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Debromination of Cinnamic Acid Dibromides by Potassium Iodide in 80 % Aqueous Ethyl Alcohol

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Debromination of Cinnamic Acid Dibromides by Potassium Iodide in 80 % Aqueous Ethyl Alcohol (a)

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In the potassium iodide promoted debromination of the erytho cinnamic acid dibromides in 80 % aqueous ethyl alcohol at 40°, trans cinnamic acids are obtained in the satisfactory yields, which means that the reaction is a trans-stereospecific. The debromination reaction is found to be a second order, being first order in the acid dibromide and first order in the nucleophile used. The reaction rate decreases approximately two-fold as the temperature decreases from 40° to 30°. There is a small increase in the reaction as the polarity of the solvent is increased. Sodium chloride and lithium bromide exert a negative salt effect on the iodide reaction. The value of rho (ρ) for this reaction series is found to be –0,84 and the intercept ($\log k_0$) is equal to-2.81. The rho value is negative because electron withdrawing substituents decrease the rate of reaction whereas the electron donating substituents accelerate it.

INTRODUCTION

Nowadays different methods are available for the removel of the two adjacent bromine atoms from vicinal dibromides and this phenomenon is known as debromination. In earlier attempts many workers have made use of zinc as a debrominating agent.

$$CH_2BrCH_2Br + Zn \rightarrow ZnBr_2 + CH_2 = CH_2$$

but this method has one disadvantage that zinc may cause the polymerisation of the olefinic product so obtained.

Other metals like magnesium and sodium have also been very frequently used for debromination[1]. But the most excellent met-

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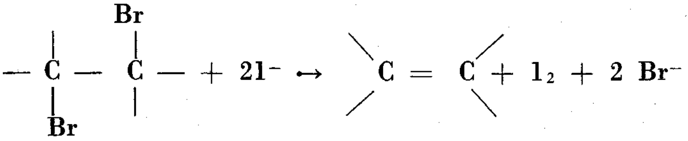
hod for debromination which has been extensively studied from kinetic and mechanistic point of view[2-6], is the reaction of vicinal dibromides with iodide ion.

$$C_6H_5CHBrCHBrCOOH + 3I^- \rightarrow I^-_3 + 2Br^- + C_6H_5CH{=}CH\,COOH$$

Erythro Cinnamic acid dibromide Trans-cinnamic acid

Winstein and his coworkers[7] have found that the second order (first order in each reactant) debromination of 2, 3-dibromobutanes by iodide ion transforms the meso-isomer to trans 2-butene and the dl-isomer to cis 2-butene, showing that the elimination goes trans.



$$\text{Rate} = k_2\,(I^-)\,(\text{dibromide})$$

Later on Slator[8] investigated the kinetics of various vicinal dibromo-and iodo bromo-compounds with iodide and thiosulphate ions. According to the valuable studies of Van Duin[9] on the reactions of many vicinal dibromides with iodide ion, the elimination is trans-stereospecific, and the cis and trans olefins were obtained from the corresponding dibromides in almost quantitative yields. Later on this idea was again strongly supported by the work of E. R. Trumbull[10].

The debromination of vicinal dibromides is important for several reasons. It is used to prepare unsaturated compounds in the pure state, by purifying them through their easily crystallisable dibromides, followed by debromination to regenerate the pure olefin. The reaction is also useful in analysing the mixture of geometrically isomeric olefins by converting the olefins into their corresponding dibromides and then measuring the rates of debromination with iodide ion. Finally in complex molecules, a double bond can be protected through bromination, the double bond can be later on regenerated easily by reaction with iodide ion. It is worth- mentioning that thiourea and thiocyanate ion have also proved almost as effective debrominating agents[11] as iodide and thiosulphate ions, for reasons of easy experimental conditions and high yields of the olefinic products. So it is seen that all those nucleophiles which have high values of Edward's polarizability parameters and low basicity constants can be used for the purpose of of debrominating vicinal dibromides. Comparatively less effective nucleophiles such as sulphide, azide and sulphite ions also give some encouraging results despite their draw-backs and weakness.

EXPERIMENTAL SECTION

The Cinnamic Acids were prepred by the Perkin[12] reaction in which a suitable benzaldehyde is condensed with the anhydride of an aliphatic carboxylic acid, in the presence of sodium salt of that acid at a high temperature of 180°. Due to the high temperatures and the failure of some aromatic aldehydes like p-dimethyl amino benzaldehyde to give corresponding acids, this reaction was modified by replacing the mono basic components by malonic acid. Some cinnamic acids were prepared by the Knoevenagel[13] modification in which malonic acid was made to condense with benzaldehydes in the presence of ammonia or primary or secondary amines, whereas other cinnamic acids were made by Doebner[14] modification of the Perkin reaction in which the malonic acid is used in the solvent pyridine and a little piperidine which acts as a catalyst. The latter methods are easier to control and give high yields. In the following table I are listed some important characteristics of the differently substituted cinnamic acids:

TABLE I

Trans Cinnamic Acids

Substituent	Equiv. Wt.	M. Pt°. C	Reaction	% Yield
H	148.2	132–133[b]	Perkin	61
m-OH	162.2	190–191[d]	Doebner	90–91
p-OH	164.2	205–206[d]	Perkin	Good
p-N $(CH_3)_2$	190.2	224–225[e]	Doebner	88
p-NO_2	193.2	286	Perkin	64
m-NO_2	193.2	203–204[b]	Perkin	63
p-CH_3	162.2	197–198[c]	Perkin	40
p-Cl	182.6	243.244[a]	Doebner	77
m-OCH_3	178.2	116–117[a]	Knoevenagel	50
p-OCH_3	178.2	166–168[b]	Knoevenagel	45

(a) Lock and Bayer, Ber; 72, 1064 (1939).
(b) E. Knoevenagel, ibid; 31. 3596 (1898).
(c) J. Dippy and J. Page, J. Chem. Soc; 357 (1938).
(d) F. Konek and E. Pascu, Ber; 51, 855 (1918).
(e) C. W. Shoppee, J. Chem. Soc; 968 (1930).

The dibromides of the cinnamic acids were prepared by bringing together the calculated quantities of the corresponding acid and bromine both dissolved in the same solvent, chloroform or acetic acid.

$$RCH{=}CHCOOH + Br_2 \rightarrow RCHBrCHBrCOOH$$

The following table 2 gives the melting points of the vicinal dibromides of the different cinnamic acids:

TABLE 2

Dibromide	Melting point, °C
Cinnamic acid dibromide	202–203[a]
M-nitro cinnamic acid dibromide	172[b]
P-chloro cinnamic acid dibromide	190–191[c]
P-hydroxy cinnamic acid dibromide	97–101[d]
P-methoxy cinnamic acid dibromide	147–148[d]
P-methyl cinnamic acid dibromide	182–183[e]
P-nitro cinnamic acid dibromide	204–205
M-hydroxy cinnamic acid dibromide	151–152
M-methoxy cinnamic acid dibromide	158
P-dimethyl amino cinnamic acid dibromide	Product not isolated

(a) E. Grovenstein and D. E. Lee, J. Am. Chem. Soc; 75, 2639 (1953).
(b) Reich and Koehler, Ber; 3732 (1913).
(c) Harry Willstaedt, ibid; 64, 2688 (1931).
(d) Eigel, ibid; 20, 2530 (1887).
(e) Th. Kröber, ibid; 23, 1033 (1890).

Kinetic Procedures:

The debromination of erythro cinnamic acid dibromides with iodide ion in the solvent 80 % aqueous ethyl alcohol was kinetically studied[17]. A typical kinetic run is described as follows.

Sodium thiosulphate solution was prepared (O, OIN) and then standardised against brominating mixture[15–16] using starch as an indicator. The normality of sodium thiosulphate solution was checked by the above method after known interval of time. In a one litre long necked flask were placed 0.89012 g. (0.01445M) of erythro cinnamic acid dibromide dissolved in 160 ml of ethyl alcohol and in 250 ml. flask were placed 7.968 g. (0.24M) of potassium iodide dissolved in 40 ml. of distilled water and both the flasks were placed separately in the constant temperature bath (thermostat) for half an hour until they attained the desired temperature of 40°. After the two solutions had attained the bath temperature, they were mixed together and shaken vigorously for a few seconds. The time of mixing these solutions was taken as zero time. 10 ml. of the mixture were removed from the reaction flask with the help of a 10 ml. pipette at the known intervals (5, 15, 25. . . . minutes) and poured into 250 ml. titration flask containing very finely crushed ice and the liberated iodine was titrated against standard solution of sodium thiosulphate taken in a 50 ml. rette using starch as an indicator.

A parallel blank run in which only 7.968 gr. (0,24M) of potassium iodide in 80 % aqueous ethyl alcohol was taken, showed no remarkable reaction because the volume of 0,0IN sodium thiosulphate solution consumed for this was zero. The same procedure was applied for the other differently substituted cinnamic acid dibromides. The process was also carried out at 30° in order to determine the temperature effect on the rate of the reaction and it was observed that for every 10° rise of the temperature, the rate of the reaction increases twofold. In other words the reaction is directly dependent on temperature and it increases with the increase of temperature as is shown in the table 3

TABLE 3

Rate Constants and Temperature Effect for the reaction

$$R\ C_6H_4CHBrCHBrCOOH + 3\,I^- \rightarrow I^-_3 + 2\,Br^- + R\ C_6H_4CH{=}CHCOOH$$

(Here R is any substituent)

Substituent, R	$K_2 X 10^{-4}$ LM^{-1} sec^{-1}	$K_2 X 10^{-4} LM^{-1} sec^{-1}$
	30± 1 °C	40± 1°C
H	3.5	8.6
m-OCH_3	1.2	2.7
p-Cl	3.1	7.64
m-NO_2	1.7	3.8
P-NO_2	1.6	3.5
P-CH_3	10.3	24
m-OH	0.88	2.6

Usually an average of 7 runs was taken but in case of p-CH_3 m-OH and p-Cl, an average of 3–4 runs was taken after necessary corrections. The rate constants for the reaction were calculated by using the following rate equation.

$$k_2 = \frac{2.303}{t(b-3a)} \log \frac{a(b-3x)}{b(a-x)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (A)$$

which is the integral form of the following differential equation:

$$\frac{dx}{dt} = k_2\ (a-x)\ (b-3x) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (B)$$

where

a= Initial concentration of acid dibromide in moles per litre

b= Initial concentration of potassium iodide in moles per litre

and x= The number of moles per litre of the acid dibromide which has reacted at time t.

The stoichiometry of the iodide- cinnamic acid dibromide reaction is substantially that given below:[18–19]

$$C_6H_5CHBrCHBrCOOH + KI \rightarrow KBr + IBr + C_6H_5CH{=}CHCOOH$$

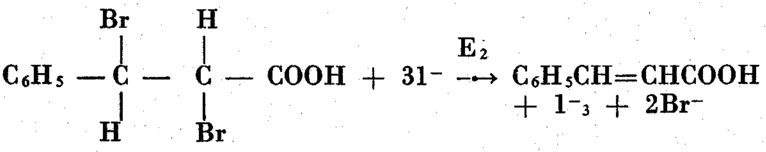
$$KI + IBr \rightarrow KBr + I_2$$

$$I_2 + KI \rightarrow KI_3\ (KI.I_2)$$

The applicability of the equation (A) depends upon several factors; (i) that initially formed IBr is rapidly transformed into I'_3 (ii) that there is sufficient iodide ion such that $b > 3x$ (iii) that the triiodide I'_3 formed is stable under the experimental conditions. The rate constants of the differently substituted cinnamic acid dibromides are given in table 3.

RESULTS AND DISCUSSION

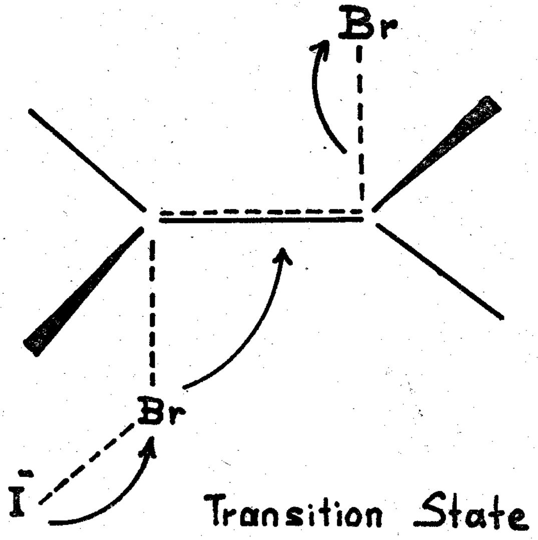
The debromination of the vicinal dibromides with iodide ion is a clear-cut second order reaction, first order in the substrate and first order in the nucleophie. The elimination so resulted is always trans-stereospecific.



$$C_6H_5-\underset{\underset{H}{|}}{\overset{\overset{Br}{|}}{C}}-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-COOH+31^- \xrightarrow{E_2} C_6H_5CH{=}CHCOOH + 1^-_3 + 2Br^-$$

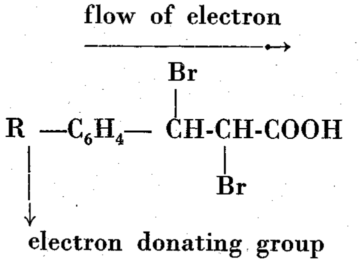
$$\text{Rate} = k_2\ [I^-]\ [\text{dibromide}]$$

The transition state for the above mechanism may be pictured as:



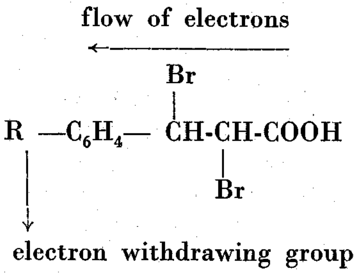
Here the nucleophile iodide ion attacks at one of the two bromine atoms donating its electron pair to the bromine atom and IBr is formed. The double bond character is developed and the second bromine atom is pushed away from the molecule with its electron pair; all this happens in a single step thus giving rise to E_2 (Elimination bimolecular). Also we see that there is a more charge separation in the transition state than in the ground state of the reaction. From the rate data for the reactions of meta and para substituted erythro cinnamic acid dibromides with iodide ion in 80 % aqueous ethanol at 40°, it is observed that the electron donating groups (p-OCH_3, p-OH, p-$(CH_3)_2$ N... etc.) when present at the para position, record a remarkable increase in the rate of the reaction; whereas the election withdrawing groups (p-NO_2, p-Cl and p-CN) show a considerable decrease in the rate of the reaction. P-methoxy, p-hydroxy and p-dimethyl amino groups increase the rate of the reaction so much that the kinetic studies were impossible under the present laboratory conditions. It is due to the direct resonance between the substituent group and the reaction centre and that is why these substituents are named by Jaffe[20] as "difficult substituents". The lone pair of electrons on the oxygen and nitrogen atoms is available to the reaction site and consequently causes the easy rupture of the carbon-halogen bond, thus the reaction proceeds in the forward direction much easily. Whereas the presence of an electron withdrawing group at the para position decreases the rate of the reaction because it wants to acquire a pair of electrons and accordingly the carbon atom holds the halogen atom more strongly to it. From table 3, we see that rate for p-nitro group is lower than that for m-nitro group because in the para position, both resonance and inductive effects are present whereas in the meta case, only inductive effect is present. This is why rate for meta nitro group is higher than that for paranitro group. Diagramatically we can show it as under:

(a)



$$R-C_6H_4-\underset{}{\overset{Br}{\overset{|}{C}}}H-\underset{\underset{Br}{|}}{C}H-COOH$$

(b)



$$R-C_6H_4-\overset{Br}{\overset{|}{C}}H-\underset{\underset{Br}{|}}{C}H-COOH$$

SOLVENT EFFECT

The rate of debromination shows a slight increase as the polarity[21] of the solvent is increased. It may be due to the reason that the solvation is more pronounced in the transition state than in the ground state due to the more charge separation in the transition state, thus compelling the reaction to go to the forward direction. Also the bromide ion gets solvated more than the more polarizable iodide ion. The solvent effect is given in the table 4.

TABLE 4

Solvent	$k_2 X 10^{-4} LM^{-1} Sec^{-1}$
80 % aqueous ethanol	8.6
70 % " "	8.9
60 % " "	10.7
50 % " "	12.49

Determination of ρ Value for the Reaction Series:

Substitution in a molecule alters its reactivity. This effect is more remarkable when the substitution is at the para position, because here the resonance interaction is more important. That is why some substituents have special sigma values (σ) when present at the para position. It was experimentally verified when we correlated our results with the Hammett[22] equation by plotting the logarithms of the rate constants of different substituents (log k) against the corresponding sigma values (σ) of these substituents. p-Cl, p-CH_3, p-NO_2 and m-NO_2 lie on the same line but m-OH and m-OCH_3 groups fall well below the curve. Now log k was taken along the Y- axis and sigma (σ) values were taken along the X-axis. The use was made of the least square method in order to determine the rho value (ρ) of this reaction series, which was found to be-0,84 and the intercept (log k_0) was equal to -2.81 as shown in the figure no. I.

The Effect of Lithium Bromide.

Observations of salt effects in debrominations have often been scattered and unsystematic.[6,9,23] According to some workers, lithium bromide depresses the rate of the reaction of iodide with meso-stilbene dibromide in acetone[24] and also LiBr depresses the rate of the reaction of bromide ion with fumaric ester dibromide in dimethyl formamide[25]. Our observations are also in harmony with their view-points but contradict the reported results of Miller and his coworkers, who have reported a small positive salt effect for similar type of debrominations. LiCl and NaCl salts were also tried and everytime a negative salt effect was observed. Table 5 gives the negative salt effects in the debromination reactions.

TABLE 5

Salt Effects in the Reactions of Cinnamic Acid Dibromide with Iodide Ion in 80 % Aqueous Ethyl Alcohol at 40±1°,

System	Added Salt	M. of salt	$K_2X10^{-4}LM^{-1}SEC^{-1}$
Erythro Cinnamic Acid	NaCl	0	8.6
Dibromide, 0,01445M		0.2M	5.9
KI, 0,24 M		0.2M	4.4
	LiCl	0.IM	5.6
	LiBr	0.005M	7.5
		0.0IM	6.9
		0.05M	6.6
		0.10M	6.03
		0.15M	5.5

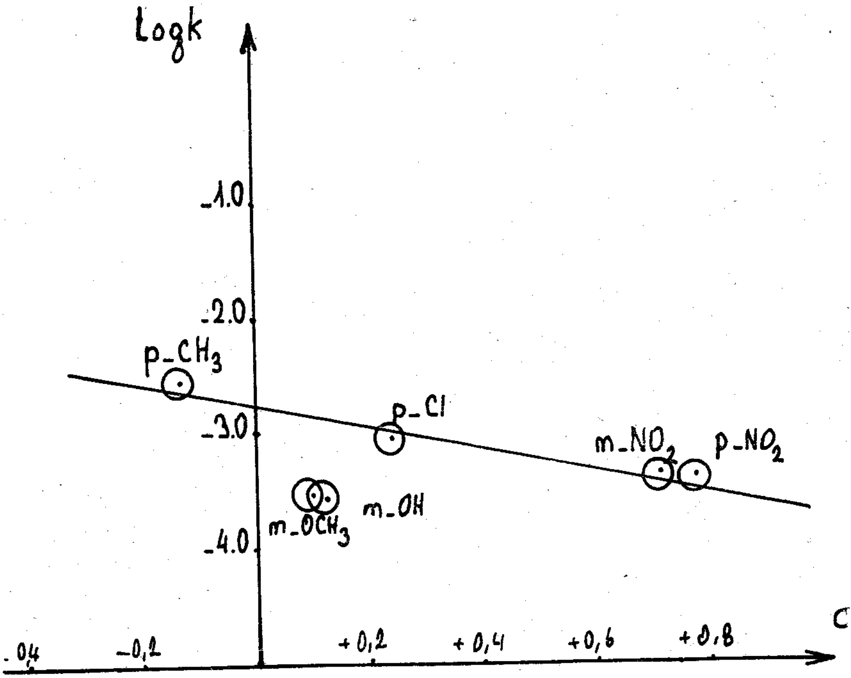


Fig. 1 : Plot between log k and the Hammett Substitution Constant σ $\log k_0 = -2.8$ $\rho = -0.84$

As the Li Br concentration increases, the rate constant for its reaction goes on decreasing. These results are within the experimental errors of the applied techniques. One reason may be due to the common ion effect. This means that there is an accumulation of bromides ions in the solution and due to their excess and their less solubility in ethyl alcohol, the whole mass does not enter into the reaction, thus causing a decrease in the rate constant of the reaction.

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ÖZET

Eritro sinamik asit dibromürlerinin % 80 etil alkol su karışımında ve 40°C de potasyum iyodür etkisiyle debrominasyon reaksiyonları incelenmiş ve sinamik asitler elverişli verimlerle elde edilmiştir ki bu reaksiyonun trans-stereospesifik olduğunu gösterir. Debrominasyon reaksiyonunun kinetik incelenmesiyle her bir reaktanta göre birinci mertebeden, dolayısiyle toplu reaksiyonun ikinci mertebeden olduğu bulunmuştur. Sıcaklığın 40°C den 30°C ye inmesiyle reaksiyon hızı yaklaşık olarak iki kat azalmaktadır. Çözücü polarlığı artınca reaksiyon hızında az bir artma gözlenmiştir; sodyum klorür ve lityum bromür bu reaksiyonda negatif tuz etkisi göstermiştir. Bu reaksiyon için ρ reaksiyon sabiti –0,84; $\log k_0 = 2.81$ olarak bulunmuştur. Elektron çekici substitüentlerin reaksiyon hızını azlttığı ve elektron verici sübstitüenlerin reaksiyon hızını artırdığı için ρ negatif bulunmuştur.

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