XLVII.—*The Addition of Bromine to Unsaturated Compounds. Part I.*

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IN a preliminary note (Proc., 1906, **22**, 318) we were able to show that the reaction between cinnamic or crotonic acid and bromine in carbon tetrachloride solution is a typical bimolecular reaction, and that the replacement of the acid by a methyl or ethyl ester affects the velocity of addition only to a very slight extent. It was also pointed out that the reaction is influenced to an appreciable extent by light, the effect of bright sunlight raising the constant some 200 times its value in the dark.

Subsequent experiments have proved that the addition of bromine to *αβ*-unsaturated acids takes place but slowly, whereas isomeric *βγ*-acids, or, generally, olefine acids in which the double linking is not in the *αβ*-position with regard to the carboxyl group, unite with bromine extremely readily, and we have suggested (Proc., 1907, **23**, 147) this as a method of determining in any given acid whether the double linking is in the *αβ*-position or not.

Hugo and Bauer (*Ber.*, 1904, **37**, 3317) have drawn attention to the inhibiting effect on the addition of bromine which the presence of several negative radicles, such as CO_2H, CO_2R, Ph, Br, and CN, in the ethylene molecule produces; but they have not determined the velocities of the reactions in any case.

Herz and Mylius (*Ber.*, 1906, **39**, 3817) have conducted experiments on the addition of bromine to cinnamic acid in chloroform solution. They worked with sealed bulbs placed in a thermostat, and at the end of the given time broke the bulbs under potassium iodide solution. They found that the reaction was bimolecular, and that certain impurities, especially iodine, had a considerable accelerating action. The combination was also found to be somewhat quicker in carbon tetrachloride than in chloroform solution, and still quicker in carbon disulphide solution; but in the latter case the values for K varied considerably.

Still more recently K. A. Hofmann and Kirmreuther (*Ber.*, 1909, **42**, 4481) have examined the addition of bromine to the chloroethylenes. They used a large excess of the chloroethylene, and found that the reaction became practically unimolecular. The results prove that dichloroethylene combines with bromine more readily than tetrachloroethylene. With trichloroethylene the values obtained for K varied considerably, and with both tri- and tetra-chloro-derivatives the reaction was disturbed by the production of a catalyst, probably carbonyl chloride.

Barrett and Lapworth (Proc., 1907, **23**, 18) have studied the addition of bromine to certain unsaturated acids in aqueous solution. With cinnamic acid, even in 0·001*N*-solutions, the reaction proceeds so quickly that the time has to be measured in seconds, and it was found that nearly the whole of the bromine was combined in thirty seconds. With crotonic acid the addition was not quite so rapid. The sodium salts were also used, and the effect of introducing potassium bromide into the mixture was examined.

Bauer and Moser (*Ber.*, 1907, **40**, 918) have studied the addition of bromine to stilbene and to methylstilbene in chloroform, and also in carbon tetrachloride solution. They found that the presence of the methyl group facilitates the addition of the halogen, and also proved that the reaction between bromine and α-phenylcinnamonitrile is a balanced one.

In all our experiments we have used carbon tetrachloride as solvent. We selected this solvent as the molecule does not contain hydrogen atoms which can react with the halogen. The solvent was purified by shaking with dilute alkali, then with dilute hydrochloric acid, and finally with water until free from acid. It was then kept for a day over fused calcium chloride and distilled over phosphoric oxide. We conducted experiments in order to determine whether the cinnamic acid or its additive compound, αβ-dibromo-β-phenylpropionic acid, had any action on sodium thiosulphate. This was necessary, as in all our experiments the concentration of the unaltered bromine, and hence of the cinnamic acid, was determined by the addition of potassium iodide solution and the titration of the free iodine by means of standard thiosulphate solution. Twenty c.c. of a 0·05*N*-solution of thiosulphate required 18·95 c.c. of standard iodine solution; 20 c.c. of the same solution were shaken for some minutes with 20 c.c. of a 0·066*N*-solution of cinnamic acid in carbon tetrachloride. In three experiments the amounts of iodine were 18·95, 18·90, and 18·95 c.c. respectively. Similar experiments were conducted with a 0·066*N*-solution of αβ-dibromo-β-phenylpropionic acid; 20 c.c. of thiosulphate required 18·95 c.c. of iodine, and three mixtures of thiosulphate and dibromide required respectively 19·05, 19·10, and 19·10 c.c. of iodine. These results indicate that there is a slight reaction between the bromo-acid and the thiosulphate, but we are of the opinion that even this effect will not be met with in the actual titrations, as an excess of thiosulphate is never present during the titration, and the amount of dibromo-acid is always considerably less than the amount used in the above experiments.

In the determination of the amount of uncombined bromine by adding potassium iodide and titrating the liberated iodine by means of standard thiosulphate and starch, it was noticed that after the titration was completed the blue colour was restored in the course of a short time. This appears to be due to the fact that the cinnamic acid dibromide can slowly liberate iodine from potassium iodide. A solution of cinnamic acid dibromide in carbon tetrachloride when kept for a week did not give a blue coloration with potassium iodide and starch, indicating that the dibromo-acid does not give rise to free bromine, but when the above mixture was kept for half an hour a distinct blue colour was observable. It is thus necessary to titrate the liberated iodine immediately after the addition of the potassium iodide.

The following numbers obtained with carbon tetrachloride solutions of cinnamic acid and bromine at 15° in colourless glass bottles in diffused daylight indicate that the reaction is bimolecular:

$C_{acid} = 52{\cdot}72.$ $C_{Br} = 26{\cdot}25.$

t (in hours).	$a - x$.	$K = \frac{1}{(a-b)t}\log\frac{b(a-x)}{a(b-x)}$.
0·25	20·65	$1{\cdot}92 \times 10^{-2}$
0·50	15·05	1·66
0·75	12·60	2·19
1·00	12·50	1·66
1·25	9·30	1·96
1·50	8·10	1·90

The effect of light was clearly shown by two sets of experiments with ethyl cinnamate and bromine at 15°; the one series was carried out in colourless bottles in fairly bright sunlight, and the other in amber-coloured bottles in the dark. The value for K obtained in the first set was $4{\cdot}0 \times 10^{-2}$, and 7/8ths of the bromine were used up at the end of an hour and a-half. In the second series of experiments only 1/24th of the bromine had been used up in the same time (1·5 hours).

Comparative experiments with crotonic acid in the dark and in ordinary daylight were also made. The solutions of acid and of bromine were of equivalent strength (practically 1/30th of the gram-molecule per litre). The constant calculated from the formula $K = 1/t.x/a(a-x)$ varied between $1{\cdot}7 \times 10^{-5}$ and $2{\cdot}4 \times 10^{-5}$ in the dark, and between $2{\cdot}6 \times 10^{-3}$ and $4{\cdot}9 \times 10^{-3}$ in daylight. Somewhat similar results were obtained with cinnamic acid and methyl cinnamate.

In all the above-mentioned experiments the bromine was purified by shaking with concentrated sulphuric acid. In subsequent experiments the bromine used was subjected to the following method of purification. About 150 c.c. were shaken with concentrated sulphuric acid, and the clear liquid was run into a test-tube surrounded by a freezing mixture of calcium chloride and ice.

After the bromine had solidified, the tube was removed from the freezing mixture, and the portion which melted first was poured off. This process was repeated several times, until about 50 grams were obtained, melting at −6° to −7°.

The general method of procedure was to make carbon tetrachloride solutions of the unsaturated compound and of bromine of the same concentration (namely, 250 c.c. of a solution containing 1/30th of the gram-molecular weight per litre). The two solutions were standardised, the acid solution by means of standard barium hydroxide solution, using phenolphthalein as indicator, and the bromine solution by means of potassium iodide and thiosulphate, using starch as indicator. When esters were used, the ester solution was not standardised, but was made of the strength required by weighing out the exact amount necessary. The two solutions were placed in the thermostat regulated for 15°, and after some little time equal volumes of the two were mixed in the dark. Thirty c.c. of the mixture were run into each of several brown bottles, and these were kept in the dark at 15°. At the end of the given time excess of potassium iodide solution was added, the whole removed to a colourless bottle, and titrated with standard thiosulphate. Several litres of the thiosulphate were prepared and stored in a large bottle attached to the burette. The thiosulphate was protected from atmospheric carbon dioxide by means of a soda-lime tower. As the two solutions were of equivalent strength, the equation $K = 1/t . x/a(a-x)$ was used for calculating K. The values for a and $a-x$ were denoted by the number of c.c.'s of thiosulphate required at the beginning and after given intervals of time. As the same number of c.c.'s of mixture were used in each case, and as the thiosulphate solution was the same throughout, the values for K given in the following table are comparable. In this table $a = 25{\cdot}30$ c.c. (of thiosulphate). In all cases t in the equation $K = 1/t . x/a(a-x)$ is calculated in hours.

The compounds used in these experiments were all purified before use. The values of K obtained for any given compound are not very concordant. Other authorities have noticed this fact (compare Herz and Mylius; Hofmann and Kirmreuther, *loc. cit.*). The only reason for this that we can offer is that a trace of some impurity has a considerable effect on the velocity of the reaction.

When acids were used in which the double linking was not in the $\alpha\beta$-position, the reaction proceeded so rapidly that titrations every few seconds were necessary. Under such conditions the experimental errors which arise in measuring t are great, and a close agreement between the values of K is not to be expected.

The conclusions we draw from these experiments are: (1) The

TABLE I.

					$1/t\,.\,x/a(a-x)$.	
Unsaturated compound.	Formula.	Series.	Maximum time.	Number of titrations.	Minimum.	Maximum.
Crotonic acid:	$CHMe{:}CH{\cdot}CO_2H$	*a*	332 hours	4	$1{\cdot}8 \times 10^{-5}$	$2{\cdot}4 \times 10^{-5}$
Cinnamic acid:	$CHPh{:}CH{\cdot}CO_2H$	*a*	240 ,,	4	$1{\cdot}8 \times 10^{-4}$	$2{\cdot}6 \times 10^{-4}$
		b	120 ,,	5	$0{\cdot}9 \times 10^{-4}$	$1{\cdot}4 \times 10^{-4}$
Methyl cinnamate:	$CHPh{:}CH{\cdot}CO_2Me$	*a*	143 ,,	5	$1{\cdot}22 \times 10^{-4}$	$2{\cdot}35 \times 10^{-4}$
		b	146 ,,	3	$1{\cdot}41 \times 10^{-4}$	$2{\cdot}21 \times 10^{-4}$
Ethyl cinnamate:	$CHPh{:}CH{\cdot}CO_2Et$	*a*	122 ,,	5	$1{\cdot}2 \times 10^{-4}$	$1{\cdot}7 \times 10^{-4}$
		b	240 ,,	5	$1{\cdot}1 \times 10^{-4}$	$1{\cdot}3 \times 10^{-4}$
		c	144 ,,	5	$1{\cdot}3 \times 10^{-4}$	$2{\cdot}6 \times 10^{-4}$
β-Ethylacrylic acid:	$CHEt{:}CH{\cdot}CO_2H$	*a*	265 ,,	4	$3{\cdot}3 \times 10^{-5}$	$6{\cdot}0 \times 10^{-5}$
αβ-Oleic acid:	$CH_3{\cdot}[CH_2]_{14}{\cdot}CH{:}CH{\cdot}CO_2H$	*a*	173 ,,	4	$2{\cdot}3 \times 10^{-5}$	$2{\cdot}6 \times 10^{-5}$
Phenyl-βγ-crotonic acid:	$CHPh{:}CH{\cdot}CH_2{\cdot}CO_2H$	*a*	120 secs.	4	3·5	6·3
		b	120 ,,	4	2·6	4·8
Allylacetic acid:	$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$	*a*	30 ,,	4	$1{\cdot}4 \times 10^{2}$	$2{\cdot}3 \times 10^{2}$
		b	30 ,,	4	$1{\cdot}4 \times 10^{2}$	$2{\cdot}2 \times 10^{2}$
Ethylidenepropionic acid:	$CH_3{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2H$	*a*	60 ,,	4	10·0	48·0
		b	60 ,,	4	11·0	58·0
Undecylenic acid:	$CH_2{:}CH{\cdot}[CH_2]_8{\cdot}CO_2H$	*a*	480 ,,	5	0·5	1·4
		b	480 ,,	4	0·7	1·5
Oleic acid:	$CH_3{\cdot}[CH_2]_7{\cdot}CH{:}CH[CH_2]_7{\cdot}CO_2H$	*a*	60 ,,	4	14·0	31·3
		b	75 ,,	5	12·7	30·9
Elaidic acid:	$CH_3{\cdot}[CH_2]_7{\cdot}CH{:}CH[CH_2]_7{\cdot}CO_2H$	*a*	120 ,,	5	2·9	10·7
		b	120 ,,	5	3·0	11·8
Erucic acid:	$CH_3{\cdot}[CH_2]_7{\cdot}CH{:}CH[CH_2]_{11}{\cdot}CO_2H$	*a*	120 ,,	4	3·0	15·7
		b	120 ,,	4	3·1	14·6
Brassidic acid:	$CH_3{\cdot}[CH_2]_7{\cdot}CH{:}CH[CH_2]_{11}{\cdot}CO_2H$	*a*	90 ,,	4	3·5	7·4
		b	120 ,,	4	3·1	7·1

reaction between bromine and an olefine acid in carbon tetrachloride solution is bimolecular, and is practically non-reversible. (2) The rate of addition is accelerated to an enormous extent under the influence of light. (3) The reaction is comparatively slow with all αβ-unsaturated acids, but is completed in the course of a few minutes, when the double linking is further removed from the carboxylic group. According to Hugo and Bauer (*loc. cit.*), this is to be attributed to the "negative" character of the carboxylic group rather than to any stereochemical effects.

The difference between the rate of esterification of an αβ-unsaturated and its βγ- or γδ-isomeride (Trans., 1907, **91**, 1033;

1909, **95**, 315) and the difference in the rates of addition of bromine afford two simple methods for determining whether the double linking in a simple olefine acid is in the *αβ*-position or not.

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