

XLIX.—*The Addition of Bromine to Ethylenic Compounds in Non-hydroxylic Solvents.*

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IT is generally stated that the addition of halogens to unsaturated ethylenic compounds in dilute solution takes place in accordance with the bimolecular law (Herz and Mylius, *Ber.*, 1906, **39**, 3816; Hofmann and Kirmreuther, *Ber.*, 1909, **42**, 4481; Barrett and Lapworth, *P.*, 1907, **23**, 18; Bauer and Moser, *Ber.*, 1907, **40**, 918; Sudborough and Thomas, *J.*, 1910, **97**, 715, 2450). In aqueous solution, the reaction takes place very rapidly, whilst in non-aqueous solvents the rate of addition is said to vary according to (i) the position of the ethylenic linkage, (ii) the presence of certain substituent groups, (iii) the solvent, and (iv) the presence of catalysts and especially of light. Published results indicate that the rate of reaction is extremely sensitive to slight variation of these conditions; *e.g.*, Sudborough and Thomas's values for the velocity coefficient for cinnamic acid and bromine vary from 0.9×10^{-4} to 2.6×10^{-4} in series of experiments carried out under apparently identical conditions.

We have examined the addition of bromine to a number of unsaturated acids and their derivatives in dry chloroform and carbon tetrachloride in the dark, and although these results are of a preliminary nature, we have reached the following general conclusions:

1. The substances examined can be divided into three classes: (a) Those to which bromine is added with considerable rapidity, the addition being accompanied by substitution and the formation of hydrogen bromide: the bimolecular velocity coefficient steadily decreases as the reaction proceeds. This class includes such diversely constituted substances as oleic and elaidic acids, *cis*- and *trans*-*o*-methoxycinnamic acids, acids containing conjugated double bonds such as cinnamylideneacetic acid and its methyl ester, phenylstyrylacrylic acid and furfurylacrylic acid. (b) Those to which bromine adds on slowly but with a measurable and increasing velocity, exhibiting a preliminary inhibition period. This class includes cinnamic acid and its methyl ester, crotonic acid, and methyl cinnamylidenemalonate. (c) Those to which no measurable addition takes place under the conditions investigated. This class includes compounds possessing cyclic structures, *e.g.*, maleic anhydride and coumarin, and also α -phenylcinnamionitrile.

The evidence obtained seems to show that the difference between the classes is not so much a question of degree as of type, and every substance examined fell naturally into one class or other.

2. The position of the double bond, especially in the α -position to the carboxyl group, and of substituent groups in close proximity to the double bond (*e.g.*, the nitrile group in α -phenylcinnamionitrile) have an important effect on the rate of addition (compare Sudborough and Thomas, *loc. cit.*, p. 2452), but these are not the deciding factors as is shown by the behaviour of the *o*-methoxycinnamic acids and of the isomeric *p*-acid (Hariharan and Sudborough, *J. Ind. Inst. Sci.*, 1925, 8A, 193).

3. The rapidity of addition to substances of class (a) above, is due to preliminary substitution, with the formation of hydrogen bromide in small amounts. This is borne out by the effect of the addition of quantities of hydrogen bromide to the reacting substances of class (b), whereby the rates of addition are much accelerated and vary with the concentration of the catalyst. Hydrogen chloride and water produce similar effects to hydrogen bromide, although not of the same degree. In each case, the inhibition period disappears and the reaction becomes bimolecular. Addition to substances of class (c) does not occur under the influence of any of the above catalysts.

In general, the reactions were more rapid in chloroform than in carbon tetrachloride.

EXPERIMENTAL.

Purification of Materials.—The solvents (carbon tetrachloride and chloroform) were washed with acid, alkali, and water, then dried for extended periods over calcium chloride, and finally distilled over phosphorus pentoxide. The bromine was shaken with concentrated sulphuric acid, purified by freezing several times until of constant melting point, and then distilled over pure potassium bromide. The acids and their derivatives were recrystallised until of constant melting point and finally dried for long periods in a vacuum.

The method described by Sudborough and Thomas (*loc. cit.*) was followed in all essential details. Equal volumes of *M*/30-solutions of the unsaturated compound and of bromine in the purified solvent were mixed in brown bottles and kept in a thermostat at 13° in a dark room. After definite intervals of time the reaction was stopped by the addition of a definite volume of 0.1*N*-potassium iodide, followed, after shaking, by a definite excess of *N*/30-sodium thiosulphate. After shaking until the iodine had been completely absorbed from the solvent layer, the excess of thiosulphate was estimated by back titration with *N*/30-iodine solution. From these data, calculation gave the amount of unabsorbed bromine remaining in the reaction mixture.

In subsequent experiments it was possible, for substances of class (b), to use a single reaction vessel with all-glass, air-tight fittings, from which samples of the reaction mixture were expelled into potassium iodide solution by forcing in dry air. These samples were weighed and analysed as before. Results obtained in this way were in general agreement with those previously obtained but more consistent amongst themselves.

In studying the effects of hydrogen chloride and hydrogen bromide as catalysts, small, definite volumes of saturated solutions of these gases in carbon tetrachloride were added to the reaction mixture, the decrease in the initial concentration of the reactants being thus known. Saturated solutions of hydrogen chloride and hydrogen bromide in carbon tetrachloride at 13° contain 0.42 and 1.80% of the gases, respectively.

TABLE I.

Temperature 13°, unless otherwise stated.

Substance.	Approx. inhibition period (hours).	Period for 25% change.	<i>k</i> ,	
			first value.	last value.
Class (a).				
* <i>trans</i> - <i>o</i> -C ₆ H ₄ (OMe)·CH:CH·CO ₂ H	—	0.01	1,074	102
† <i>cis</i> - „ „	—	0.02	1,578	126
* <i>cis</i> - „ „	—	0.01	1,824	144
*C ₆ H ₅ ·CH:CH·CH:CH·CO ₂ H	—	0.01	882	174
†C ₆ H ₅ ·CH:CH·CH:CH·CO ₂ Me ...	—	0.02	97.8	5.4
* „ „ „	—	0.01	2,562	420
*C ₆ H ₅ ·CH:CH·CH:CPh·CO ₂ H	—	0.3	65.4	42.0
*C ₆ H ₄ O·CH:CH·CO ₂ H	—	0.01	1,134	162
†Oleic acid	—	0.001	78,000	780
†Elaidic acid	—	0.001	102,000	3840
Class (b).				
*C ₆ H ₅ ·CH:CH·CO ₂ H	12	65	0.078	0.792
† „ „	20	156	0.066	0.246
† „ „ (at 0°)	20	206	0.039	0.096
† „ „ (at 25.5°) ...	10	31	0.426	0.702
†C ₆ H ₅ ·CH:CH·CO ₂ Me	42	280	0.039	0.063
†CH ₂ ·CH:CH·CO ₂ H	18	195	0.063	0.120
†C ₆ H ₅ ·CH:CH·CH:C(CO ₂ Me) ₂	22	117	0.126	0.234
Class (c).				
†C ₆ H ₅ $\begin{matrix} \diagup \text{CH:CH} \\ \diagdown \text{O-CO} \end{matrix}$				7.0% change in 352 hours.
† $\begin{matrix} \text{CH-CO} \\ \diagdown \text{O} \\ \text{CH-CO} \end{matrix}$				5.4% change in 306 hours.
†C ₆ H ₅ ·CH:CPh·CN				5.8% change in 280 hours.

* Indicates reactions in chloroform as solvent.

† Indicates reactions in carbon tetrachloride as solvent.

A constant water content in the solvent was obtained by the introduction of sodium sulphate-decahydrate salt-pair (compare Bury and Roberts, J., 1923, 123, 2037). If the vapour pressure of the salt-pair be taken as 7.91 mm. at 13° and that of water at 13° as 11.23 mm., the solvent will be 70% saturated with water in the presence of the salt-hydrate pair.

The use of carbon tetrachloride as a solvent was limited, since many of the substances examined were not sufficiently soluble in it. In those cases, chloroform only was used.

The results are shown in the tables, the bimolecular velocity coefficient, $k = 1/t \cdot x/a(a - x)$, being based upon time (t) in hours and concentrations (a and x) in g.-mols. per litre. Two typical results illustrating the variation of k in the addition of bromine to substances of classes (a) and (b) are afforded respectively by *trans*-*o*-methoxycinnamic acid in chloroform, in which k fell continuously from 1074 to 102 during 2½ hours, and by cinnamic acid in carbon tetrachloride, in which, after an induction period of some 15–25 hours, k rose from 0.066 at 69 hours to 0.246 at 247 hours.

Table I summarises the results for all the substances used. Table II shows the effects of the three catalysts used.

TABLE II.
Solvent CCl₄.

	Catalyst.	(a).	(b).	k_1 .	k_2 .
Cinnamic acid	HBr	0.26	1.25	18.0	15.6
" "	"	0.53	0.37	58.2	72.0
" "	"	1.08	0.16	132	156
" "	HCl	1.10	50	0.474	0.510
" "	H ₂ O	—	104	0.168	0.186
Crotonic acid	HBr	0.53	5.2	5.94	0.98
" "	H ₂ O	—	15	1.74	2.46
Methyl cinnamylidenemalonate	HBr	0.53	0.05	384	408
" " " "	HCl	1.10	2.8	10.8	5.52
" " " "	H ₂ O	—	55	0.642	0.588
Methyl cinnamate	"	—	72	0.210	0.102

Column (a) gives the molar ratio of catalyst : bromine; column (b) gives the time (in hours) for 25% change; k_1 and k_2 are respectively the first and last values of k (generally up to 80% addition). With water as catalyst the solvent was 70% saturated.

Summary and Conclusion.

The results tabulated above indicate that hydrogen bromide is a very effective catalyst in the addition reaction between ethylenic acids and bromine. Further, they suggest that when an unsaturated acid and bromine are brought into contact, the first reaction that occurs is substitution with the formation of hydrogen bromide; this

in turn catalyses the addition reaction, which then proceeds in general much more rapidly than the substitution reaction.

It is to be noted that the reactions described in this paper have been conducted in the absence of light. There is reason to believe that radiant energy gives rise to reactions of different type.

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