128. *The Addition of Halogens to Unsaturated Acids and Esters. Part IV. The Rate of Addition of Bromine to Cinnamic Acid in Acetic Acid.*

By DAVID MATTHEW WILLIAMS.

THE kinetics of the addition of bromine to ethylenic compounds has been hitherto studied only in non-hydroxylic solvents such as carbon tetrachloride and chloroform. Comparison of the velocity of reaction in these two solvents has shown that it is invariably more rapid in the latter (Williams and James, J., 1928, 343), and since this is a polar solvent ($\mu = 1{\cdot}0 \times 10^{-18}$) the increased velocity has been ascribed to the effect of the solvent molecules. Evidence in support of this idea is derived from the study of the gaseous reaction between ethylene and bromine, which is essentially a surface reaction and varies with the polarity of the surface (Norrish, J., 1923, **123**, 3006). But it is significant that the addition of bromine to an ethylenic compound such as cinnamic acid in a non-polar solvent such as carbon tetrachloride and in a polar one such as chloroform is essentially an autocatalytic reaction (Williams and James, *loc. cit.*), the catalyst being apparently hydrogen bromide. It seems that the polar chloroform molecules only influence the catalysed reaction and are unable to cause reaction by their own effect.

The velocity of addition to cinnamic acid in hydroxylic solvents such as water and alcohol is very much more rapid than in chloroform, and that the solvent molecules take part in the reaction is proved by the formation of the bromohydrin and the bromoethoxy-compound respectively. There is no apparent reason, however, why the addition reaction should be so extremely rapid in comparison with that in chloroform. It seemed that information as to the cause of this reactivity could be obtained by studying the kinetics of the addition of bromine in a hydroxylic solvent. Acetic acid was chosen for this purpose : purified by the method of Orton and Bradfield (J., 1927, 983), it is not reacted upon by bromine at ordinary temperatures; further, the complications that would arise from the use of water and alcohol are avoided, since the addition of the acetoxy-group instead of the second bromine atom does not take place to a detectable extent.

A preliminary experiment at 15° showed that the addition reaction in acetic acid is quite different from that in chloroform. It approximated very closely to a bimolecular reaction until about the half-way stage, but then it was obvious from the velocity constants that a second reaction was producing a catalyst so that the constants had an upward trend. This was more apparent at 18° and still more so at 20° and at 25° : the higher the temperature the greater was the amount of catalyst formed and the more the reaction deviated from the bimolecular type. The most probable side reaction is substitution either in the nuclear part of the cinnamic acid or, perhaps, in the solvent under the influence of the cinnamic acid. The hydrogen bromide formed in this way would then be the actual catalyst. To prove that this substitution occurred, the addition was followed at 18° in sealed tubes, more bromine being used than was equivalent to the cinnamic acid taken, and it was found that the reaction proceeded slowly beyond its theoretical end. Further evidence on this point was obtained when hydrogen bromide was added to the reaction mixture : the reaction was catalysed considerably and approximated very closely to the bimolecular type. The efficiency of hydrogen bromide as a catalyst, however, is not so great in acetic acid as in carbon tetrachloride, and had it been used in the same concentration in the latter solvent the reaction would have been very much more rapid (compare the results of Williams and James, *loc. cit.*).

Thus the immediate production of hydrogen bromide is not sufficient to account for the fact that there is no inhibition period when the addition occurs in acetic acid. Neither does a comparison of the polarity of the two solvents, chloroform and acetic acid, as far as can be gathered from the dielectric-constant data for the latter, account for the absence of an inhibition period in this solvent.

Owing to the difficulty of preparing and keeping pure acetic acid of m. p. 16·6°, an acid of m. p. 16·2°, corresponding to 0·2% of water, was used for this work. This small amount of water might have a very important effect on the reaction, and in order to investigate this, the addition was studied in acetic acid containing more water. When the water content is still small (0·7%), a reaction of a different type is observed, the values of the velocity constant calculated for a bimolecular reaction tending to diminish as the reaction proceeds. When the amount of water is considerably greater, the velocity is very much increased, and the decrease in the constant with time becomes very marked. Thus two facts have to be explained: (1) Why is the reaction velocity accelerated so much by the presence of relatively small amounts of water, and (2) why does the character of the reaction differ from that in the solvent when the amount of water is very small? A possible explanation was found from a study of the effect of hydrogen bromide on the reaction in aqueous acetic acid. It had a definite but not a very strong anticatalytic effect, and this is quite specific, since added hydrogen chloride, on the other hand, had a catalytic effect. It seems probable that the hydrogen bromide exerts its influence by disturbing the equilibrium $Br_2 + H_2O \rightleftharpoons HBr + HOBr$, and that the really active catalyst in aqueous acetic acid is the hypobromous acid, although hydrogen bromide may also be a catalyst, like hydrogen chloride, but a much less efficient one. When the water content is very small, as in the acid of m. p. 16·2°, the effect of the added hydrogen bromide more than counteracts its effect on the equilibrium, but as the water content increases, its own effect does not counteract the retardation due to loss of hypobromous acid. The latter does not in this case react with the cinnamic acid, since its concentration is very small and the dibromide can be isolated in almost theoretical yield from such a solvent.

The rapidity of addition reactions in hydroxylic solvents seems from the above argument to be due to an equilibrium XOH + $Br_2 \rightleftharpoons HBr + XOBr$, where both substances on the right-hand side of the equation are catalysts, and in ionising solvents hypobromous acid is a more efficient catalyst than hydrogen bromide. The choice of solvents with a high dielectric constant, and towards which bromine is quite inert, is so small that the actual effect of the solvent molecules on the reaction cannot at present be discussed; but, partially at least, the rapidity of addition in hydroxylic solvents must be due to the above equilibrium and the catalytic effect of the bromine compounds so formed.

EXPERIMENTAL.

Purification of Materials.—The bromine was dried by sulphuric acid and then distilled from a mixture of potassium bromide and zinc oxide, the middle fraction being collected. The cinnamic acid was thrice recrystallised from carbon tetrachloride–alcohol. Acetic acid of m. p. 16·2° (water = 0·2%) was obtained by applying Orton and Bradfield's oxidation method (*loc. cit.*) to ordinary acid which had been fractionally frozen three times, the only impurity then present in it being water. Finally, the acid was distilled with the amount of acetic anhydride required to react with the water present, as calculated from the freezing point, a small amount of β-naphthalenesulphonic acid being added to catalyse the hydrolysis of the anhydride. (Excess anhydride must be carefully avoided.) The acid so prepared was perfectly stable towards bromine at the temperatures used.

Velocity Measurements.—All the velocity determinations for the slow reactions, *i.e.*, those with a half-time reaction period exceeding 50 hours, were carried out in an all-glass reaction vessel, from which samples could be forced out into a weighing bottle containing a solution of potassium iodide by means of dry, carbon dioxide-free air. These samples were weighed and titrated against standard thiosulphate, starch being used as indicator and sodium acetate being added to decrease the acidity of the solution. An appreciable time was required for the thorough mixing of large volumes of reactants in the reaction vessel, and this would have caused considerable error in fixing the initial time for the rapid reactions. More accurate results could be obtained by mixing small equal volumes of the solutions of the reactants in bottles of brown glass, the reaction being stopped by addition of excess of potassium iodide solution. The contents were then washed out and titrated. Unless otherwise stated, all the experiments were carried out in a thermostat at 18° ± 0·1° in a dark room. A trial experiment was done at room temperature (15° ± 0·5°). When finding the effect of temperature on the reaction, thermostats at 20° ± 0·05° and 25° ± 0·05° were used.

The cinnamic acid and bromine solutions were of the same concentration within 0·2%, in most cases $M/30$. The velocity constants could thus be calculated without any appreciable error according to the simplified equation $k = x/ta(a - x)$.

The aqueous acetic acid used as solvent was prepared by weight, except that when the water content was 0·7% this was calculated from the lowering of the freezing point. Hydrogen bromide and hydrogen chloride were introduced into the reaction mixture by adding small volumes of concentrated solutions of the dry gases in the solvent. These volumes were measured from a burette graduated in 0·05 c.c. This small dilution factor had to be taken into account when calculating the velocity constant.

Results.—The results are given in the following tables, where the time t is expressed in hours, the change x in percentage reaction, a is the initial concentration of the reactants, and w the percentage

I.

$T = 15°$; $a = M/53·3$; $w = 0·2$.

t.	*x*.	*k*.
4·5	5·07	0·620
22·25	20·30	0·608
46·25	34·65	0·613
70·5	45·20	0·624
119·0	58·35	0·629
142·5	63·28	0·645

II.

$T = 18°$; $a = M/60$; $w = 0·2$.

t.	*x*.	*k*.
23·0	18·60	0·594
47·0	34·88	0·678
72·0	46·27	0·714
97·0	54·98	0·756
120·0	60·99	0·780
167·0	73·14	0·978

III.

$T = 20°$; $a = M/60$; $w = 0·2$.

t.	*x*.	*k*.
23·0	22·56	0·762
31·6	29·26	0·786
47·0	38·79	0·810
71·0	50·31	0·852
97·3	61·03	0·966
144·0	77·45	1·434

IV.

$T = 25°$; $a = M/60$; $w = 0·2$.

t.	*x*.	*k*.
4·5	7·25	1·04
10·0	15·05	1·06
23·0	30·79	1·27
47·0	52·53	1·41
72·0	70·96	2·03
80·0	76·64	2·46

V.

$T = 18°$; $a = M/60$; $w = 0·69$.

t.	*x*.	*k*.
10·0	16·37	0·114
30·0	38·32	0·124
54·5	53·37	0·126
71·0	59·44	0·124
120·0	69·31	0·113
167·0	75·25	0·109

VI.

$T = 18°$; $a = M/60$; $w = 5·36$.

t.	*x*.	*k*.
0·5	9·71	12·9
1·0	17·09	12·4
2·0	28·48	11·9
4·0	41·81	10·8
12·3	65·43	9·2
24·0	75·67	7·8

VII.

$T = 18°$; $a = M/60$; $w = 9·67$.

t.	*x*.	*k*.
0·167	11·81	48·2
0·5	27·82	39·7
1·5	44·44	32·0
3·0	57·72	27·1
10·0	76·65	19·7
23·0	85·67	15·5

VIII.

$T = 18°$; $a = M/63$; $w = 0·2$.

$[HBr]/[Br_2] = 2·90$.

t.	*x*.	*k*.
4·0	15·32	2·87
6·33	21·80	2·75
13·5	37·26	2·83
19·75	47·21	2·85
23·75	55·04	3·25
28·0	60·54	3·45

IX.

$T = 18°$; $a = M/63$; $w = 5·36$.

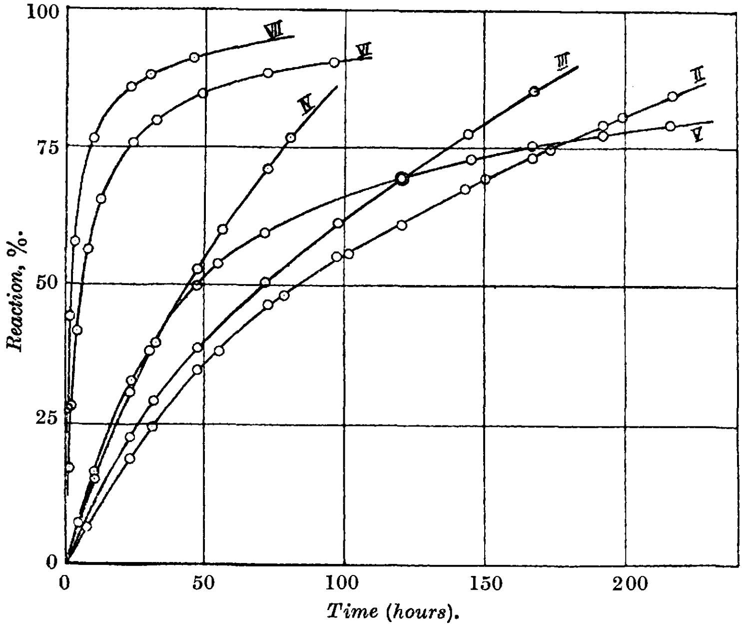
$[HBr]/[Br_2] = 2·90$.

t.	*x*.	*k*.
0·8	7·67	6·54
1·6	13·93	6·37
3·0	22·53	6·09
6·0	35·40	5·75
10·0	47·03	5·59
24·0	65·00	4·87

X.

$T = 18°$; $a = M/63$; $w = 5·36$. $[HCl]/[Br_2] = 2·90$.

t.	x.	k.
0·2	8·11	27·8
0·5	15·47	23·1
0·8	21·28	21·3
1·5	30·40	18·4
3·6	45·74	14·7
5·5	53·37	13·1



of water in the solvent. In series VIII, IX, and X, the effects of added hydrogen bromide and hydrogen chloride are shown. Only sufficient values of *k* are given to indicate how the main reaction is influenced by the side reactions, but all the experimental data for series II—VII are shown graphically in the figure.

In conclusion, the author wishes to express his gratitude to Professor T. C. James for much helpful advice and criticism during this investigation.

THE EDWARD DAVIES CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH.

[*Received, February 5th*, 1932.]