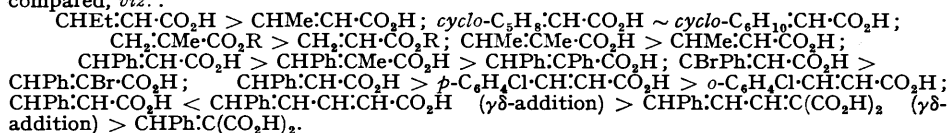### 336. *The Kinetics of Halogen Addition. Part XVI.* αβ-*Ethylenic Acids.*

By D. A. Evans, T. R. Watson, and P. W. Robertson.

Certain new compounds have been investigated, and rates of electrophilic halogen addition compared, *viz.* :

$CHEt{:}CH{\cdot}CO_2H > CHMe{:}CH{\cdot}CO_2H$; $cyclo\text{-}C_5H_8{:}CH{\cdot}CO_2H \sim cyclo\text{-}C_6H_{10}{:}CH{\cdot}CO_2H$;
$CH_2{:}CMe{\cdot}CO_2R > CH_2{:}CH{\cdot}CO_2R$; $CHMe{:}CMe{\cdot}CO_2H > CHMe{:}CH{\cdot}CO_2H$;
$CHPh{:}CH{\cdot}CO_2H > CHPh{:}CMe{\cdot}CO_2H > CHPh{:}CPh{\cdot}CO_2H$; $CBrPh{:}CH{\cdot}CO_2H >$
$CHPh{:}CBr{\cdot}CO_2H$; $CHPh{:}CH{\cdot}CO_2H > p\text{-}C_6H_4Cl{\cdot}CH{:}CH{\cdot}CO_2H > o\text{-}C_6H_4Cl{\cdot}CH{:}CH{\cdot}CO_2H$;
$CHPh{:}CH{\cdot}CO_2H < CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO_2H$ (γδ-addition) $> CHPh{:}CH{\cdot}CH{:}C(CO_2H)_2$ (γδ-addition) $> CHPh{:}C(CO_2H)_2$.

Also certain nucleophilic rates of bromine addition in the presence of hydrogen bromide have been compared, *viz.* : $CH_2{:}CH{\cdot}CO_2R > CH_2{:}CMe{\cdot}CO_2R$; $CHPh{:}CH{\cdot}CH{:}C(CO_2H)_2$ (αβ-addition) $\sim CHPh{:}C(CO_2H)_2$.

CERTAIN αβ-unsaturated acids have already been investigated and their kinetics of halogen addition discussed in earlier papers in this series; they include acrylic, crotonic, and ββ-di-

methylacrylic acids, cinnamic acid and its methyl and nitro-derivatives, and the dibasic acids, maleic, fumaric, citraconic, mesaconic, glutaconic, and β-methylglutaconic (*J.*, 1945, 129, 891). The carboxyl group, by its combined inductive and tautomeric effects, has a deactivating influence on electrophilic reactivity, but, on the other hand, if the electronic flow towards the ethylenic link is not considerable, it can cause compounds to react by the nucleophilic mechanism, for example when hydrogen tribomide is the reagent. It is inferior to the more strongly electron-attracting aldehyde group, which in general confers on compounds a lower electrophilic and a higher nucleophilic reactivity (*J.*, 1945, 888). These investigations are now extended to include certain other αβ-unsaturated acids, which have been examined for special reasons. The velocities quoted are second-order rate coefficients, k_2 (min.$^{-1}$ g.-mol.$^{-1}$ l.).

β-*Methyl- and* β-*Ethyl-acrylic Acids.*—These compounds were compared with reference to the relative effectiveness of the electron-contributing alkyl groups. The following rates were found for electrophilic bromine addition in 25% aqueous acetic acid solution at 25°, the reactants being M/40 :

	CHMe:CH·CO₂H.	CHEt:CH·CO₂H.
k_2	0·74	1·1
k_2 (+ M/5-H₂SO₄)	0·62	0·92

Owing to the slight dissociation of the acids in the mixed solvent the rates are increased as a result of the superior reactivity of the unsaturated anion (cf. *J.*, 1937, 341). Sulphuric acid represses this ionisation, and the rates for the undissociated acids are thus obtained. The relative reactivities due to the two alkyls, Et 1·5 times Me, may be compared with the values for the alkylbenzenes for chlorination, Me 1·2 times Et (*J.*, 1943, 279), and the values for phenyl ethers, Et twice Me (cf. Bradfield and Jones, *Trans. Faraday Soc.*, 1941, 37, 743). In this last mode of reaction, *i.e.*, in a compound such as anisole, an inductive effect only is possible, and in the other two reactions combined inductive and hyperconjugation effects are in operation. In the alkylacrylic acids the inductive effect is relatively more important than hyperconjugation, and the reverse is true for the alkylbenzenes. This is in accordance with expectation as the inductive effect is short-range and should therefore operate more powerfully in an ethylene than in a larger benzene molecule. A similar conclusion has been reached from measurements of the electronic spectra of ethylenic and aromatic hydrocarbons (for discussion, cf. Walsh, *Annual Reports*, 1947, 32).

The nucleophilic rates of the two acids were also measured, reactants being M/40 with M/5-hydrogen bromide at 25° : for β-ethylacrylic acid k_2 = 0·073, and for β-methylacrylic acid k_2 = 0·054, in acetic acid solution. The reactivities remain in the electrophilic order, as sometimes happens (cf. *J.*, 1945, 888 : 1948, 980), since the two stages of the nucleophilic reaction have opposing electronic requirements.

cyclo*Pentylidene- and* cyclo*Hexylidene-acetic Acids.*—These two compounds were examined as part of a more general investigation of the influence of steric factors on the rate of halogen addition. Rates of bromine addition were measured in acetic acid at 25°, and are now given as second-order coefficients for M/40-reactants :

$$
\begin{array}{cccc}
\underset{\text{CH}_3}{\overset{\text{CH}_3}{>}}\text{C=CH·CO}_2\text{H} & \text{CH}\!\!<\!\!\underset{\text{CH}_2-\text{CH}_2}{\overset{\text{CH}_2-\text{CH}_2}{>}}\text{C=CH·CO}_2\text{H} & \underset{\text{CH}_2-\text{CH}_2}{\overset{\text{CH}_2-\text{CH}_2}{|}}\!\!>\!\!\text{C=CH·CO}_2\text{H}
\end{array}
$$

k_2 (x = 50)   0·28   1·65   1·96

There is therefore no evidence that halogenation of these compounds is sterically hindered. A corresponding difference, indicating also a greater electron-repelling power of the cyclic group than of ββ-dimethyl, is shown by reference to the dissociation constants : cyclohexyl-ideneacetic acid, K = 0·26 × 10^{-6}; dimethylacrylic acid, K = 2·2 × 10^{-6}.

Acrylic and α-*Methylacrylic Esters.*—These compounds were examined to discover the influence of the α-methyl group on the electrophilic and nucleophilic rates, which were measured in acetic, acid solution at 25°.

	CH₂:CH·CO₂Et.	CH₂:CMe·CO₂Me.*
k_2 (Cl₂)	0·056	3·4
k_2 (HBr₂)	0·42	0·165

* Me and Et esters of other αβ-unsaturated acids show only slightly differing rates.

An approximately 60-fold increase in velocity is caused by the α-methyl group, and the order of the nucleophilic is the reverse of that of the electrophilic reactivity, as similarly found for related compounds (*J.*, 1945, 129).

Crotonic and Tiglic Acids.—For these two compounds also the influence of an α-methyl group is to cause a considerable (60-fold) increase in the electrophilic rate of chlorine addition in acetic acid at 25° :

	CHMe:CH·CO$_2$H.	CHMe:CMe·CO$_2$H.
k_2 (Cl$_2$)	0·62	36
k_2 (Br$_2$) (+ LiBr)	0·069	0·22

The bromine rates are for M/40-reactants, with M/40-sodium acetate and M/10-lithium bromide, and are less spaced than the values for chlorine addition owing to a contribution from a nucleophilic rate in the crotonic acid reaction.

Cinnamic Acid, its α-Methyl and α-Phenyl Derivatives.—The rates of chlorine addition have been measured in acetic acid at 25°.

	CHPh:CH·CO$_2$H.	CHPh:CMe·CO$_2$H.	CHPh:CPh·CO$_2$H.
k_2	5·0	3·0	0·36

The influence of the α-methyl group, in contrast with that for the preceding compounds, is to reduce the electrophilic rate. The methyl thus acts as if it lessened the $+T$ influence of the phenyl. The α-phenyl group would be expected to act in a similar manner and, as it also exerts a $-T$ effect in this position, the rate for α-phenylcinnamic acid is lower than that of α-methylcinnamic acid.

α- and β-Bromocinnamic Acids.—When attached to an ethylenic carbon atom, a halogen may exert a $+T$, $-I$ effect as in a compound such as CHBr:CH$_2$, or a $-I$ effect only, when the electrophilic attack is on the carbon to which the halogen is attached, as in CHPh:CHBr. The deactivating influence of the bromine atom in such compounds is considerable, and there is a large rate reduction in comparison with the unsubstituted compound. Similar effects are apparent with the two compounds now under consideration, although the deactivation is smaller; the following are rates of chlorine addition in acetic acid at 25° :

	CHPh:CH·CO$_2$H.	CBrPh:CH·CO$_2$H.	CHPh:CBr·CO$_2$H.
k_2	5·0	0·21	0·0077

p- and o-Chlorocinnamic Acids.—The following rates of chlorine and bromine addition have been measured in acetic acid at 25°; in the bromine additions the reactants were M/40, with M/40-sodium acetate, and in the catalysed reactions, the lithium bromide was at M/10 :

	CHPh·CH:CO$_2$H.	p-C$_6$H$_4$Cl·CH:CH·CO$_2$H.	o-C$_6$H$_4$Cl·CH:CH·CO$_2$H.
k_2 (Cl$_2$)	5·0	2·5	0·27
k_2 (Br$_2$)	0·080	0·036	0·0041
k_2 (Br$_2$) (+ LiBr)	0·074	0·045	0·014

The electrophilic rates of chlorine addition may be compared with the rates, under the same conditions, of the benzylideneacetophenones, CHPh:CH·COPh ($k_2 = 60$) and its p- ($k_2 = 23$) and o-chloro-derivatives ($k_2 = 1·8$) (cf. *J.*, 1948, 980). The $+T$, $-I$ effects of the chlorine atom tend to balance each other in the *para*-position, but in the *ortho*-position the deactivating influence of the chlorine becomes superior. Similarly o-nitrocinnamic acid was found to add chlorine at a slower rate than did its *para*-isomer (*J.*, 1945, 891). As the second stage of halogen addition involves a Walden-like inversion, it was suggested that there might be a steric effect in such cases. There is, however, gradually accumulating evidence that such steric hindrance does not operate in these reactions.

The rates of bromine addition in the presence of sodium acetate are in the same ratio as the rates of chlorine addition, *i.e.*, the reactions with bromine also proceed by the electrophilic mechanism. Whereas lithium bromide reduces the rate for cinnamic acid (the catalytic effect of the Br$^-$ ion being obscured by LiBr$_3$ formation), it causes an increase in rate for the chlorocinnamic acids, in which compounds the chlorophenyl group exerts a $-I$ as well as a $+T$ effect. According to the classification of modes of catalysis by electrolytes in acetic acid solution (*J.*, 1949, 294), cinnamic acid belongs to Class I, and the chlorocinnamic acids to Class II, and for all three compounds lithium chloride is found to be superior to lithium bromide as a catalyst.

Cinnamylidene-acetic and -malonic Acids.—The rates of bromine addition to these two compounds are compared with the values for cinnamic and benzylidenemalonic acids, reactants

being M/80 in the presence of sodium acetate to eliminate any acid-catalysed nucleophilic addition, in acetic acid at 25° :

$$CHPh{=}CH{\cdot}CH{=}CH{\cdot}CO_2H.$$
(I.)

$$CHPh{=}CH{\cdot}CO_2H.$$
(II.)

k_2 ($x = 20$) 200   0·040

$$CHPh{=}CH{\cdot}CH{=}C(CO_2H)_2.$$
(III.)

$$CHPh{=}C(CO_2H)_2.$$
(IV.)

k_2 ($x = 20$) .... 0·42   ~0·0004

The great reactivity of (I) compared with (II), and of (III) as compared with (IV), suggests that, in the compounds (I) and (III), electrophilic attack is initiated, as shown by the arrows, at the γ- rather than at the α-position, as found for the related compound $CHMe{:}CH{\cdot}CH{:}CH{\cdot}CO_2H$ by Ingold *et al.* (*J.*, 1934, 79). The claim by Hinrichson (*Annalen*, 1904, **336**, 168) that $\alpha\beta$-addition takes place with (III) seems to be based on insufficient evidence. The latter compound is less reactive than (I) because of the combined effect of the two carboxyl groups attached to the same carbon atom, and this deactivation becomes still greater in (IV).

In the presence of hydrogen bromide, nucleophilic reactions will proceed; but in compounds (I) and (II) their contribution is relatively small, especially in the case of (I), for which the electrophilic reaction, although reduced in rate somewhat by hydrogen bromide, is very rapid. For (III) [k_2 (HBr$_3$) = 44] and (IV)[k_2 (HBr$_3$) = 28], however, owing to the increased electron-attracting power of the two carboxyl groups acting in concert, the nucleophilic reactions become dominant. Since the phenyl group hinders nucleophilic attack on an adjacent carbon atom, and since the tautomeric effect of the carboxyl groups will become weakened by transmission through the CH:CH group, the initial nucleophilic attack on (III) is probably on the β- rather than on the δ-position. The use of different reagents might, therefore, enable the isolation of $\alpha\beta$- and $\gamma\delta$-addition products with bromine, but actually there are complications owing to secondary changes. On bromine addition in the presence of hydrogen bromide, the product was the compound $CHPh{:}CH{\cdot}CH{:}CBr{\cdot}CO_2H$, formed by loss of carbon dioxide and elimination of hydrogen bromide; in the presence of sodium acetate, the $\gamma\delta$-addition product is accompanied by the bromoacetate formed by the intervention of solvent molecules in the final (non-rate-determining) stage of electrophilic addition. However, Hinrichson (*loc. cit.*) has shown that there is $\gamma\delta$-addition to the ester in an aprotic solvent.

EXPERIMENTAL.

The following compounds were used in this investigation : a-methylcinnamic acid, m. p. 82°; a-phenylcinnamic acid, m. p. 172°; crotonic acid, m. p. 72°; tiglic acid, m. p. 64°; methyl crotonate, b. p. 121°/760 mm.; methyl a-methylacrylate, b. p. 100°/755 mm.; β-ethylacrylic acid, m. p. 8°, b. p. 108°/17 mm.; *cyclo*hexylideneacetic acid, m. p. 90—91°; *cyclo*pentylideneacetic acid, m. p. 52°; a-bromocinnamic acid, m. p. 128°; β-bromocinnamic acid, m. p. 134°; *o*-, m. p. 200°, and *p*-chlorocinnamic acid, m. p. 243°; cinnamylideneacetic acid, m. p. 165°; cinnamylidenemalonic acid, m. p. 208°.

As small differences in reactivity were involved for crotonic and β-ethylacrylic acids and the latter compound is liable to be contaminated with the very much more highly reactive $\beta\gamma$-unsaturated isomer, a special check was made on the purity of the β-ethylacrylic acid. After purification by the method given by Sudborough and Thomas (*J.*, 1911, 2314) and several recrystallisations from light petroleum, the liquid sample was cooled until about half had crystallised; the solid and the liquid fraction on separation had identical m. p.s. Similarly the purity of the *cyclo*pentylidene- and *cyclo*hexylideneacetic acids (which likewise tend to be contaminated with more reactive isomers) was especially tested. The purified specimens were crystallised from light petroleum, and after separation of the crystals the filtrate was evaporated to dryness; the two samples thus obtained had identical rates.

All measurements were made in duplicate in tightly stoppered bottles protected from light. Volatility corrections were applied to all chlorine reactions as previously described. The following are details of one of the measurements :

M/40-Tiglic acid + M/40-Br$_2$ + M/40-NaOAc in acetic acid at 25°; 1-ml. samples were titrated with N/80-sodium thiosulphate.

Time (mins.)	0	32·75	99·5	219·5;	0	17	66·3	197
Titre (ml.)	4·01	3·47	2·73	2·06;	4·01	3·73	3·04	2·12

From the separate curves : $x = 20$, $t = 54·5$; $x = 20$, $t = 56$.

Additional results are expressed as times (minutes) for $x\%$ of halogen absorption at 25° in acetic acid, unless otherwise shown :

M/80-CHPh:CPh·CO$_2$H + M/80-Cl$_2$, $x = 50$, $t = 226$. M/40-CHPh:CPh·CO$_2$H + M/40-Br$_2$: + M/40-NaOAc, $x = 20$, $t = 8330$; + M/10-LiCl, $x = 20$, $t = 2380$; + M/10-LiBr, $x = 20$, $t = 5560$. M/80 CHPh:CMe·CO$_2$H + M/80-Cl$_2$, $x = 50$, $t = 26·5$. M/40-CHPh:CMe·CO$_2$H + M/40-Br$_2$: + M/40-NaOAc,

$x = 50$, $t = 1905$; $+ \text{M}/10\text{-LiCl}$, $x = 50$, $t = 714$; $+ \text{M}/10\text{-LiBr}$, $x = 50$, $t = 1482$. $\text{M}/40\text{-}$CHMe:CH·CO$_2$H $+ \text{M}/40\text{-Br}_2$: $+ \text{M}/40\text{-NaOAc}$, $x = 20$, $t = 420$; $+ \text{M}/10\text{-LiCl}$, $x = 20$, $t = 114$; $+ \text{M}/10\text{-LiBr}$, $x = 20$, $t = 145$. $\text{M}/40\text{-CHEt:CH·CO}_2\text{H} + \text{M}/40\text{-Br}_2$ in HOAc : $+ 25\%$ of H$_2$O, $x = 50$, $t = 54$; $+ \text{M}/5\text{-H}_2\text{SO}_4$, $x = 50$, $t = 64$. $\text{M}/40\text{-CHMe:CH·CO}_2\text{H} + \text{M}/40\text{-Br}_2$, in HOAc : $+ 25\%$ of H$_2$O, $x = 50$, $t = 36·3$; $+ \text{M}/5\text{-H}_2\text{SO}_4$, $x = 50$, $t = 43·5$. $\text{M}/40\text{-CHMe:CMe·CO}_2\text{H} + \text{M}/40\text{-Cl}_2$, $x = 50$, $t = 1·1$. $\text{M}/40\text{-CHMe:CMe·CO}_2\text{H} + \text{M}/40\text{-Br}_2$: $+ \text{M}/40\text{-NaOAc}$, $x = 50$, $t = 220$; $+ \text{M}/10\text{-LiCl}$, $x = 50$, $t = 86$; $+ \text{M}/10\text{-LiBr}$, $x = 50$, $t = 197$. $\text{M}/40\text{-CH}_2\text{:CMe·CO}_2\text{Me}$: $+ \text{M}/40\text{-Br}_2 + \text{M}/5\text{-HBr}$, $x = 50$, $t = 234$; $+ \text{M}/40\text{-Cl}_2$, $x = 50$, $t = 11·7$. $\text{M}/40\text{-CHMe:CH·CO}_2\text{Me} + \text{M}/40\text{-Br}_2 + \text{M}/5\text{-HBr}$, $x = 20$, $t = 125$. $\text{M}/40\text{-}cyclo\text{Hexylideneacetic acid} + \text{M}/40\text{-Br}_2$, $x = 50$, $t = 30·5$. $\text{M}/40\text{-}cyclo\text{Pentylidene-acetic acid} + \text{M}/40\text{-Br}_2$, $x = 50$, $t = 28·8$. $\text{M}/40\text{-}\alpha\text{-Bromocinnamic acid} + \text{M}/40\text{-Cl}_2$, $x = 20$, $t = 1300$. $\text{M}/40\text{-}\beta\text{-Bromocinnamic acid}, + \text{M}/40\text{-Cl}_2$, $x = 20$, $t = 46$. $\text{M}/80\text{-}o\text{-Chlorocinnamic acid} + \text{M}/80\text{-Cl}_2$, $x = 20$, $t = 73$; $\text{M}/40\text{-}o\text{-chlorocinnamic acid} + \text{M}/40\text{-Br}_2$: $+ \text{M}/40\text{-NaOAc}$, $x = 20$, $t = 2450$; $+ \text{M}/10\text{-LiBr}$, $x = 10$, $t = 715$. $\text{M}/80\text{-}p\text{-Chlorocinnamic acid} + \text{M}/80\text{-Cl}_2$, $x = 20$, $t = 73$; $\text{M}/40\text{-}p\text{-chlorocinnamic acid} + \text{M}/40\text{-Br}_2$: $+ \text{M}/40\text{-NaOAc}$, $x = 20$, $t = 275$; $+ \text{M}/10\text{-LiBr}$, $x = 20$, $t = 223$. $\text{M}/80\text{-}$Cinnamylidenemalonic acid $+ \text{M}/80\text{-Br}_2 + \text{M}/80\text{-NaOAc}$, $x = 10$, $t = 47·5$. $\text{M}/80\text{-Cinnamylidenemalonic}$ acid $+ \text{M}/80\text{-Br}_2 + \text{M}/40\text{-HBr}$, $x = 20$, $t = 0·45$. $\text{M}/80\text{-Cinnamylideneacetic acid} + \text{M}/80\text{-Br}_2 + \text{M}/80\text{-}$NaOAc, $x = 20$, $t = 0·09$.

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