236. *The Kinetics of Halogen Addition to Unsaturated Compounds. Part IX. Nitrocinnamic Acids.*

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The rates of electrophilic addition of chlorine to the methyl nitrocinnamates have been measured in acetic acid solution. Those of HBr_3 addition to these esters in chloroform solution, and to the acids in acetic acid solution, have also been investigated. The relative velocity order, *m* > *p* > *o*, remains the same for each type of reaction, and the results are discussed with reference to electronic theory.

The rates of bromine addition to cinnamic acid and its derivatives have been reported by various observers (Sudborough, J., 1910, **97**, 715, 2450; Williams and James, J., 1928, 343; Hanson and James, J., 1928, 1955, 2982; Hanson and Williams, J., 1930, 1059; Robinson and James, J., 1933, 1453; Jones and James, J., 1935, 1600). These measurements, however, were for the most part in carbon tetrachloride or chloroform solution, and in these solvents the reactions tend to be slow and are frequently autocatalytic. The establishment of the reaction mechanisms for halogen addition to the αβ-olefinic acids (Part V, this vol., p. 129) has led to the examination of the nitrocinnamic acids, and their more soluble methyl esters, under conditions for which the reaction mechanism is known.

Chlorine addition to αβ-olefinic acids in acetic acid solution proceeds by an electrophilic mechanism. The following are the bimolecular rates of addition of chlorine to methyl cinnamate and its nitro-derivatives in acetic acid at 24° :

Methyl cinnamate.	*m*-NO_2.	*p*-NO_2.	*o*-NO_2.
10·0	0·011	0·0049	0·0011

There is the expected reduction in rate due to the electron-attracting nitro-group, and this effect is greater in the *p*- than in the *m*-position, where the inductive effect only operates. The still slower rate for the *o*-compound is attributed to steric hindrance. According to the theory proposed by Roberts and Kimball (*J. Amer. Chem. Soc.*, 1937, **59**, 947) to explain *trans*-halogen addition to ethylenic compounds, the addition of the second halogen atom involves a steric (Walden) inversion, for this type of compound, at the β-carbon atom of the system. This inversion is hindered, but not prevented, by an *o*-nitrophenyl group in the β-position. The possibility of such stereo-hindrance has been discussed by Willstaedt (*Ber.*, 1931, **64**, 2688) for the halogenocinnamic acids : *o*-chlorocinnamic acid adds bromine more slowly than its *p*-isomer, and in the *o*-compounds the rate sequence is F > Cl > Br > I. These observations, however, were approximate only, as the measurements were carried out in saturated solutions in presence of the solid phase. This type of steric hindrance becomes especially evident in a compound such as coumarin, owing to the locking caused by the ring structure. The low rate of addition of bromine to coumarin has been reported, and is now confirmed for addition of chlorine in acetic acid solution (cinnamic acid, k_2 at 24° = 6·2; coumarin, k_2 at 24° = 0·0030).

With phenylpropiolic acid derivatives such steric hindrance is not to be expected, and this is confirmed by the small rate difference between the potassium nitrophenylpropiolates for iodine addition in alcoholic solution: $k_2\ (p) = 4{\cdot}9 \times 10^{-4}$; $k_2\ (o) = 6{\cdot}4 \times 10^{-4}$ (James and Sudborough, J., 1907, **91**, 1037). In a related reaction that requires electron accession at the point of attack, *viz.*, chlorine substitution of the nitrodiphenyls, there is likewise no expectation of steric hindrance for the *o*-compound, and its rate is approximately the same as that for its *p*-isomer. This is shown by the following bimolecular rates; the value for diphenyl is included for comparison, and in the two electrophilic reactions, substitution of chlorine in the diphenyls and addition of chlorine to the cinnamic acids, the influence of the *p*-nitro-group is of the same general order.

	Ph·Ph.	$Ph{\cdot}C_6H_4{\cdot}NO_2(p)$.	$Ph{\cdot}C_6H_4{\cdot}NO_2(o)$.
k_2 ($HOAc,H_2O$ 10%) 24°	1·5	0·0029	0·0022

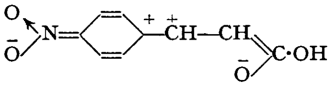
The mechanism of HBr_3 addition to αβ-olefinic acids appears to be electrophilic when there is considerable electron accession to the ethylene link, as in ββ-dimethylacrylic acid, and nucleophilic when such electron accession becomes small, as in acrylic acid. For compounds of the second type, addition of bromine is slow and that of HBr_3 relatively rapid, so that hydrogen bromide acts as a catalyst for the former addition. The nitrocinnamic acids, owing to the electron attraction of the nitro-group, should behave like acrylic acid, and correspondingly show marked catalysis by hydrobromic acid, whereas for cinnamic acid itself the catalysis should be relatively small. This is experimentally found, and the following bimolecular rates have been obtained for M/30-reactants + 0·015M-HBr in chloroform solution:

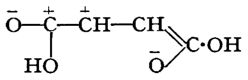
	Methyl cinnamate.	*m*-NO_2.	*p*-NO_2.	*o*-NO_2.
k_2 (24°)	0·033	0·0076	0·0041	0·00081

As in the electrophilic addition of chlorine, there seems to be a steric effect for the *o*-compound, and the rate order *m* > *p* remains the same for both modes of reaction. A further comparison shows that the nitrocinnamic acids have a lower nucleophilic rate than acrylic acid, as is seen from the values for HBr_3 addition, *i.e.*, M/80-reactants + M/80-HBr in acetic acid solution:

	$CH_2{:}CH{\cdot}CO_2H$.	*m*-$NO_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$.	*p*-$NO_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$.
k_2 (24°)	0·44	0·0057	0·0033

These rates are for the *trans*-stereoisomers, whereas a stricter comparison would be one between acrylic acid and the *cis*-compounds. If such a comparison were made (the ratio for HBr_3 addition to maleic and to fumaric acid is 15 : 1) the nucleophilic rate for the *cis*-nitrocinnamic acids must still be considerably less than that of acrylic acid. This effect can be explained by electronic considerations. The conjunction of


(I.)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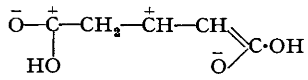
(III.)

the two electron-attracting groups involves an unfavourable resonance structure (I) having adjacent polarities, with the consequence that the likelihood of nucleophilic attack on the β-carbon atom is reduced. Consequently, the β-nitrophenyl derivatives have a lower nucleophilic rate than acrylic acid, and the *p*-nitro-compound reacts more slowly than the *m*-isomer.

Similar considerations explain the magnitude of the nucleophilic rates of HBr_3 addition to the dibasic unsaturated acids, reported previously (this vol., p. 129), but only partly discussed. There is a similar unfavourable structure (II) for maleic acid, whose HBr_3 addition rate ($\frac{1}{2}k_2 = 0{\cdot}13$, the half rate being comparable as there are two symmetric points of attack) is lower than that of acrylic acid ($k_2 = 0{\cdot}50$). On the other hand, *trans*-glutaconic acid ($k_2 = 0{\cdot}090$), for which adjacent polarities are not established (III), has a higher rate than *trans*-crotonic acid ($k_2 = 0{\cdot}051$) for HBr_3 addition.

The electron-repelling methyl group increases the rate of electrophilic addition in accordance with theory, and the relative effects of methyl and the nitro-group are shown by a comparison of the compounds, *p*-$C_6H_4X{\cdot}CH{:}CH{\cdot}CO_2H$:

X:	Me.	H.	NO_2.
Cl_2 addition, rel. rates	16	1	0·0005

EXPERIMENTAL.

The compounds used were methyl nitrocinnamates, *o*-, m. p. 72°, *m*-, m. p. 125°, *p*-, m. p. 160°; nitrocinnamic acids, *m*-, m. p. 195°, *p*-, m. p. 284°; *p*-methylcinnamic acid, m. p. 194°; cinnamic acid, m. p. 134°; methyl cinnamate, m. p. 34°. The solvents, acetic acid and chloroform, and reagents, bromine and chlorine, were purified as previously described.

For the fast additions of chlorine the modified procedure for volatility correction (J., 1943, 279) was employed. The following values in acetic acid solution at 24° are from curves relating addition % (x) to time (mins.): methyl cinnamate, M/20, $x = 50$, $t = 2{\cdot}0$, $k_2 = 10{\cdot}0$; ethyl cinnamate, M/20, $x = 50$, $t = 2{\cdot}0$, $k_2 = 10{\cdot}0$; cinnamic acid, M/40, $x = 50$, $t = 6{\cdot}0$, $k_2 = 6{\cdot}6$ (earlier value 6·2; J., 1939, 1511); phenylpropiolic acid, M/40, $x = 50$, $t = 17{\cdot}0$, $k_2 = 2{\cdot}4$ (showing that addition of chlorine, like that of bromine, to phenylpropiolic acid is slower than to *trans*-cinnamic acid, and still slower than to *cis*-cinnamic acid, $k_2 = 21$). Addition of chlorine to *o*-nitrophenylpropiolic acid, like that of bromine to propylpropiolic acid, is accompanied by polymerisation. *p*-Methylcinnamic acid, $x =$ (*a*) 55, (*b*) 58, $t = 0{\cdot}50$, $k_2 = 103$.

In the slow additions of chlorine the reaction vessel was opened only once, the experimental results for the methyl nitrocinnamates in acetic acid at 24° being, for M/20-reactants :

m-NO_2 .... (*a*) $t = 180$, $x = 9{\cdot}5$ (*b*) $t = 300$, $x = 13{\cdot}7$
p-NO_2 .... (*a*) $t = 240$, $x = 6{\cdot}0$ (*b*) $t = 360$, $x = 7{\cdot}7$
o-NO_2 .... (*a*) $t = 240$, $x = 2{\cdot}0$ (*b*) $t = 1440$, $x = 7{\cdot}5$

Measurements of the rates of HBr_3 addition to the methyl nitrocinnamates were made by Hanson and Williams (*loc. cit.*) in chloroform solution at 0° [$x = 25$; times (hours), *m*- 230, *p*- 120, *o*- 155] but no reference was made to the possibility of loss by volatility. We have found that solutions of hydrogen bromide in chloroform very readily lose hydrogen bromide—as much as 50% on dropping from a pipette into the reaction vessel. The method of experiment adopted was to make up reaction mixture from 2 ml. of M/10-methyl nitrocinnamate, 2 ml. of 0·045M-hydrogen bromide (stock solution tested before experiment) delivered with the pipette ***under*** the surface of the liquid, and finally 2 ml. of M/10-bromine. The reaction vessel (stopper specially ground until no volatility loss could be detected) was opened only once, and, after addition of potassium iodide, the total contents were titrated with sodium thiosulphate. Both sets of experiments (*a*) and (*b*) were started together in each case.

Methyl cinnamate .... (*a*) $t = 120$; $x = 10{\cdot}0$ (*b*) $t = 360$, $x = 31{\cdot}4$
m-NO_2 .... (*a*) $t = 720$, $x = 14{\cdot}0$ (*b*) $t = 1440$, $x = 28{\cdot}9$
p-NO_2 .... (*a*) $t = 1440$; $x = 17{\cdot}0$ (*b*) $t = 1440$, $x = 17{\cdot}5$
o-NO_2 .... (*a*) $t = 1440$, $x = 4{\cdot}0$ (*b*) $t = 2880$, $x = 7{\cdot}6$

A similar technique was employed for measurements of HBr_3 addition to the nitrocinnamic acids in acetic acid at 24°, the acid, bromine, and hydrogen bromide all being M/80 :

m-NO_2 .... (*a*) $t = 1800$, $x = 11{\cdot}5$ (*b*) $t = 3420$, $x = 19{\cdot}1$
p-NO_2 .... (*a*) $t = 1800$, $x = 6{\cdot}3$ (*b*) $t = 3420$, $x = 11{\cdot}7$

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