlorocinnamic acid dibromides. It is, therefore, suggested that at least *p*-methoxycinnamic acid dibromide does involve this nonsynchronous transition state, presumably due to the resonance stabilisation of the positive charge on the benzylic carbon atom, by the electron pair on the methoxy oxygen.

In the third case the small effect of the electron withdrawing groups on the rate of reaction is best explained if a synchronous transition state is implicated in the debromination of these dibromides. The small decelerating effect on the rate is in accordance with the views of Bunnett¹⁴ who has pointed out that for truly synchronous transition state the substituent effect should be small.

In short our data shows that for erythrocinamic acid dibromide and its *p*-nitro-, *m*-nitro and *p*-chloro-analogues the transition state is synchronous in that the formation of the double bond at the transition state is quite significant whereas for *p*-methoxycinnamic acid dibromide the mechanism is nonsynchronous.

The observed values of the entropy of activation (Table 2) are in the range of -15 to -21 entropy units. In the ground state of debromination, one of the reactant, i.e. the iodide ion, is highly solvated whereas in the transition state some of the charge of iodide ion is distributed over the dibromide also thus decreasing the charge density on the iodide ion. Therefore, some of the solvent shell is freed in the transition state. This factor alone would increase the entropy of the system. However, there is another factor and that is, that in the transition state the two reactant molecules are linked together suffering loss of certain degree of freedom. Furthermore, an E2 type mechanism as is suggested for our reactions, requires a highly oriented state. These two factors, when combined together, cause considerable loss of entropy. It appears in our system that the gain of entropy due to decreased solvation of transition state relative to the ground state is more than counter balanced by the loss of entropy due to the highly oriented geometry of the transition state.

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