CXXXII.—*The Addition of Halogens to Unsaturated Acids and Esters. Part III. The Velocity of Bromine-addition.*

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WILLIAMS and JAMES (J., 1928, 343) showed that addition of bromine to unsaturated acids and esters in the dark in non-hydroxylic solvents, such as carbon tetrachloride and chloroform, was an autocatalytic reaction, and adduced evidence that the catalyst was hydrogen bromide. Davis (*J. Amer. Chem. Soc.*, 1928, **50**, 2769) suggested that bromine-addition in the dark to olefins in carbon tetrachloride proceeded mainly through the medium of a bromine hydrate because the reaction velocity increased as the temperature was lowered from 25° to 0°. Further, the same thermal reaction was studied by Meyer and Pukall (*Z. physikal. Chem.*, 1929, **145**, 360) for the case of cinnamic acid in chloroform; here, again, the reaction was autocatalytic, and it was suggested that the catalyst was produced by the action of bromine on the solvent and that the rapidity of the photobromination was due to the rapid production of the catalyst under the influence of light rays.

The present communication is an attempt to investigate systematically the effect of constitutional differences on the velocity of bromine-addition to unsaturated acids and methyl esters. The latter were used chiefly in those cases in which the acids were insoluble in the two solvents, and where comparison was possible, the ester was found to react slightly less readily than the acid. The addition was invariably more rapid in chloroform than in carbon tetrachloride, and hence, where choice was possible, the former was used for the slow and the latter for the rapid reactions. Solutions of purified bromine in either of the purified solvents can be kept in the dark for long periods without any deterioration, so the explanation of Meyer and Pukall does not seem to apply to the dark reaction.

The rate of addition to both forms of *o*-methoxycinnamic acid is several hundred times greater than to cinnamic acid, the velocity diminishing more rapidly than would be expected for a bimolecular reaction (Williams and James, *loc. cit.*). This work has now been extended to include the methyl esters of *m*- and *p*-methoxycinnamic acids, and the reaction velocities are all of the same order of magnitude. The attachment of the strongly activating methoxyl group to the nucleus greatly intensifies the rate of nuclear substitution, and hence it seems that the enhanced rate of reaction is due to the ease with which hydrogen bromide is produced. This suggestion is in accordance with the observations of Davies and Davies (J., 1928, 602) and of Reimer and Tobin (*J. Amer. Chem. Soc.*, 1930, **52**, 341), that addition of bromine respectively to *m*-methoxycinnamic acid and to 2 : 4-dimethoxycinnamic acid always results in considerable substitution in the nucleus. It was anticipated that a nuclear deactivating group directly attached to the nucleus in cinnamic acid would have the converse effect, decreasing the rate of addition and causing a long inhibition period. This expectation has been realised, for the nitro-group in the methyl esters of *o*-, *m*-, and *p*-nitrocinnamic acids was found to have the anticipated effects on the velocity of addition of bromine. Further, the inhibition periods vanished when hydrogen bromide was added initially as a catalyst.

Halogen atoms attached to the carbon atoms of the double linkage show interesting contrasts, for an α-halogen atom completely inhibits addition, even in the presence of hydrogen bromide, while a β-halogen atom does not noticeably affect the rate. Although no other substituents in these positions have yet been studied, it is clear that the character of the groups attached to the doubly linked carbon atoms is an important factor in determining the rate.

Comparison of rates of addition to a number of *cis*- and *trans*-isomerides has shown that in every case addition of bromine to the *cis*-form occurs more readily, but the difference in rate varies considerably from pair to pair. An important fact relating to this point was discovered by the study of methyl fumarate and methyl maleate. Neither of these esters reacts with bromine in the dark in carbon tetrachloride at 18°. The fumarate is perfectly stable towards bromine even if heated in sealed tubes at 100° for several days, but the maleate is not so inactive at high temperatures : being an oil at ordinary temperature, it is more difficult to purify, and probably its impurities, by producing traces of hydrogen bromide, cause it to react slowly with bromine. In the presence of hydrogen bromide, the fumarate reacts with bromine very slowly, but the maleate reacts very rapidly and an apparent equilibrium is attained, after which the reaction is exceedingly slow. This is probably due to the fact that a proportion of the maleate is converted into the fumarate under the influence of hydrogen bromide, concurrently with the addition. This shows that a third factor influencing the rate of addition is the rate of conversion of the unstable or *cis*-form into the stable or *trans*-form, and this seems to point to the existence of the same intermediate form in the conversion and in the addition. The same conclusion was reached by Schmidt (*Z. physikal. Chem.*, 1928, *B*, **1**, 205) as regards the photochemical action of bromine on methyl maleate and methyl fumarate.

EXPERIMENTAL.

Exactly the same methods of purification of bromine and solvents were adopted as in the previous work. The solid esters were repeatedly recrystallised, and the liquid esters were twice redistilled under reduced pressure. The methyl maleate on standing for a few weeks deposited crystals of the fumarate, and since the presence of the latter does not interfere with the bromination of the former, a saturated solution of the fumarate in the maleate at 13° was used. This solution, as shown by the melting-point curve of mixtures of the two esters (Schmidt, *loc. cit.*), contains 4% of fumarate.

The procedure for the velocity measurements was modified accordingly as the reaction was rapid or slow. Equal volumes of *M*/30-solutions of the substance and of bromine at 0° were mixed either in well-stoppered brown bottles or in tubes, and the latter were at once sealed in a very faint red light. The vessels were then kept at 0° in the dark for the required period, the reaction being stopped either by adding excess of potassium iodide solution or by breaking the bulb under the solution. A definite volume (excess) of standard sodium thiosulphate solution was then added, the whole shaken until colourless, and the excess thiosulphate titrated against *N*/50-iodine solution.

In studying the catalytic effect of hydrogen bromide, definite volumes of a solution of the carefully dried gas in the solvent were added to the reaction mixture, a separate bottle being used for each determination. The concentration of the hydrogen bromide solution was determined either by titration with baryta or by precipitation as silver bromide. The catalytic effect on the addition of bromine to methyl maleate was so great that the best results were obtained by mixing 100 c.c. of each reacting solution in a large brown bottle, adding a definite volume of hydrogen bromide solution, and withdrawing samples of 20 c.c. for analysis at definite intervals.

The velocity measurements are summarised in the following tables. Since in no case was the reaction bimolecular in the absence of added hydrogen bromide, no velocity coefficients are given. For a comparison of rates, the approximate inhibition period and the time for 25% change are given, time being in hours throughout.

Table I shows the influence on the rate of the nitro- and methoxy-groups attached to the nucleus. The position of the substituent in the ring is a secondary factor compared with its nature. It will be seen that both types of addition, (*a*) and (*b*), are considerably accelerated by hydrogen bromide.

TABLE I.

	Without initial HBr.		With initial HBr.	
Isomeride.	Inhibition period.	Time for 25% change.	$[HBr]/[Br_2]$.	Time for 25% change.
(*a*) Methyl nitrocinnamates. Solvent, $CHCl_3$. Temp., 0°.				
ortho	*ca.* 60	750	0·758	155
meta	*ca.* 50	540	0·758	230
para	*ca.* 50	390	0·758	120
(*b*) Methyl methoxycinnamates. Solvent, CCl_4. Temp., 0°.				
ortho	—	2·7	0·053	2·1
meta	—	21·0	0·432	0·22
para	—	0·1	0·204	0·01

In Table II are given the rates of addition to various pairs of *cis*- and *trans*-isomerides, including the α and β-halogen-substituted cinnamic acids. The *cis*-acid is in every case the more reactive, and the effect of the position of the halogen atom is clearly indicated.

TABLE II.

Temperature, 0°.

Substance.	Solvent.	Inhibition period.	Time for 25% change.
trans-Cinnamic acid	CCl_4	*ca.* 22	135
cis- „ „	CCl_4	*ca.* 7	35
trans-β-Bromocinnamic acid	$CHCl_3$	*ca.* 25	280
cis- „ „	$CHCl_3$	*ca.* 5	250
trans-β-Chlorocinnamic acid	$CHCl_3$	*ca.* 25	200
cis- „ „	$CHCl_3$	*ca.* 4	210
trans-*o*-Methoxycinnamic acid	$CHCl_3$	—	0·05
cis- „ „	$CHCl_3$	—	0·02
Methyl *trans*-*o*-methoxycinnamate	CCl_4	—	2·1
Methyl *cis*- „ „	CCl_4	—	0·40
α-Bromocinnamic acid (both forms) α-Chlorocinnamic acid (both forms) αβ-Dibromocinnamic acid (both forms) β-Chloro-α-bromocinnamic acid (both forms)	Do not react to a measurable extent with bromine at 0° in either solvent, even under the influence of hydrogen bromide.		

The velocity measurements with methyl maleate and methyl fumarate were conducted in carbon tetrachloride in a thermostat at 18°. No addition took place to either of the esters unless hydrogen bromide was added, whereupon the two esters exhibited widely different rates of reaction. In Table III are given the periods for 50% change with the maleate for different amounts of the catalyst, and also the position of equilibrium, which shows the percentage change into the fumarate.

TABLE III.

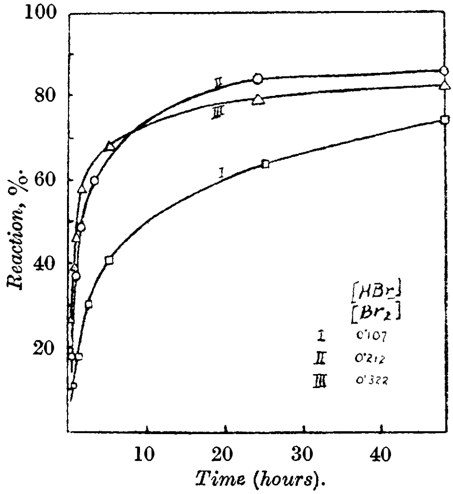
Solvent, CCl_4. Temp., 18°.

(*a*) Methyl maleate.

$[HBr]/[Br_2]$.	Time for 50% change.	Percentage change at equilibrium.
0·107	9·5	—
0·212	1·6	85·4
0·322	0·95	81·5
	(*b*) Methyl fumarate.	
0·52	9% of the bromine had reacted in 400 hours.	

The actual figures obtained for the maleate are plotted in Fig. 1, in which it is shown that when the concentration of the catalyst is small, the reaction reaches an equilibrium very slowly.

FIG. 1.



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