

235. *The Kinetics of Halogen Addition to Unsaturated Compounds. Part VIII.
 $\alpha\beta$ -Unsaturated Aldehydes.*

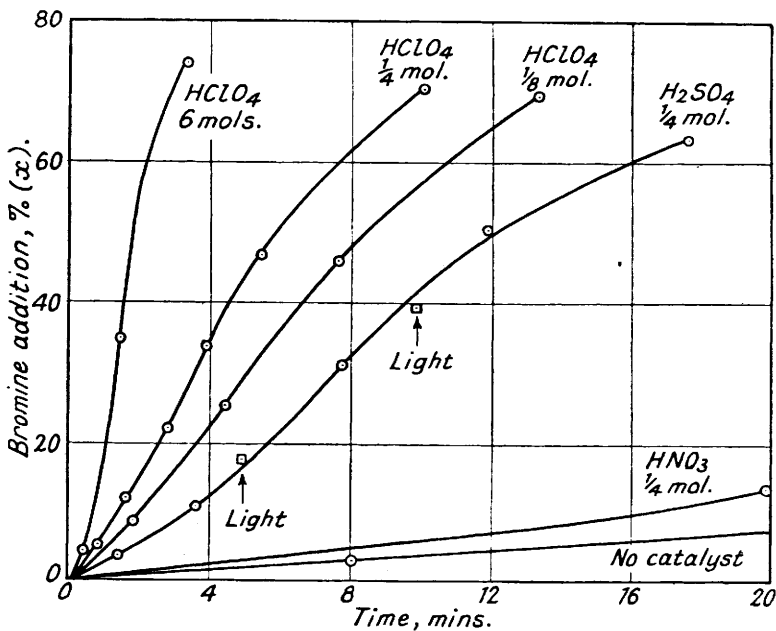
By P. B. D. DE LA MARE and P. W. ROBERTSON.

Acid-catalysed addition of chlorine and bromine to cinnamaldehyde, crotonaldehyde, and acraldehyde in acetic acid solution shows reaction kinetics and relative velocities indicating a nucleophilic mechanism. Although perchloric, sulphuric, and nitric acids have catalytic activities in the order of their acid strengths, yet hydrobromic and hydrochloric acid show an enhanced activity, due to HBr_2 (and possibly HClBr_2 and HCl_2) formation. The addition of water to the acetic acid solution reduces the nucleophilic rate; with sufficient water

the electrophilic reaction is established, and further dilution with water increases the rate. The addition of sodium acetate to the acetic acid solution eliminates the acid-catalysed reaction, and the expected electrophilic order is found for chlorine addition in the series $\text{CHPh:CH}\cdot\text{CO}_2\text{Et} > \text{CHPh:CH}\cdot\text{CHO} > \text{CHPh:CH}\cdot\text{NO}_2$.

PRELIMINARY observations (J., 1939, 1509) indicated that addition of bromine and chlorine to $\alpha\beta$ -olefinic aldehydes in acetic acid solution is catalysed by hydrochloric and sulphuric acids, whereas these acids do not influence the rate of electrophilic halogen addition, e.g., to allyl acetate. The acid catalysis of bromine addition to $\alpha\beta$ -unsaturated acids was also reported (this vol., p. 129), and the suggestion made that in these reactions a nucleophilic mechanism might be operating. The possibility of nucleophilic bromine addition was envisaged by Ingold and Ingold in their comprehensive analysis of the conditions determining halogen addition (J., 1931, 2354). Kinetic considerations and a comparison of the relative reaction rates of similar compounds make it probable that both bromine and chlorine may initiate an attack on a positive carbon atom, the charge on this atom being acquired by the addition of a hydrogen ion, $\text{CHR:CH}\cdot\text{CHO} + \text{H}^+ \rightarrow \text{CHR}^+\text{CH}\cdot\text{CHO}$.

The effect of different acids on the rate of bromine addition to cinnamaldehyde is shown in the accompanying figure. The specific conductivities ($\times 10^6$) of the $m/320$ -acids in acetic acid at 25° are: HClO_4 (3.4),



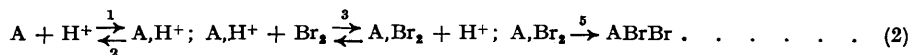
Cinnamaldehyde-bromine; reactants $m/80$ with acids.

H_2SO_4 (0.28), HNO_3 (0.011) (Kolthoff and Willman, *J. Amer. Chem. Soc.*, 1934, 56, 1007). As the corresponding relative rates of bromine addition are: HClO_4 , 8; H_2SO_4 , 4; HNO_3 , 1, it is apparent that these rates are a function of the acid strength, but are not proportional to the hydrogen-ion concentration. The simple mechanism (1) must therefore be rejected.



(In the formulations and discussions which follow, reference throughout is made to hydrogen ions, irrespective of the fact that they are largely present as H_2OAc^+ .)

The alternative process (2) is therefore suggested:



By application of the method of stationary concentrations

$$-d[\text{Br}_2]/dt = k_1 k_3 k_5 [\text{A}][\text{Br}_2][\text{H}^+] / (k_2 k_4 + k_3 k_4 [\text{H}^+] + k_3 k_5 [\text{Br}_2]) \quad (3)$$

If k_3 is small relatively to the other constants, this expression assumes the simplified form

$$-d[\text{Br}_2]/dt = k[\text{A}][\text{Br}_2][\text{H}^+] / (1 + k'[\text{H}^+]) \quad (4)$$

This would require second-order kinetics for A and Br_2 , and hydrogen-ion catalysis becoming less effective with increased hydrogen-ion concentration, as is experimentally found. A further consequence, if k_3 is relatively very small, is that a finite time might elapse before the attainment of stationary concentrations.

This would involve an initial retardation and would show itself in the rising bimolecular coefficients that characterise these reactions. An alternative explanation of this effect would be autocatalysis by hydrobromic acid; actually the amount of this acid present at the end of the reaction is very small, but on the other hand its catalytic power is considerable.

In view of the complicated nature of the expression (3), it is not surprising that one of the reactions examined (acraldehyde + chlorine catalysed by sulphuric acid) has been found to have a reaction order with respect to aldehyde and halogen of less than 2 ($n, m/80 - m/160, = 1.6$).

With regard to the catalysis by hydrobromic and hydrochloric acids of the reaction between cinnamaldehyde and bromine, it is found that these acids exert a greater influence than is expected from their relative acid strengths in acetic acid ($\text{HClO}_4 > \text{HBr} > \text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$). This is shown by the rates of bromine addition for $m/80$ -reactants + $\frac{1}{4}$ mol. of acid in acetic acid at 24° .

	HClO_4 .	HBr .	H_2SO_4 .	HCl .	HNO_3 .
$k_2(x = 20)$	7.3	~300	3.4	24	~0.8

The considerable catalysis by hydrobromic acid is attributed to the formation of HBr_3 , an active nucleophilic reagent, for which 1 : 4 addition has been proposed (Part V, this vol., p. 129). Although there is no evidence for the existence of HClBr_2 in acetic acid solution, it is theoretically possible, and its formation would explain the abnormally high catalysis by hydrochloric acid. Similarly, this acid is an especially active catalyst in acid-catalysed chlorine addition (and the effect could be explained by HCl_3 formation) as is seen in the rates for cinnamaldehyde and chlorine (each $m/80$) + $\frac{1}{4}$ mol. of acid in acetic acid at 24° , corrected by subtraction of the electrophilic rates, $k_2(\text{NaOAc}) = 1.8$:

	HClO_4 .	H_2SO_4 .	HCl .
$k_2(x = 20)$	2.9	1.3	5.1

The theory of nucleophilic halogen addition is also in accord with the order of reactivity for related compounds in these reactions. Thus the more strongly electron-attracting aldehyde group is superior in its effect to the weaker carboxyl group, as is indicated for bromine addition in acetic acid at 24° :

	$\text{CHMe:CH}\cdot\text{CO}_2\text{H}$.	$\text{CHMe:CH}\cdot\text{CHO}$.
$k_2(+\frac{1}{4}\text{H}_2\text{SO}_4)$	~0.01	~1000

Correspondingly, the electrophilic order (shown, *e.g.*, by addition of chlorine to the acids $\text{CHR:CH}\cdot\text{CO}_2\text{H}$) may become reversed in the nucleophilic acid-catalysed addition of chlorine to the corresponding aldehydes, as illustrated by the following velocities in acetic acid at 24° :

	$\text{CHPh:CH}\cdot\text{CO}_2\text{H}$.	$\text{CHMe:CH}\cdot\text{CO}_2\text{H}$.	$\text{CH}_2\text{:CH}\cdot\text{CO}_2\text{H}$.
k_2	5.0	0.62	0.017
	$\text{CHPh:CH}\cdot\text{CHO}$.	$\text{CHMe:CH}\cdot\text{CHO}$.	$\text{CH}_2\text{:CH}\cdot\text{CHO}$.
Corrected $k_2, m/80(\frac{1}{4}\text{H}_2\text{SO}_4)$	1.3 ($n = 2.0$)	43 ($n = 1.9$)	35 ($n = 1.6$)

Such a comparison, however, loses its meaning when the kinetic order of the reaction changes: in the above series the rate of addition of chlorine to crotonaldehyde is greater or less than that to acraldehyde according to the concentration chosen for the comparison.

In electrophilic addition, chlorine reacts more rapidly than bromine (J., 1939, 1513), whereas the nucleophilic rates, as illustrated by the above reactions, may be reversed. The two modes of halogen addition also show a difference with regard to the effect of illumination. Electrophilic addition of bromine is photosensitive, whereas its acid-catalysed addition to cinnamaldehyde in acetic acid is not accelerated by light (see figure).

The retarding influence of added water on HBr_3 addition in acetic acid was first demonstrated for acrylic acid (Part I, J., 1937, 335), and later found also for maleic acid (Nozaki and Ogg, *J. Amer. Chem. Soc.*, 1942, 64, 709). It was consequently to be expected that acid-catalysed nucleophilic halogen addition to unsaturated aldehydes should reveal a similar deceleration. Perchloric acid is a favourable catalyst for this comparison, as it is a strong acid both in acetic acid and in aqueous solution. The rates of addition of bromine to cinnamaldehyde (both $m/80$) + $\frac{1}{4}$ mol. of perchloric acid in acetic acid-water mixtures at 24° are:

$\text{H}_2\text{O}, \%$	0.1	1.0	2.0	4.9	10	20
$k_2(x = 20)$	7.3	1.4	0.63	0.40	1.1	~10

With *ca.* 5% of added water the electrophilic reaction begins to take control, and further dilution of the acetic acid increases the rate in the manner characteristic of electrophilic halogen addition. The conditions determining the decelerating influence of water in the nucleophilic reaction are liable to be complex, as all the constants in the rate expression (2) may be affected by the alteration in the solvent medium.

As sodium acetate is a base in acetic acid solution, it represses the hydrogen ion catalysis; the rates of halogen addition to the unsaturated aldehydes are then for the electrophilic reactions, and in a series of compounds containing electron-attracting groups of increasing power there is a descending order. The following rates have been obtained for chlorine addition in acetic acid at 24° :

	$\text{CHPh:CH}\cdot\text{CO}_2\text{Et}$.	$\text{CHPh:CH}\cdot\text{CHO}$.	$\text{CHPh:CH}\cdot\text{NO}_2$.
k_2	10.0	1.8 *	0.020
	* $m/80 + m/80\text{-NaOAc}$.		

EXPERIMENTAL.

The solvent acetic acid, bromine, and chlorine were purified as described in previous communications. As these acid-catalysed halogen additions are sensitive to small variations in the water content of the acetic acid, a bulk sample, m. p. 16.4°, was used for all the measurements now recorded. The solutions of the halogens in acetic acid were prepared before each set of measurements and used within 12 hours, for after that, especially if exposed to light, they contain traces of hydrochloric or hydrobromic acid sufficient to cause a measurable catalysis. Cinnamaldehyde, b. p. 120°/15 mm., crotonaldehyde, b. p. 102°/760 mm., and acraldehyde, b. p. 53–54°/760 mm., were fractionally distilled before use. The standard acid solutions were prepared from perchloric, sulphuric, and nitric acids by adding them to acetic acid with the theoretical amount of acetic anhydride to combine with the water; hydrochloric and hydrobromic acid solutions were standardised before measurements.

Times (t) are given in minutes; percentages of bromine absorption (x) are corrected for slight deviation from $M/80$ and $M/160$, and values of k_2 are in g.-mols./l., mins. Unless otherwise stated, the solvent is acetic acid and the temperature 24°. Herewith is a typical experiment: reactants $M/80 + \frac{1}{2}$ mol. of sulphuric acid:

1 ml. of 0.150M-cinnamaldehyde + 1 ml. of 0.0415M-H₂SO₄ + 5 ml. of HOAc + 5 ml. of 0.0307M-Br₂; 1.965 ml. pipetted into 5% KI soln. and titrated with 0.0125N-Na₂S₂O₃.

t	0	1.06	3.55	7.70	17.6
Titre (ml.)	4.03	3.97	3.64	2.89	1.51

From a curve, with additional points from a second experiment, $t(x = 20) = 5.8$, $t(x = 50) = 12.0$.

Other results are summarised below, as times for $x = 20$ and $x = 50$ in that order, except where otherwise stated.

Cinnamaldehyde + Br₂: Reactants, $M/80$: 0.077M-HClO₄, 1.0, 1.7; 0.0035M-HClO₄, 2.7, 5.8; 0.00175M-HClO₄, 3.8, 8.4; 0.0032M-HCl, 0.88, 2.0; 0.0033M-HNO₃, 24 ($x = 20$); 0.012M-NaOAc, 705 ($x = 20$). Reactants, $M/160$: 0.0035M-HClO₄, 5.8, 12.2 (hence with $M/80$ values, and same concentration of H₂SO₄, $n = 2.0$). Reactants, $M/80$, 39.5°; 0.0035M-HClO₄, 1.2, 2.7.

Cinnamaldehyde + Cl₂: Reactants, $M/80$: 0.077M-HClO₄, 2.4, 7.5; 0.0035M-HClO₄, 4.4, 17.1; 0.0032M-HCl, 2.9, 9.8; 0.0032M-H₂SO₄, 6.5, 21.0; 0.012M-NaOAc, 10.9, 47.0.

Crotonaldehyde + Br₂: Reactants, $M/80$: 0.0032M-H₂SO₄, <0.2 ($x = 50$); 0.012M-NaOAc, 164, 363.

Crotonaldehyde + Cl₂: Reactants, $M/80$: 0.0036M-H₂SO₄, 0.46, 0.95; 0.0032M-HCl, <0.3 ($x = 50$); 0.012M-NaOAc, 49 ($x = 20$). Reactants, $M/160$: 0.0036M-H₂SO₄, 0.82, 1.84.

Acraldehyde + Cl₂: Reactants, $M/80$: 0.0036M-H₂SO₄, 0.56, 1.27; 0.062M-NaOAc, 155 ($x = 20$). Reactants, $M/160$: 0.0036M-H₂SO₄, 0.83, 1.84.

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VICTORIA UNIVERSITY COLLEGE, WELLINGTON, N.Z.

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