548. *The Kinetics of Halogen Addition to Unsaturated Compounds. Part XIX. The αβ-Ethylenic Nitriles.*

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The relative rates of electrophilic chlorine addition in acetic acid solution are in the order, $\mathrm{CHPh{:}CH{\cdot}CN} > \mathrm{CHMe{:}CH{\cdot}CN} > \mathrm{CH_2{:}CH{\cdot}CN}$, and $\mathrm{CHPh{:}CH{\cdot}CN} > \mathrm{CHPh{:}CPh{\cdot}CN}$, and with respect to other deactivating groups there is the series, $\mathrm{CHPh{:}CHBr} > \mathrm{CHPh{:}CH{\cdot}CO_2H} > \mathrm{CHPh{:}CH{\cdot}CHO} > \mathrm{CHPh{:}CH{\cdot}CN} \approx \mathrm{CHPh{:}CH{\cdot}NO_2}$. The compounds $\mathrm{CHR{:}CH{\cdot}CN}$ further add bromine by the nucleophilic acid-catalysed mechanism, and the relative rates with $\mathrm{HBr_3}$ are $\mathrm{CHMe{:}CH{\cdot}CN} > \mathrm{CHPh{:}CH{\cdot}CN}$, and $\mathrm{CHPh{:}CH{\cdot}CHO} > \mathrm{CHPh{:}CH{\cdot}CN} > \mathrm{CHPh{:}CH{\cdot}NO_2}$.

THERE appears to be no record of kinetic measurements of halogen addition to the acrylonitriles, except 1-phenylcinnamonitrile. This compound adds bromine in carbon tetrachloride solution extremely slowly in the dark, but in light the addition proceeds reversibly, giving an equilibrium which is independent of the intensity of the illumination (Berthoud and Nicolet, *J. Chim. physique*, 1928, 40). This reaction is of interest in that very few examples of reversible bromine addition at ordinary temperatures are known, and a reference to the influence of temperature on the equilibrium is made on p. 2835. It is, however, more especially the nature of thermal halogen addition which is the subject of this series of investigations. The cyanide group, attached to an ethylene carbon atom, by virtue of its considerable inductive and tautomeric effects ($-I$, $-T$, in Ingold's nomenclature) should have a powerful deactivating influence on electrophilic reactivity. This is revealed in the slow rates of chlorine addition in acetic acid solution at 25° to cinnamo-, crotono-, and acrylo-nitriles:

$\mathrm{CHPh{:}CH{\cdot}CN}$	$\mathrm{CHMe{\cdot}CH{:}CN}$	$\mathrm{CH_2{:}CH{\cdot}CN}$ *
$k_2 = 0{\cdot}022$	$k_2 = 0{\cdot}0017$	$k_2 \sim 0{\cdot}0001$

* In presence of sodium acetate to prevent polymerisation.

These rates are in the same order as those for the corresponding acids, and smaller by a factor of about 200. The deactivating influence of the cyano-group on chlorine addition, in comparison with certain other groups, is shown by reference to $\mathrm{CHPh{:}CHBr}$ ($k_2 = 30$) and $\mathrm{CHPh{:}CH{\cdot}NO_2}$ ($k_2 = 0{\cdot}020$). Whereas Br reduces the rate of chlorination of $\mathrm{CHPh{:}CHBr}$ by an inductive effect only, CN has a larger dipole moment and acts both by its inductive and by its mesomeric and electromeric effects, as seen from the large difference in rates between the bromide and the nitrile. The cyano- and nitro-groups have similar dipole moments, but in certain reactions behave as if the combined mesomeric and electromeric effects of the nitro-group were superior, as, *e.g.*, in the reactions of the *p*-bromonitrobenzene and *p*-bromocyanobenzene with alkali (Barnett and Levett, *J. Amer. Chem. Soc.*, 1948, **70**, 2778).

Whereas a single phenyl group attached to the ethylene system has an activating effect on halogen addition ($+T$), another phenyl on the second ethylene carbon acts reversely ($-T$), as discussed by Ingold and Ingold (*J.*, 1931, 2354) and experimentally confirmed in Part X of this series for the compounds $\mathrm{CHPh{:}CH_2}$ and $\mathrm{CHPh{:}CHPh}$ (*J.*, 1947, 628). A similar effect is to be expected in the compounds now under consideration, and rates of chlorine addition to cinnamonitrile and its 1-phenyl derivative are now given. The measurements, owing to the low reactivities in acetic acid, are made in 25% aqueous acetic acid (at 25°), and the arrow indicates the point of electrophilic attack:

$\mathrm{CHPh}\overset{\curvearrowright}{=}\mathrm{CH{\cdot}CN}$	$\mathrm{CHPh}\overset{\curvearrowright}{=}\mathrm{CPh{\cdot}CN}$
$k_2 = 2{\cdot}0$	$k_2 = 0{\cdot}27$

The reactions so far considered have been electrophilic in character. The acid-catalysed nucleophilic mode of halogen addition has been demonstrated for compounds containing $-T$ groups, such as CHO or $\mathrm{NO_2}$, and the CN group similarly should be capable of causing this type of reaction, as it is possible to form compounds of the type $\mathrm{\overset{\oplus}{C}HR{\cdot}CH{:}C{:}NH}$ by addition of a proton.

Perchloric acid in acetic acid solution was found to cause marked catalysis of bromine addition, as indicated by the initial rates for $\mathrm{CHPh{:}CH{\cdot}CN}$ (reactants M/40) at 25°:

$$k_2(\mathrm{NaOAc,\ M/40}) < 0{\cdot}0001 \qquad k_2(\mathrm{HClO_4,\ M/40}) > 0{\cdot}26$$

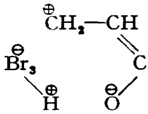
The rates for this compound with perchloric acid were not perfectly reproducible and moreover decreased considerably after the initial absorption, a behaviour apparently due to concomitant polymerisation. With excess of hydrogen bromide, however, *i.e.*, with $\mathrm{Br_3}^{\ominus}$ as the nucleophilic reagent, the bimolecular coefficients remained constant over the greater part of the addition, indicating the absence of a disturbing side reaction. With crotononitrile, on the other hand, there was a slight falling off in rate even when HBr_3 was the reagent, and this became more considerable for acrylonitrile. The following values of the initial rate were recorded in acetic acid at 25°, M/40-reactants, with M/5-HBr :

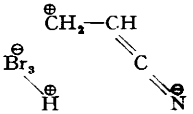
	CHPh:CH·CN	CHMe:CH·CN	CH_2:CH·CN
k_2, HBr_3 ($x = 20$)	4·1	5·7	~0·72

The rate for CHPh:CH·CN may be compared with the rates obtained under similar conditions with other compounds also containing strongly electron-attracting groups, *viz.*, CHPh:CH·CHO ($k_2 \sim 300$) and CHPh:CH·NO_2 ($k_2 = 0{\cdot}83$). Such nucleophilic rates, as pointed out in previous communications, being dependent on opposing electronic requirements, are not necessarily in the reverse order of the electrophilic rates of the compounds. It may be predicted, however, that when the electrophilic rate of chlorine addition to a compound is very low, owing to the influence of a group with a large $-T$ effect, the rate of bromine addition in the presence of hydrogen bromide will be considerably greater [*e.g.*, for CH_2:CH·CN, $k_2(Cl_2) \sim 0{\cdot}0001$, $k_2(HBr_3) \sim 0{\cdot}7$].

In earlier communications (*loc. cit.*) we have proposed the theory that, for compounds containing CHO and NO_2 groups, the reaction may proceed by way of 1 : 4-addition of HBr_3.

(I.)





(II.)

For such compounds, a one-stage process of this type is sterically possible (I), but for the αβ-unsaturated nitriles the linearity of the CH:C:N$^\ominus$ system keeps the attacked centres at a greater distance apart (II), and it seems more likely, therefore, that the addition process involves attack by H$^\oplus$ and $Br_3^\ominus$ in separate stages of the reaction, as is formulated in general terms in the following paper.

EXPERIMENTAL.

The following compounds were used in this investigation : cinnamonitrile, b. p. 255—257°/760 mm. ; crotononirile, b. p. 118—119°/757 mm. ; acrylonitrile (Light and Co.), b. p. 78°/757 mm. ; 1-phenylcinnamonitrile, m. p. 86°. The first three nitriles were purified by distillation immediately before use, as they tend to polymerise. The reactions were carried out in duplicate in tightly stoppered bottles in the dark ; for some of the slower reactions, sealed tubes were used. The following are details of a typical rate determination :

M/40-PhCH:CH·CN + M/40-Br_2 + M/5-HBr in acetic acid at 25° ;
1-ml. samples titrated with N/80-sodium thiosulphate.

Time (mins.) ...	0	3	6	9	12	16·5	0	1·2	3·2	7	10	20
Titre (ml.)	3·99	3·05	2·45	2·09	1·81	1·43	3·99	3·57	3·05	2·29	2·00	1·23

All the points lay on a smooth curve which gave constant k_2 values.

x (% addition)	10	20	30	40	50	60
k_2	4·1	4·1	4·1	4·1	4·05	4·1

Additional results are given as times (minutes) for $x = 20\%$ halogen addition, at 25°, in acetic acid, unless otherwise indicated :

M/40-CHPh:CH·CN + M/40-Br_2 + M/20-$HClO_4$, $t = 38$; M/40-CHPh:CH·CN + M/40-Cl_2, $t = 465$; M/80-CHPh:CH·CN + M/80-Cl_2 in acetic acid + 25% water, $t = 10$; M/40-CHMe:CH·CN + M/40-Cl_2, $t = 5640$; M/40-CHMe:CH·CN + M/40-Br_2 + M/5-HBr, $t = 1{\cdot}7$; M/40-CH_2:CH·CN + M/40-Br_2 + M/5-HBr, $t = 12{\cdot}5$; M/4-CH_2:CH·CN, + M/40-Cl_2 + M/40-NaOAc, $t = 13220$; M/40-CHPh:CPh·CN + M/40-Cl_2 + M/40-NaOAc, $t = 7130$; M/40-CHPh:CPh·CN + M/40-Cl_2, in acetic acid + 25% water, $t = 37$.

The influence of temperature on the equilibrium between 1-phenylcinnamonitrile and bromine was examined qualitatively. Sealed tubes of reactants, M/40 in carbon tetrachloride solution, were illuminated at 25° until attainment of equilibrium. One of these tubes was then illuminated at 0°, and a second at 50°, and kept at these temperatures for some days. The change in colour of the solutions was easily evident, the dissociation to yield bromine being greatest at 50° and least at 0°. On re-illumination at 25°, all the solutions regained the same tint, indicating the absence of concomitant polymerisation under these experimental conditions.

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