34. *The Kinetics of Halogen Addition to Unsaturated Compounds. Part V. The αβ-Unsaturated Acids and Hydrogen Bromide Catalysis.*

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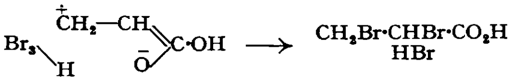
ββ-Dimethylacrylic acid unites with bromine in acetic acid solution by a rapid termolecular reaction, which is only slightly accelerated by hydrogen bromide. Unsaturated acids in which electronic regression from the ethylene system is considerable show autocatalysed addition of bromine and are strongly catalysed by hydrogen bromide. These reactions by means of HBr_3 are nucleophilic, as the rates for related compounds, *e.g.*, acrylic and crotonic, maleic and citraconic, fumaric and mesaconic, glutaconic and β-methylglutaconic acids, are in the reverse order to the electrophilic rates of bromine addition in aqueous acetic acid. Benzylidenemalonic acid gives, relatively to cinnamic acid, a high rate of HBr_3 addition in acetic acid, and a low rate of bromine addition in aqueous acetic acid. Phenyl- and *n*-propyl-propiolic acids have also been investigated.

The fact that αβ-olefinic acids may differ fundamentally with regard to addition of bromine in the presence of hydrogen bromide was pointed out in Part I (J., 1937, 335). It was found that addition of bromine to acrylic acid in acetic acid solution was strongly accelerated by hydrogen bromide, whereas *cis*-cinnamic acid under the same conditions showed no such catalysis. The acid-catalysed reaction with acrylic acid further differed from normal bromine addition in that its rate was decreased on addition of water to the solvent. Subsequently, Anantakrishnan and Venkataraman (J., 1939, 224) pointed out that crotonic and tiglic acids also showed marked catalysis by hydrogen bromide, and they proposed a chain mechanism involving the complex A, hydrogen bromide, and bromine activated by the acid. Nozaki and Ogg (*J. Amer. Chem. Soc.*, 1942, 68, 697) have investigated hydrogen bromide and lithium bromide catalysed addition of bromine to maleic and fumaric acids in acetic acid solution, and conclude that these reactions proceed by a termolecular reaction between A, Br_2, and Br^-.

In this investigation a number of αβ-olefinic acids have been examined, and it appears that a theory of nucleophilic HBr_3 addition, with elimination of hydrogen bromide, offers a reasonable explanation of catalysis by the latter. There is an analogy with the αβ-olefinic aldehydes, which also show bromine addition strongly catalysed by the acid, but the change in rate of HBr_3 addition from the one type of compound to the other may be considerable; *e.g.*, crotonaldehyde reacts at 10^5 times the rate of crotonic acid, and this corresponds with the activity of these compounds to other nucleophilic reagents. With reference to the mechanism of the reaction, 1 : 4-addition of HBr_3, analogous to 1 : 4-addition of hydrogen cyanide to the corresponding aldehydes, is proposed to represent the initial stage. The reaction between acrylic acid and HBr_3 could therefore be formulated as



$$\mathrm{Br_3}\ \mathrm{H}\ \overset{+}{\mathrm{C}}\mathrm{H_2{-}CH{=}C{\cdot}OH}\ \overset{-}{\mathrm{O}} \longrightarrow \begin{array}{c}\mathrm{CH_2Br{\cdot}CHBr{\cdot}CO_2H}\\ \mathrm{HBr}\end{array}$$

The attack is upon the positive β-carbon atom of the system, so the reaction is nucleophilic in type. The rates of related compounds should therefore decrease on replacing the hydrogen atoms of the β-carbon atom by electron-contributing groups, and consequently be in the reverse order of that found for electrophilic bromine addition. This is confirmed by the experimental results. If the relative rates of the HBr_3 reaction are taken as the difference between the rates of bromine addition with and without the same small amount of added hydrogen bromide, the order is $CH_2{:}CH{\cdot}CO_2H > CHMe{:}CH{\cdot}CO_2H > CMe_2{:}CH{\cdot}CO_2H$, and this is the reverse of the electrophilic rate of bromine addition in aqueous acetic acid (or of chlorine addition in acetic acid).

A further similarity between αβ-unsaturated acids and aldehydes is that bromine addition in acetic acid is accelerated by added acids, *e.g.*, sulphuric acid, whereas allyl compounds such as the benzoate show no such catalysis. The possibility that bromine can act under certain conditions as a nucleophilic reagent is being examined in an investigation on the αβ-unsaturated aldehydes.

The kinetics of bromine addition to an αβ-olefinic acid may vary with the nature of the compound and also, for a given compound, with the concentration. In ββ-dimethylacrylic acid the inductive effect of the two methyl groups favours electrophilic addition, and the characteristic third-order reaction holds with small deviations over the concentration range investigated. Crotonic acid, in which electronic accession to the ethylenic system is less, reacts more slowly, adding bromine at an approximately third-order rate at the concentration region 0·1M; at lower concentrations the reaction merges into an autocatalysed reaction, with its disturbing effect on the reaction order. The following are the times for 10% reaction and reaction orders for bromine addition to ββ-dimethylacrylic acid in acetic acid at 24°:

	M/20.		M/40.		M/80.		M/160.
Time, mins., for $x = 10$	3·05		13·0		56·5		240
n		3·1		3·1		3·1	

The kinetics of the hydrogen bromide-catalysed reactions in acetic acid are complex, and the interpretation uncertain, for the reaction $\mathrm{HBr + Br_2 \rightleftharpoons HBr_3}$ appears to show a variation in K with the concentration (Jones, J., 1911, **99**, 402). The rates for ββ-dimethylacrylic and crotonic acids with various amounts of hydrogen bromide show the characteristic differences between these two types of compound. For M/80-acid in acetic acid at 24°:

$[\mathrm{HBr}]/[\mathrm{Br_2}]$.	0·0.	0·25.	0·5.	1.	2.	4.
$\mathrm{CMe_2{:}CH{\cdot}CO_2H}$, k_2 ($x = 10$)	0·15	0·15	0·16	0·18	0·18	0·18
$\mathrm{CHMe{:}CH{\cdot}CO_2H}$, k_2 ($x = 10$)	<0·006	0·018	0·030	0·051	0·051	0·051

ββ-Dimethylacrylic acid, which has a high electrophilic rate for bromine addition, differs from crotonic and acrylic acids in that the rate is only slightly accelerated by hydrogen bromide. Values with allyl compounds (Part VI, following paper) indicate that $\mathrm{HBr_3}$ may act as an electrophilic reagent. This also appears probable from a consideration of the following relative rates.

Bimolecular coefficients in acetic acid at 24°.

	$\mathrm{CMe_2{:}CH{\cdot}CO_2H}$.	$\mathrm{CHMe{:}CH{\cdot}CO_2H}$.	$\mathrm{CH_2{:}CH{\cdot}CO_2H}$.
k_2 ($\mathrm{Cl_2}$)	51	0·62	0·017
k_2 ($\mathrm{HBr_3}$)	0·18	0·051	0·42

Addition of chlorine is in the normal electrophilic order; that of $\mathrm{HBr_3}$ is in the nucleophilic order for acrylic and crotonic acids, but for dimethylacrylic acid there is a reversal in rate. The conclusion is that the mechanism changes in this series, and the high rate for dimethylacrylic acid with $\mathrm{HBr_3}$ is due to electrophilic addition.

The dicarboxylic unsaturated acids show marked catalysis by hydrogen bromide of bromine addition. The values in the presence of the bromide are shown in the following table as bimolecular rates for $x = 10$ and M/80-solutions at 24°.

$[\mathrm{HBr}]/[\mathrm{Br_2}]$.	1.	4.	$[\mathrm{HBr}]/[\mathrm{Br_2}]$.	1.	4.
Maleic acid	0·27	0·56	Glutaconic acid	0·090	0·44
Fumaric acid	0·019	0·047	β-Methylglutaconic acid	0·015	0·049
Citraconic acid	0·0054	0·012	Benzylidenemalonic acid	26	26
Mesaconic acid	0·014	0·025			

In $\mathrm{HBr_3}$ addition a nucleophilic mechanism operates, for the rates for related compounds are in the reverse order to the velocities of bromine addition in aqueous acetic acid, *i.e.*, under conditions favourable for the electrophilic reaction. This is evident from the following comparison, for which the rates with 4 mols. of hydrogen bromide are taken as a relative measure of $\mathrm{HBr_3}$ addition.

Relative rates of nucleophilic and electrophilic addition.

$\mathrm{HBr_3}$ in HOAc.	$\mathrm{Br_2}$ in HOAc (25%) + $\mathrm{H_2O}$ (75%).
Maleic : Citraconic = 45 : 1	Citraconic : Maleic = 15 : 1
Fumaric : Mesaconic = 2 : 1	Mesaconic : Fumaric = 15 : 1
Glutaconic : β-Methylglutaconic = 9 : 1	β-Methylglutaconic : Glutaconic = 45 : 1

In benzylidenemalonic acid the combined electronic pull of the two carboxyl groups favours the nucleophilic reaction and is unfavourable to the electrophilic reaction. This compound gives in acetic acid a high rate with $\mathrm{HBr_3}$, about 40 times as rapid as cinnamic acid, whereas its electrophilic rate of bromine addition in 25% aqueous acetic acid is low, being about 100 times slower than that of cinnamic acid.

Phenylpropiolic acid in acetic acid solution at 24° shows third-order kinetics:

	M/10.		M/20.		M/40.		M/80.
Time, mins., for $x = 20$	55		240		980		3750
n		3·1		3·0		2·9	

At each concentration the termolecular coefficients remain constant over the first 60% of the reaction:

x	10	20	30	40	50	60
k_3 (M/40)	1·9	1·9	1·9	1·9	2·0	2·0

As hydrogen bromide is a catalyst, this constancy indicates it is not formed during the reaction, and this was confirmed by testing the reaction mixture. The catalytic effect of hydrogen bromide is shown by the following initial rates in acetic acid at 24°, calculated as bimolecular coefficients;

[HBr]/Br$_2$	0	0·25	0·5	1	4	6
k_2, M/80 ($x = 10$)	0·0053	0·012	0·018	0·030	0·032	0·032

With addition of water to the acetic acid, the rate of bromine addition increases in the manner characteristic of the electrophilic addition, and the reaction becomes bimolecular.

n-Propylpropiolic acid adds bromine rapidly, the initial rate at M/20 being 300 times that of phenylpropiolic acid, but this falls off considerably on reducing the concentration; in acetic acid at 24° :

	M/20.	M/40.	M/80.
Time, mins. ($x = 5$)	0·35	2·5	100

At each concentration there is a deceleration as the reaction proceeds, becoming more pronounced at lower concentrations, and less than 1 mol. of bromine reacts with 1 mol. of the propylpropiolic acid. These results are interpreted as indicating a chain mechanism, with partial polymerisation to less unsaturated products. Addition of water to the solvent reduces the rate and makes the reaction proceed normally.

This investigation provides data for the comparison of the velocity of bromine addition to related olefinic and acetylenic compounds :

	cis-CHPh⁚CH·CO$_2$H.	CPh⋮C·CO$_2$H.
k_3 (HOAc), 24°	21	2·0
	trans-CHMe⁚CH·CO$_2$Me.*	CEt⋮C·CO$_2$Me.
k_2 (50% H$_2$O/HOAc), 24°	2·4	0·035

* Methyl- and ethyl-acrylic acids have approximately the same rate of bromine addition in carbon tetrachloride solution (Sudborough and Thomas, J., 1910, **97**, 719).

It is apparent that acetylenic compounds add halogen by the electrophilic mechanism less rapidly than the corresponding olefinic compounds. This effect appears to be general and is being further investigated.

EXPERIMENTAL.

The technique is as previously described. The following compounds were used: crotonic acid, m. p. 71·5°; ββ-dimethylacrylic acid, m. p. 70°; maleic acid, m. p. 128·5°; fumaric acid, m. p. 285°; citraconic acid, m. p. 90°; glutaconic acid, m. p. 135°; β-methylglutaconic acid, m. p. 147°; phenylpropiolic acid, m. p. 146°; *n*-propylpropiolic acid, m. p. 24°; methyl ethylpropiolate, b. p. 47°/10 mm. We are indebted to Professor J. Packer, Christchurch, N.Z., for the specimens of glutaconic acids, and to Dr. G. F. Henion, Notre Dame, Indiana, for the alkylpropiolic acid compounds.

Details of a typical experiment are:

M/20-*Dimethylacrylic acid and* M/20-*bromine in acetic acid at* 24°.

Reaction mixture, 10 ml.; 1-ml. samples titrated with 0·05N-Na$_2$S$_2$O$_3$.

Time, mins.	0	1·95	3·95	5·90	8·65
Titre, ml.	2·00	1·88	1·72	1·64	1·49

From curve: $x = 10$, $t = 3·0$; $x = 20$, $t = 6·6$. Second expt.: $x = 10$, $t = 3·1$; $x = 20$, $t = 6·8$.

The times for this compound at other concentrations have been given on p. 130.

For experiments with added hydrogen bromide, portions of a concentrated solution of hydrogen bromide (standardised at intervals) were added. The times for 4 mols. of hydrogen bromide have been given; those for $x = 10$ for M/80-acid and M/80-bromine in acetic acid at 24° are: ββ-dimethylacrylic, $t = 50$; crotonic, $t = 175$; maleic, $t = 15$; fumaric, $t = 190$; citraconic, $t = 700$; mesaconic, $t = 350$; glutaconic, $t = 20$; β-methylglutaconic, $t = 180$; benzylidenemalonic, $t = 0·48$.

Reactions with sulphuric acid showed the following ratios to uncatalysed reactions. For M/80-crotonic acid + M/80-bromine: [H$_2$SO$_4$], 1·5; 4[H$_2$SO$_4$], 3·1. For M/80-allyl benzoate + M/80-bromine: 2[H$_2$SO$_4$], 1·0.

The times in aqueous acetic acid (25% acid) at 24° were as follows (M/80-reactants, $x = 10$): maleic, $t = 36$; fumaric, $t = 80$; citraconic, $t = 2·3$; mesaconic, $t = 6·4$; glutaconic, t ($x = 50$) $= 13·7$; β-methylglutaconic, t ($x = 50$) $= 0·30$; benzylidenemalonic (in 75% acid), t ($x = 10$) $= 8·5$.

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