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Kinetics and Mechanism of Bromine Addition to Derivatives of Unsaturated Aliphatic Carboxylic Acids in Aqueous Solution

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This paper deals with the kinetics of bromine addition to unsaturated compounds in presence of added bromide ions at 22, 30, 38, 46, and 54 °C. The substrates used were acrylamide (AAm), methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), *t*-butyl acrylate (*t*BA), methacrylamide (MAAm), methyl methacrylate (MMA), ethyl methacrylate (EMA), methyl crotonate (MC), and ethyl crotonate (EC). The kinetics was followed potentiometrically. The activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$) were calculated and compared. Estimation of product ratio of bromohydrin to dibromide showed the absence of any correlation of the product formation with reactivity of the substrates. The observed parameters are discussed in relation to the proposed reaction mechanisms.

Although a number of mechanisms have been proposed for the bromination in presence of bromide ions,[1—3] controversy still persists regarding the electrophilic activity of the tribromide species.[2—8] We reinvestigated these mechanisms with the help of kinetic experiments, product analysis and salt effects.

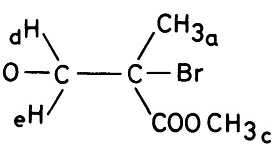
Experimental

Materials. Acrylamide,[9] methacrylamide,[10] and esters[11] were purified. Crotonates were prepared according to the reported procedures.[12] Sodium bromide was recrystallised three times from distilled water, and dehydrated at 120 °C for 5 d and kept in a vacuum desiccator over sodium hydroxide. All other inorganic chemicals used were of guaranteed reagents.

Kinetic Procedures. All the kinetic experiments were carried out by potentiometric method using Pt, Br_2/Br^-, and glass electrodes fitted into a specially fabricated reaction vessel.[13,14]

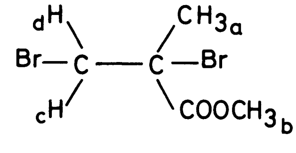
Analysis of Products. To study the regioselectivity factor mainly by ^1H NMR technique for the substrates, MMA and EMA a slight excess of bromine at various bromide concentrations was employed. After completion of the reaction potassium iodide and then sodium thiosulfate were added to remove unreacted bromine. After saturation with NaCl the products were ether extracted, dried over anhydrous sodium sulfate and then distilled off ether. The remaining liquid was used for analysis by TLC, GC, IR, and ^1H NMR studies, as the case may be.

Authentic bromohydrins were prepared[15] and separated by column chromatography. The ^1H NMR spectrum of methyl 2-bromo-3-hydroxy-2-methylpropionate (CCl_4/TMS) showed a singlet (3H, H_a) at δ 1.90, a singlet (1H, H_b) at δ 3.31,



(exchangeable with D_2O), a singlet (3H, H_c) at δ 3.85, and a pair of doublets (2H, $H_{d,e}$) one pair at δ 3.72 and another pair at δ 4.90 resulting from the diastereotropic and hence anisochronous hydrogens on the carbon bearing the hydroxyl group (J_{gem}, 11 Hz). Similarly, the ^1H NMR spectrum of methyl 3-bromo-2-hydroxy-2-methylpropionate (CCl_4/TMS) showed a characteristic singlet at δ 1.49 for 2-methyl group.

The ^1H NMR spectrum of methyl 2,3-dibromo-2-methylpropionate (CCl_4/TMS) showed a singlet (3H, H_a) at δ 2.0, a singlet (3H, H_b) at δ 3.8 and a pair of doublets (2H, $H_{c,d}$) situated at δ 3.66 and δ 4.19 resulting from the diastereotropic and hence anisochronous hydrogens on the carbon bearing the bromine (J_{gem}, 10 Hz).



Results and Discussion

In each reaction, the emf falls linearly with time (Fig. 1) showing first-order in bromine. The pseudo-first-order rate constants (k_1) were obtained from the slope of the plots.[16] The second-order rate constant, k_2(obsd),

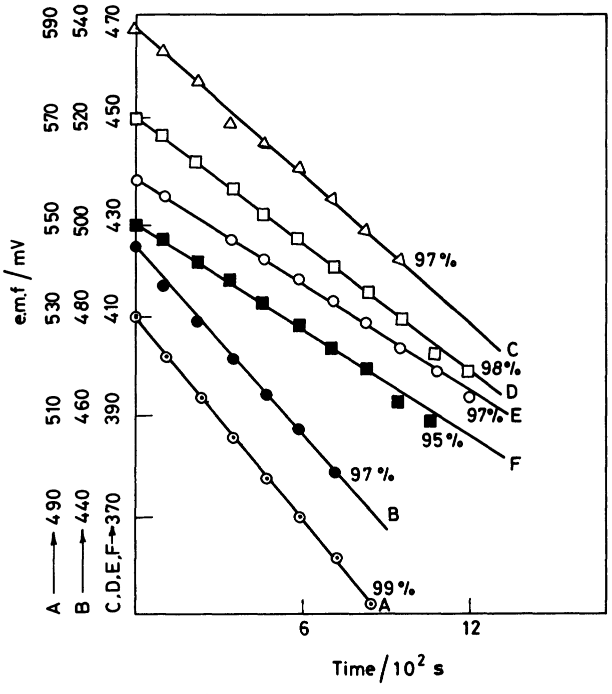


Fig. 1. Pseudo first-order plots for AAm–Br_2 reaction in water at 22 °C. The various $[Br^-]$'s/mol dm^{-3} used are A: 0.01, B: 0.05, C: 0.10, D: 0.20, E: 0.3, F: 0.40. $[AAm]=8.0\times10^{-3}$ mol dm^{-3}, $[Br_2]=6.0\times10^{-5}$ mol dm^{-3}, $[HClO_4]=1.0\times10^{-2}$ mol dm^{-3}.

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can be obtained by dividing k_1 by the substrate concentration (S). The constancy in k_2(obsd) values for AAm and MAAm for a variation of the substrate concentration by a factor of 6 indicates the first-order in substrate.

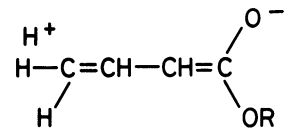
The acids like $HClO_4$, HNO_3, and H_2SO_4 had no effect on the rate constant even for a 100 times variation in concentration thus excluding the contribution of hypobromous acid to reaction. Further, the possibility of the reaction by bromine cation can be neglected in presence of such a high concentration of bromide used. It is therefore reasonable to assume that the reaction may proceed mainly by Br_2 and Br_3^- species. Hence, k_2(obsd), a composite parameter, is given by the equation:[2]

$$k_2(\text{obsd}) = (k_{Br_2} + k_{Br_3^-} K[Br^-])/(1 + K[Br^-]), \qquad (1)$$

where k_{Br_2} is the rate constant for the attack by Br_2 species and $k_{Br_3^-}$ for the Br_3^- species; and K, the tribromide formation constant for $Br_2 + Br^- \rightleftharpoons Br_3^-$. Employing least square method for the K values of Scaife and Tyrrell,[17] the values at other required temperatures have been evaluated. Values of k_{Br_2} and $k_{Br_3^-}$ were calculated from the plots of k_2(obsd) $(1+K[Br^-])$ *vs.* $[Br^-]$ (Fig. 2). Activation parameters were calculated by employing k_{Br_2} and $k_{Br_3^-}$ (Table 1). The values of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ (at 303 K) are given in Tables 2 and 3.

It is clear from the Table 2 that the $\Delta H^{\ddagger}$ values for the methyl-substituted alkenic compounds are lower than that of the corresponding unsubstituted ones. It is evident that the introduction of a methyl group, which causes electron accession to the alkenic linkage by both inductive (+I) and hyperconjugative effects, brings down the activation enthalpy and correspondingly the reaction rate of the methyl-substituted compound increases.

The methacrylic esters react faster than their isomeric crotonates (Table 2). In MMA and EMA, resonance structure-**2** facilitates the retention of the negative charge on the alkenic carbon atom whereas in alkyl crotonates, where the methyl group is present on β-carbon, resonance structure-**1** reduces the electron density on the alkenic carbon atom,



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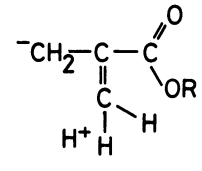

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where $R = -CH_3$ or $-C_2H_5$

When $\Delta H^{\ddagger}$ values of all these substrates were compared, it was observed that the activation enthalpy remains almost constant in each of the following sets of

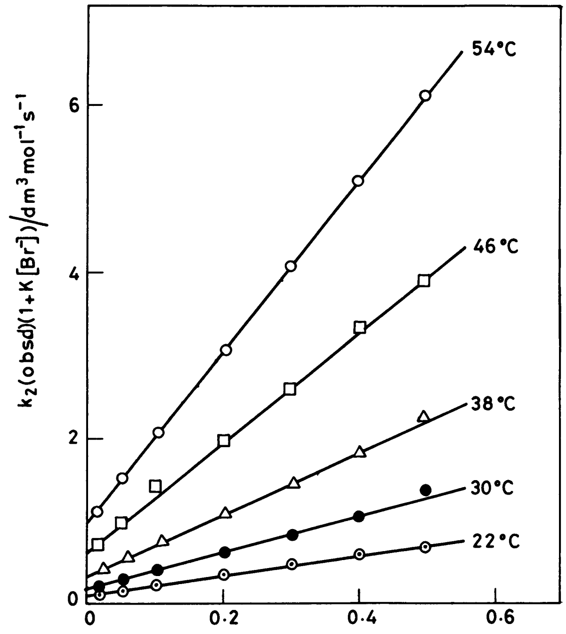


Fig. 2. Determination of k_{Br_2} and $k_{Br_3^-}$ at different temperatures for EA–Br_2 reaction in water.

Table 1. Rate constants (k_{Br_2} and $k_{Br_3^-}$) at different temperatures

Compound	22 °C		30 °C		38 °C		46 °C		54 °C		Average value of
	k_{Br_2}	$k_{Br_3^-}$	k_{Br_2}	$k_{Br_3^-}$	k_{Br_2}	$k_{Br_3^-}$	k_{Br_2}	$k_{Br_3^-}$	k_{Br_2}	$k_{Br_3^-}$	$k_{Br_2}/k_{Br_3^-}$
AAm	0.82	0.30	1.67	0.58	3.10	1.03	5.35	1.97	9.20	3.36	2.82
AAM at μ=0.5 mol dm^{-3}	1.25	0.24	2.54	0.45	4.15	0.88	8.05	1.61	13.80	2.69	5.14
MA	0.06	0.04	0.12	0.09	0.23	0.18	0.40	0.32	0.68	0.49	1.35
MA at μ=0.5 mol dm^{-3}	0.08	0.04	0.17	0.08	0.36	0.16	0.71	0.28	0.95	0.44	2.21
EA	0.10	0.07	0.17	0.13	0.33	0.25	0.66	0.46	1.00	0.77	1.36
BA	0.09	0.07	0.21	0.14	0.38	0.23	0.65	0.46	1.01	0.77	1.43
tBA	0.34	0.21	0.67	0.49	1.19	0.70	2.40	1.43	3.60	2.78	1.53
MAAm	24.50	7.85	47.00	13.55	81.50	24.50	139.00	39.26	215.00	70.32	3.30
MMA	3.10	1.44	5.80	2.67	10.60	4.62	16.80	8.16	28.00	13.60	2.15
MMA at μ=0.5 mol dm^{-3}	4.75	1.24	8.75	2.30	13.40	4.24	26.80	7.04	39.00	11.84	3.56
EMA	5.90	2.59	9.30	4.30	18.40	8.10	27.60	13.57	50.00	25.18	2.15
MC	1.38	0.55	2.83	1.06	5.15	1.96	8.95	3.26	13.70	5.24	2.63
EC	2.35	0.82	4.68	1.65	8.30	2.95	14.00	5.12	22.80	7.87	2.83

Units for k_{Br_2} and $k_{Br_3^-}$ are in $dm^3\ mol^{-1}\ s^{-1}$.

Table 2. Activation parameters for the addition of Br_2 species

Compound	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1} mol^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}
AAm	55.3	−59.0	73.3
AAm[a)]	54.9	−56.1	72.0
MA	57.0	−75.3	79.6
MA[a)]	57.8	−68.7	78.7
EA	55.3	−77.0	78.7
BA	55.7	−75.3	78.3
*t*BA	55.3	−66.1	75.3
MAAm	49.4	−49.8	64.5
MMA	49.8	−66.1	69.9
MMA[a)]	48.6	−67.0	69.1
EMA	48.6	−65.7	68.7
MC	52.8	−62.8	71.6
EC	51.5	−62.4	70.3

a) At μ=0.5 mol dm^{-3}.

Table 3. Activation parameters for the addition of Br_3^- species

Compound	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1} mol^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}
AAm	56.1	−64.9	75.8
AAm[a)]	56.1	−66.1	76.2
MA	57.0	−77.4	80.0
MA[a)]	56.1	−80.8	80.4
EA	57.0	−74.1	79.5
BA	55.6	−78.3	79.5
tBA	57.4	−62.8	76.2
MAAm	49.8	−59.4	67.4
MMA	51.5	−67.0	72.0
MMA[a)]	51.5	−68.2	72.0
EMA	51.9	−61.1	70.3
MC	51.5	−74.9	74.1
EC	51.9	−70.3	72.8

a) At μ=0.5 mol dm^{-3}.

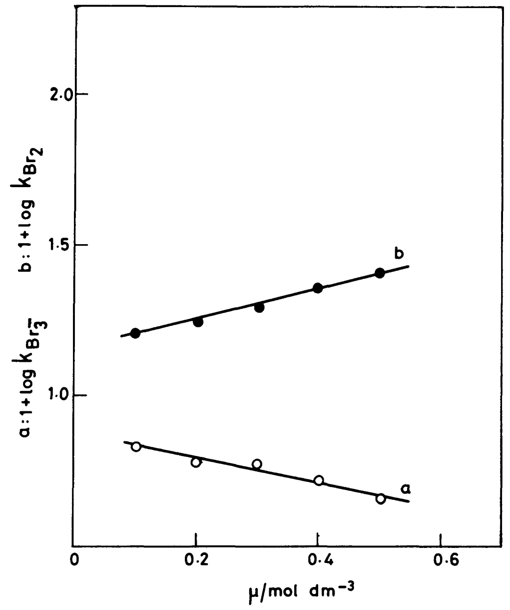


Fig. 3. Effect of ionic strength on k_{Br_2} and $k_{Br_3^-}$ for AAm-Br_2 reaction in water at 30 °C.

compounds: (i) CH_2=$CHCOR_1$; R_1=-NH_2, -OBu^t, -OBu, -OEt, -OMe, (ii) CH_2=C(Me)COR_2; R_2=-NH_2, -OEt, -OMe, and (iii) CHMe=$CHCOR_3$; R_3=-OEt, -OMe. In spite of constancy in $\Delta H^{\neq}$, the variations in the rate constant for the compounds in each set are reflected in their $\Delta S^{\neq}$ values (Table 2). That the values of $\Delta G^{\neq}$ remain more or less constant indicates a similar reaction mechanism operating in these cases.

It was observed that the value of k_{Br_2} increases in much the same manner as does k_2(obsd) with increasing ionic strength (Fig. 3). The observed increase in rate is in accord with Hughes-Ingold theory of solvent action for a reaction in which the transition state is stabilised more than the initial state.[18)] While k_{Br_2} increased with increasing ionic strength $k_{Br_3^-}$ decreased (Fig. 3). This trend was observed at all the experimental temperatures in the bromination of substrates such as AAm, MA, and MMA. However, the added $NaNO_3$ does not affect the activation enthalpy of the reaction (Table 2).

It was observed that the ratio (*Q*) of k_{Br_2} to $k_{Br_3^-}$ is greater for the extra methyl-substituted compounds. For each substrate, *Q* remains constant at all the experimental temperatures. In the present investigation, a comparison was, therefore, made between the reactivity of the substrate and the mean value of the ratio of k_{Br_2} to $k_{Br_3^-}$ obtained at all temperatures. It was observed that *Q* varied regularly in a set of compounds. For example, in compounds having the common structure CH_2=CHCOR (R= -OMe, -OEt, -OBu, -OBu^t, -NH_2), CH_2=C(Me)COR R=-OMe, -OEt, -NH_2) and CHMe=CHCOR R= -OMe, -OEt), *Q* increased with the increasing order of the reactivity of the substrate in each set.

Both by potentiometry and by titrimetry, the stoichiometry of alkene-bromine reactions was found to be 1:1. The values of product ratio, (P_r= [Bromohydrin]/[Dibromide]) were determined in order to find out the relation, if any, between the two reaction paths namely the attack by Br_2 and Br_3^- species, on the one hand, and the different products (bromohydrin and dibromide), on the other. When 1 mol of bromohydrin was formed by the attack of water, 1 mol of HBr will be liberated. The estimation of the liberated acid gave directly the amount of bromohydrin formed. The difference between the amount of bromine initially taken and the bromohydrin formed gave the amount of dibromide formed during the reaction. The product ratio of bromohydrin to dibromide did not agree with that calculated on the basis of Kanyaev's view[1)] (Table 4).

When the observed product ratio values of all the substrates studied were compared at any particular bromide concentration, it did not fall under any correlation. The values of P_r neither follow the reactivities of the substrates[1)] nor the relative reactivity ratio of Br_2 and Br_3^-.[2)] Instead of comparing different substrates for the correlation of reaction rate and the product composition, an attempt was made in the present investigation to study such effect on a single substrate itself. According to Kanyaev[1)] and Atkinson[2)]

TABLE 4. PRODUCT RATIO THE VALUES OF [BROMOHYDRIN]/[DIBROMIDE] AT VARIOUS $[Br^-]$'S AT 30 °C

$[Br^-]$	AAm		MA		EA		BA		tBA		MAAm	
mol dm^{-3}	Obsd	Calcd[a]	Obsd	Calcd[a]	Obsd	Calcd[a]	Obsd	Calcd[a]	Obsd	Calcd[a]	Obsd	Calcd[a]
0.01	—	—	18.18	8.45	48.08	8.06	9.02	9.54	7.54	8.54	131.37	21.83
0.05	—	—	—	—	4.82	1.61	2.14	1.91	2.72	1.71	9.61	4.37
0.10	4.20	1.80	2.59	0.84	1.88	0.81	1.16	0.95	1.63	0.85	3.88	2.18
0.15	—	—	—	—	—	—	0.72	0.64	1.17	0.57	2.54	1.46
0.20	1.74	0.90	1.04	0.42	1.10	0.40	0.59	0.48	0.92	0.43	2.07	1.09
0.25	—	—	—	—	—	—	0.48	0.38	0.75	0.34	1.75	0.87
0.30	1.25	0.60	0.83	0.28	0.72	0.27	0.41	0.32	0.67	0.28	—	—
0.40	1.03	0.45	0.74	0.21	0.50	0.20	—	—	—	—	—	—
0.50	0.85	0.37	0.58	0.17	0.37	0.16	—	—	—	—	—	—

a) The calculated values of [bromohydrin]/[dibromide] based on Kanyaev's view.[1)]

the ratio of bromohydrin to dibromide should increase with k_{Br_2}. To examine this fact P_r was determined by carrying out the acrylamide-bromine reaction at various concentrations of added salts like $NaNO_3$ and Na_2SO_4. Though the ratio $k_{Br_2}/k_{Br_3^-}$ increases with the increase of ionic strength by adding $NaNO_3$, P_r decreased; and the product analysis in presence of nitrate revealed that this is due to the incorporation of NO_3^- in the product. In presence of added Na_2SO_4 P_r remained almost constant (Table 5). The present investigation reveals therefore, the following facts: i) the effect of ionic strength on the ratio in presence of non-participating radicals like SO_4^{2-} clearly indicates that there exists no relation between reaction rates and product distribution; ii) P_r was unaffected much by temperature and iii) the increase of acid concentration even by 100 fold did not alter P_r.

TABLE 5. EFFECT OF $[NaNO_3]$, $[Na_2SO_4]$, AND TEMPERATURE ON THE PRODUCT RATIO, P_r=[BROMOHYDRIN]/[DIBROMIDE] AT $[Br^-]$=0.1 mol dm^{-3} FOR AAm–BROMINE REACTION

Effect of $NaNO_3$		Effect of Na_2SO_4		Effect of temperature	
$[NaNO_3]$ mol dm^{-3}	P_r	$[Na_2SO_4]$ mol dm^{-3}	P_r	Temp °C	P_r
0.0	4.18	0.0	4.10	22	4.02
0.1	3.94	0.1	4.07		
0.2	3.69	0.2	3.80	30	4.10
0.3	3.29	0.3	4.07		
0.4	3.29	0.4	4.07	38	4.18
0.5	3.24	0.5	3.80		
0.6	2.65	0.6	3.80	46	4.18
1.0	2.53	—	—		

Contrary to the earlier observations[7,15)] the present investigation shows the formation of a small amount of bromohydrin (2.3%) even at $[Br^-]=2$ mol dm^{-3} and an appreciable amount of bromohydrin at $[Br^-]=0.5$ mol dm^{-3} (Tables 4 and 6). The products are, therefore, formed by the competitive attack by bromide, water, *etc.*

The aspect of regioselectivity was considered for the bromination of MMA and EMA. The product analysis by GC has shown the formation of three products and they were identified as a dibromide and two isomeric bromohydrins by comparing the retention time with those of authentic samples. Further, NMR spectrum showed three singlets at δ 2.00, δ 1.90, and δ 1.49 for C-2 methyl protons of 2,3-dibromo-, 2-bromo-3-hydroxy-, and 3-bromo-2-hydroxy- compounds as identified by the spectra of authentic samples. The nucleophilic attack by Br^-, Br_3^-, solvent molecule, *etc.*, may be on either of the two carbon atoms of the alkenic linkage giving rise to a dibromide and isomeric bromohydrins. The results also show that the bromonium ion formed in these cases did not favour any unsymmetrical bromonium structure. The regioselectivity value[19)] is fluctuating around 0.5. In spite of unsymmetrical nature of the substrate, the intermediate behaves almost like a symmetrical one. This may probably be due to the fact that in methyl acrylates a Me(+I) group on C-2 partially compensates for the influence of ester group

TABLE 6. THE PERCENT OF VARIOUS PRODUCTS (BY NMR SPECTRAL ANALYSIS) AT DIFFERENT $[B_r^-]$'S FOR MMA, EMA-BRONINE REACTION IN AQUEOUS MEDIUM

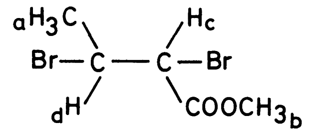
$[B_r^-]$	MMA				EMA			
mol dm^{-3}	A(%)	B(%)	C(%)	*R*(B)	A(%)	B(%)	C(%)	*R*(B)
0.01	25.48	34.08	40.44	0.46	17.86	39.29	42.85	0.48
0.05	26.09	35.87	38.04	0.49	42.17	16.87	40.96	0.29
0.10	45.71	30.00	24.29	0.55	70.37	14.81	14.81	0.50
0.20	63.58	18.17	17.10	0.50	—	—	—	—
0.30	75.83	12.92	11.25	0.54	—	—	—	—
0.40	—	—	—	—	73.21	7.15	19.65	0.27
0.50	78.22	14.22	7.56	0.65	—	—	—	—
2.00	97.72	0.91	1.37	0.40	—	—	—	—

A: 2,3-dibromo-, B: 2-bromo-3-hydroxy-, C: 3-bromo-2-hydroxy-compounds.

R: Regioselectivity factor, $R(\mathrm{B})=\dfrac{\mathrm{B}}{\mathrm{B}+\mathrm{C}}$.

(—I) on the same C-2 position. Thus the occurrence of isomeric compounds almost in equal proportion gives evidence for non-regiospecificity or non-regioselectivity in its product formation.

In order to find out the possibility of any cis-addition (*via* the addition of Br_3^- whose structure is slightly bent in the solid state[20] which may be favourable for a cis-addition) the study of stereochemistry was extended to methyl crotonate-bromine reaction in water in presence of bromide ions. The reaction mixture was fractionated by silica-gel column chromatography and a number of small fractions were collected and ^{1}H NMR spectra were taken for the first, the middle and the last fractions. The ^{1}H NMR spectrum of the dibromo compound namely the methyl 2,3-dibromobutanoate (CCl_4/TMS) showed a doublet at δ 1.92 (3H, $J=6$ Hz, H_a) a singlet at δ 3.82 (3H, H_b) and a multiplet centered at δ 4.42 (2H, $\text{H}_{\text{c,d}}$); the methyl-decoupled spectrum showed a doublet at δ 4.36 ($J=5.2$ Hz) instead of a complex multiplet present in the original spectrum. This is compared with similarly methyl-decoupled spectrum of an authentic sample of erythro-dibromo product of methyl crotonate prepared, where bromination occurs only by trans addition.[21] Comparison shows that the dibromo compound obtained in the bromination in aqueous medium in the present case is also an erythro isomer (trans addition). Spectra for other fractions of dibromo compounds were also found to be similar for protons at C-2 and C-3 positions ($J=5.2$ Hz).[22] Absence of threo isomer completely rules out a cis-addition. The attempts to detect the presence of π-complex, if any, in water by UV spectrophotometric method were not successful. However, interactions between alkene and bromine leading to a π-complex cannot be ruled out and π-complex may be small to be detected spectrophotometrically. From a kinetic point of view, however, such a small concentration is quite sufficient, as the π-complex is formed in a fast equilibrium step. The absence of spectrophotometric evidence for alkene-bromine π-complex could not be considered as a total negative evidence for its formation. Dewar *et al.*[23] have also stressed this point.

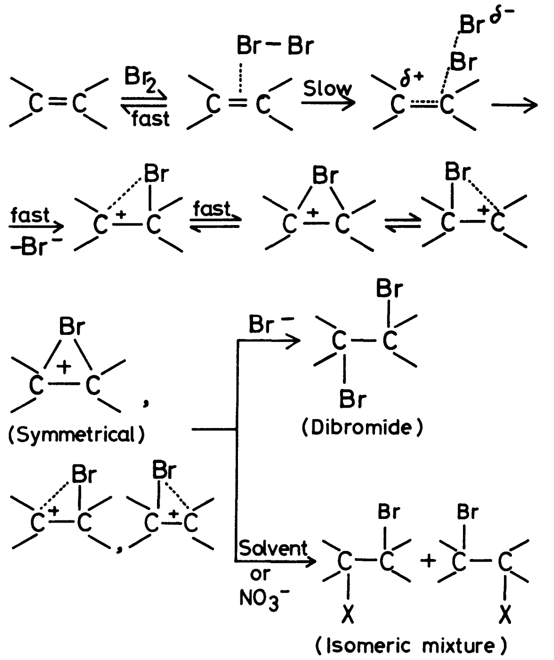


Reaction Mechanism. The experimental results show that the contribution to the reaction by Br_2 and Br_3^-, species is quite appreciable. The fact that the experimental values of $k_2(\text{obsd})\,(1+K[\text{Br}^-])$ and the calculated values, $(k_{\text{Br}_2}+k_{\text{Br}_3^-}\,K[\text{Br}^-])$ are in total agreement with each other indicates that bromination, under the experimental conditions, occurs mainly by Br_2 and Br_3^- species. As a representative example, the observed and calculated values of $k_2(\text{obsd})\,(1+K[\text{Br}^-])$ for the bromination of AAm in water at 22 °C are provided in Table 7. In the following two sections are discussed two mechanisms one for the reaction between alkene and Br_2 species and the other for alkene and Br_3^- species.

TABLE 7. THE OBSERVED AND CALCULATED VALUES OF $k_2(\text{obsd})\,(1+K[\text{Br}^-])$ FOR THE BROMINATION OF AAm IN WATER AT 22 °C

$[\text{Br}^-]$/mol dm^{-3}	0.01	0.05	0.10	0.20	0.30	0.40	0.50
Obsd	1.73	2.15	2.64	3.30	4.44	5.15	6.15
Calcd	1.76	2.13	2.59	3.52	4.43	5.37	6.06

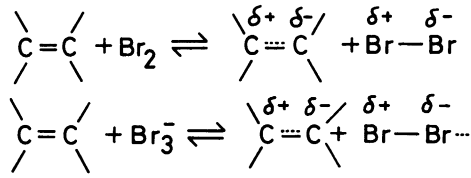
Mechanism of the Bromination of Alkenes by Br_2 Species. Based on the effect of ionic strength on k_{Br_2} and on the formation of exclusive stereospecific but non-regiospecific, anti-addition products and in the light of the points discussed, the kinetic scheme for the bromination of alkene by Br_2 species in aqueous medium may be represented as follows:



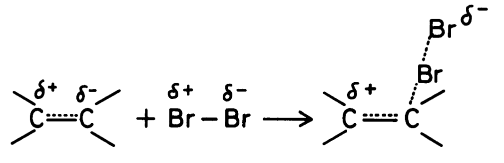
Thus it may be formulated that molecular bromine first attaches to double bond of alkenic compounds in a fast equilibrium step to form an intermediate complex, which then decomposes to give a carbonium ion. The carbonium ion rearranges to a bromonium ion which by subsequent fast steps readily forms dibromide, bromohydrin or bromo nitrates by the reaction with bromide, water molecule or with nitrate ions, respectively.

Mechanism of the Bromination of Alkenes by Br_3^-, Species. A number of mechanisms for the bromination of alkenes by Br_3^- species have been proposed by earlier workers.[2–8] The data collected on the rate constants correspond well with the following rate expression: $\text{rate}=k_{\text{Br}_3^-}[\text{S}][\text{Br}_3^-]$. Alternatively, the rate expression can also be represented as, $\text{rate}=k_{\text{Br}^-}[\text{S}][\text{Br}_2][\text{Br}^-]$. These two rate expressions cannot be distinguished kinetically. While the former represents the addition of Br_3^- by a bimolecular mechanism, the latter represents Br^- catalysed termolecular mechanism.

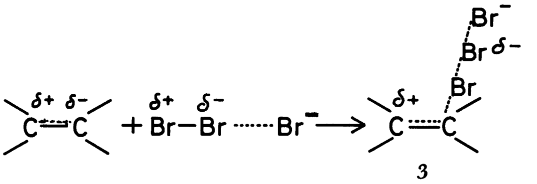
A possible mechanism for Br_3^- addition is envisaged in the present investigation for the first time on the basis of experimental kinetic parameters and the product analysis. Irrespective of whether the bromination is between alkene and Br_2 or between alkene and Br_3^-, the value of $\Delta H^{\ne}$ is observed to be the same in either case for a given substrate. There is thus every reason to believe that the approach of Br$_2$ or Br$_3^-$ towards alkene should be quite similar. Since the structure of Br$_3^-$ species even in solid state was predicted to be linear[20] and unsymmetrical[24] and carrying a single negative charge and since the Br$_3^-$ structure in solution is even more uncertain, the approach to alkene by both Br$_2$ and Br$_3^-$ species (in keeping with more or less same $\Delta H^{\neq}$ obtained in either case) can be unequivocally depicted as



It should be stressed at this point that the ionic strength effect is to increase the rate ($k_{\mathrm{Br_2}}$) of alkene–Br$_2$ species reaction while decreasing that of alkene–Br$_3^-$ species. As already stated the rate enhancement in the former case is due to the formation of polar or ionic intermediate from neutral molecules and can be represented in all probability as



On the other hand, the decrease in rate ($k_{\mathrm{Br_3^-}}$) with μ found in the reaction between alkene and Br$_3^-$ species may be attributed to the less polar character of the transition state as compared to the reactants, a neutral molecule and an ionic species, and may be represented as follows:



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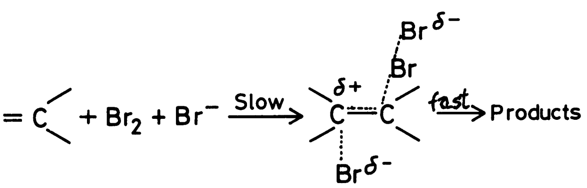
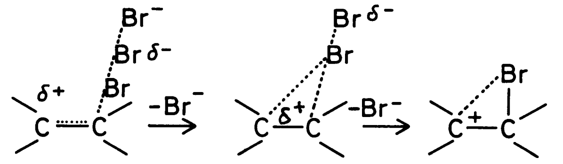
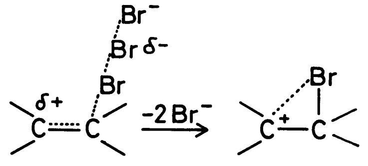
Similarly, a less-charged activated complex can be equivally possible in Br$^-$-catalysed mechanism too, as shown below



Further, the Br$^-$-catalysed reaction is stereospecific whereas structure **3** formed by Br$_3^-$ can still lead to non-stereospecific products. However, in the present study, the product analysis made on the reaction between methyl crotonate and bromine showed a nil contribution of threo product. To account for this stereospecificity it is necessary to propose bromonium ion structure in Br$_3^-$-addition also. Hence the activated complex (Structure **3**) giving rise to a bromonium ion should involve breakage of two Br–Br bonds in contrast to the addition by Br$_2$ species where only one bond needs to be broken. Thus the breakage of two Br–Br bonds may take place one at a time as in



or the two Br–Br bonds may break simultaneously as in



Futhermore, this bromonium ion must be either symmetrical or equilibrium mixture of two unsymmetrical forms in accordance with regioselectivity factor around 0.5. Otherwise, a single unsymmetrical structure formed by Br$_3^-$ alone (and not by Br$_2$) might result in a regioselective products. The participation by Br$_3^-$ as an electrophile is proved further in the present study as follows.

Substitution of a methyl group at the alkenic carbon increases both $k_{\mathrm{Br_2}}$ and $k_{\mathrm{Br_3^-}}$. The methyl substitution accordingly, decreases activation enthalpy in either case. If we assume that $k_{\mathrm{Br_3^-}}$ is especially due to Br$^-$-catalysed reaction, then the product formed by this step should be only dibromide. And the solvent incorporated and salt (NO$_3^-$) incorporated products should then result from bromonium ion formed due to addition of Br$_2$ species. It is evident that if Kanyaev's view[1] namely bromohydrines are exclusively formed by the addition to alkene by Br$_2$ species and dibromide by Br$_3^-$ species, is correct, then one can expect that both the observed and calculated product ratios, [bromohydrin]/[dibromide], should agree with each other. As already pointed out, the bromonium ion formation during the course of the reaction seems inevitable to explain the observed 'stereospecific *cum* non-regioselective' products. Also the dibromide formation in this situation is warranted. If this were so, the amount of bromohydrin formed should be actually lower than that predicted by calculation. This means that the observed ratio of bromohydrin to dibromide should be less than the calculated value. This expectation arises from the assumption that $k_{\mathrm{Br_3^-}}$ is due to Br$^-$ catalysis. However, the experimental P_r has been found to be greater than the calculated one (Table 4). It is quite clear that the formation of more of bromohydrin than the expected amount should have resulted only from Br$_3^-$-addition. So the observation that bromohydrin is formed in rather large quantity than dibromide, cannot be explained by Br$^-$-catalysed mechanism alone. All the foregoing arguments strongly suggest that Br$_3^-$ species acts as an electrophile. Otherwise either nucleophilic attack by Br$_3^-$ or bromide-catalysed reaction should have resulted only in a dibromide compound, which is not found to be the case.

In conclusion, the addition of bromine to alkenes in aqueous medium in presence of bromide in the present investigation is stereospecific and non-regioselective antiaddition. Though $k_{\mathrm{Br_3^-}}$ is a composite term, in the present set of substrates, electrophilic-bimolecular addition by Br_3^- species is more favourable. The activated complex formed by Br_3^- species is less polar than the one formed from the alkene–Br_2 species. The formation of activated complex is the slow step of the bromination. Besides dibromide, other products such as bromohydrins and bromonitrates too are formed due to incorporation of solvent and added salts like nitrates.

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