116. *The Kinetics of Halogen Addition to Unsaturated Compounds.*
Part X.   Styrene, Stilbene, and their Derivatives.

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The factors determining the relative rates of addition of bromine to styrene, dimethyl-styrene, and stilbene are discussed.   Addition to stilbene in acetic acid is decelerated by hydrogen bromide and catalysed only to a small extent by lithium chloride.   β-Nitrostyrene adds halogen by the electrophilic mechanism 10^6 times more slowly than styrene, and its rate of bromine addition in acetic acid is accelerated by sulphuric acid and very considerably by hydrogen bromide.   It thus resembles cinnamaldehyde, and a similar nucleophilic mechan-ism is possible for the two compounds.   Dinitrostilbene shows both a low electrophilic and a low nucleophilic rate of halogen addition.

Bromine addition to styrene has been measured by the competition method (Ingold and Ingold, *J.*, 1931, 2354), and the relative rates established, CHPh:CH₂ 3 >CHMe:CH₂.   The superiority of Ph to Me as an electron donor in electrophilic halogen addition was confirmed by direct kinetic measurement of the rates of chlorine addition to the compounds, CHPh:CH·CO₂H 9 >CHMe:CH·CO₂H (Part V, *J.*, 1945, 129).   Bauer and Moser (*Ber.*, 1907, **40**, 918) found that stilbene added bromine slowly in carbon tetrachloride and more rapidly in chloroform, without, however, making a detailed kinetic study of the reactions.   In methyl-alcoholic solution, addition of bromine becomes more rapid, the products being *s*.-dibromodibenzyl and α-bromo-β-methoxydibenzyl, and Meinel (*Annalen*, 1934, **510**, 219; 1935, **516**, 237) concluded that the brominating agent was MeOBr.   A comprehensive investigation of this reaction by Bartlett and Tarbell (*J. Amer. Chem. Soc.*, 1936, **58**, 466) revealed that the results were in accord with a mechanism of electrophilic attack by the bromine molecule.
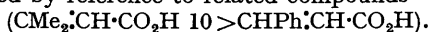
Styrene adds bromine in acetic acid solution at a rate too rapid for detailed kinetic measure-ment.   Substitution of a β-hydrogen atom in this compound by Ph causes a large rate reduction, as is indicated by the following relative rates (values for CMe₂:CHPh and CMe₂:CHMe added for comparison) :

CMe₂:CHMe	CMe₂:CHPh	CHPh:CH₂	CHPh:CHPh
>10	1·3	1	0·012

As two methyl groups joined to the same carbon atom are superior to a phenyl group in electron-donating power, the electrophilic attack is chiefly on the α-carbon atom (*A*).   The

(*A*.)   Me₂C═══CHPh   ∓ ⟨══⟩=CH—CH=⟨══⟩ ±   (*B*.)

phenyl group now acts in the reverse sense and tends to attract electrons, causing the rate for CMe₂:CHPh to be inferior to that of CMe₂:CHMe (although Ph is superior to Me as an electron-donor).   The rate for stilbene should be less than for CMe₂:CHPh but not to so con-siderable an extent, as judged by reference to related compounds

(CMe₂:CH·CO₂H 10 >CHPh:CH·CO₂H).

It is possible that resonance stabilisation (*B*) as well as a steric effect may operate to reduce the rate of halogen addition to stilbene.

Bromine addition to stilbene in acetic acid solution shows mixed third- and second-order kinetics in the concentration region M/80—M/160 at 24°, as is found for other compounds in this solvent.   Rate measurements have also been made with added hydrogen bromide and lithium chloride :

k_2, M/80, = 18   + M/20-HBr, k_2 = 7·8   +M/20-LiCl, k_2 = 28

The ratios of catalysed to uncatalysed addition thus obtained, *viz.*, for HBr 0·43, for LiCl 1·6, correspond with the values at the same concentrations for such compounds as allyl benzoate, HBr 0·67, LiCl 1·9 (Part VI).   These reactions are considered to proceed by an electrophilic mechanism, and differ from the reactions of compounds which constitutionally tend to favour a nucleophilic mechanism and show considerable catalysis, *e.g.*, CH₂:CHBr, HBr 10·5, LiCl 7·0 (following communication).

The introduction of the strongly electron-attracting nitro-group in the β-position in styrene causes a very large reduction in the electrophilic rate of halogen addition (CHPh:CH₂ 10^6 > CHPh:CH·NO₂), and nitrostyrene has its expected position in the series, CHPh:CH·CO₂H > CHPh:CH·CHO > CHPh:CH·NO₂ (Part VIII, *J.*, 1945, 888).   The nitro-group, moreover,

resembles the aldehyde group in being structurally favourable for hydrogen-ion addition (see C and D), and consequently acid-catalysed nucleophilic halogen addition is possible. Nitro-

$$\text{(C.)} \quad \begin{array}{c} \text{PhC}\overset{+}{\text{H}}\text{—CH} \\ \diagdown\text{CH} \\ \text{H—O} \end{array} \qquad\qquad \text{PhC}\overset{+}{\text{H}}\text{—CH} \begin{array}{c} \\ \diagdown\text{N}\rightarrow\text{O} \\ \text{H—O} \end{array} \text{(D.)}$$

styrene is catalysed by sulphuric acid and hydrogen bromide; herewith are the rates for nitro styrene plus bromine, each M/40 ($x = 20$), in acetic acid at 24° :

$+$ M/40-NaOAc, $k_2 = 0.0019$ $+$ M/40-H_2SO_4, $k_2 = 0.0090$ $+$ M/40-HBr, $k_2 = 0.83$

The superiority of hydrogen bromide to sulphuric acid as a catalyst, as in the corresponding reactions with cinnamaldehyde, is in accordance with the theory of 1 : 4-addition of HBr_3. With 2 : 4-dinitrostilbene, to which reference is made later, such addition cannot take place, and correspondingly there is no such large difference in effect between the two catalysts for bromine addition.

The nitro-group, which is more strongly electron-attracting than the aldehyde group and consequently has a greater decelerating influence on electrophilic halogen addition, is found to be inferior to it in promoting nucleophilic addition, as is evident from the relative velocities (CHPh:CH·CHO $3 \times 10^4 >$ CHPh:CH·NO_2) for sulphuric acid catalysed bromine addition in acetic acid solution. A rate-determining change in this mode of addition is the initial reaction, $A + H^+ \rightleftharpoons A^+H$ By reference to the formulations (C) and (D), it is apparent that in (D) the $N \rightarrow O$ group by electron attraction tends to cause the splitting off of H^+, and hence to make the rate of acid-catalysed nucleophilic addition to the nitro-compound less than to the aldehyde.

The introduction of nitro-groups into stilbene causes a large reduction in the electrophilic rate of halogen addition, as is apparent from the relative velocities :

CHPh:CH—⟨ ⟩   CHPh:CH—⟨ ⟩NO₂ (NO₂)   CHPh:CH—⟨ ⟩NO₂ (NO₂, NO₂)

1   1×10^{-3} 4×10^{-6}
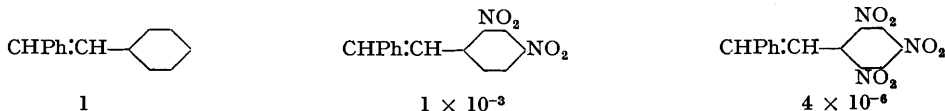
The dinitrophenyl group attached to the ethylene system has a smaller electron-attracting power than the nitro-group; this is shown by the electrophilic rates of chlorine addition in acetic acid at 24° :

CHPh:CH·$C_6H_3(NO_2)_2$ CHPh:CH·NO_2
$k_2 = 12.8$ $k_2 = 0.020$

Correspondingly, dinitrostilbene reacts less rapidly than nitrostyrene by the nucleophilic mechanism; herewith are the rates of bromine addition to dinitrostilbene, both M/160, in presence of catalysts in acetic acid at 24° :

$k_2 = 0.014$ $+$ M/160-H_2SO_4, $k_2 = 0.017$ $+$ M/160-HBr, $k_2 = 0.033$
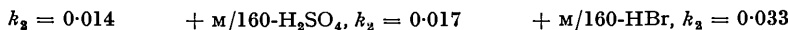
It is evident that the tendency to the tautomeric change involving the nitro-group becomes weakened in being relayed through the benzene nucleus. The relatively small difference in catalytic activity betwen sulphuric acid and hydrogen bromide is ascribed to the impossibility of 1 : 4-addition of HBr_3 to dinitrostilbene.

EXPERIMENTAL.

The following compounds were used in this investigation : styrene, freshly distilled, b. p. 146°/760 mm.; $\beta\beta$-dimethylstyrene, b. p. 184°/760; β-nitrostyrene, m. p. 57°; stilbene, m. p. 124°; 2 : 4-dinitrostilbene, m. p. 143°; 2 : 4 : 6-trinitrostilbene, m. p. 155°.

The method of experimentation was as previously described and is illustrated for one reaction. Stilbene, M/80 $+$ Br_2, M/80 in HOAc, 24°; reaction mixture, 10 ml.; 1-ml. samples pipetted into KI and titrated with N/80-$Na_2S_2O_3$:

Time (mins.)	0	0.6	1.7	2.9	4.3	5.5	7.3
Titre (ml.)	1.95	1.73	1.33	1.12	1.00	0.90	0.78

From curve, $x = 50$, $t = 4.40$. Second expt., $x = 50$, $t = 4.30$. The reaction is typically termolecular.

Br_2 addition, x, %	10	20	30	40	50
$k_3 \times 10^{-3}$	8.5	8.0	8.0	8.3	8.7

Other measurements are given as times (mins.) for $x = 20$ or $x = 50\%$ halogen absorption, reactions in HOAc in the dark, 24°. Stilbene, $\text{M}/80 + \text{Br}_2$, $\text{M}/80 + 4[\text{HBr}]$, $x = 50$, $t = 10\cdot0$; $+ 3\cdot2[\text{LiCl}]$, $x = 50$, $t = 2\cdot1$; $\text{M}/160 + \text{Br}_2$, $\text{M}/160$, $x = 50$, $t = 13\cdot6$. Dinitrostilbene, $\text{M}/160 + \text{Cl}_2$, $\text{M}/160$, $x = 50$, $t = 12\cdot5$; $+ \text{Br}_2$, $\text{M}/160$, $x = 20$, $t = 2800$; $+ [\text{H}_2\text{SO}_4]$, $x = 20$, $t = 2400$; $+ [\text{HBr}]$, $x = 20$, $t = 1200$. Trinitrostilbene, $\text{M}/160 + \text{Cl}_2$, $\text{M}/160$ (solvent HOAc $+ \text{H}_2\text{O}$, 5%), $x = 50$, $t = 570$. Styrene, $\text{M}/320 + \text{Br}_2$, $\text{M}/320$, $x = 50$, $t = 0\cdot028$; $\beta\beta$-dimethylstyrene, $\text{M}/320 + \text{Br}_2$, $\text{M}/320$, $x = 50$, $t = 0\cdot021$ (these two results from a group of observations at $x = {\sim}50\%$). β-Nitrostyrene, $\text{M}/40 + \text{Cl}_2$, $\text{M}/40$, $x = 20$, $t = 480$; $\text{M}/40 + \text{Br}_2$, $\text{M}/40$, $x = 20$, $t = 5100$; $+ [\text{H}_2\text{SO}_4]$, $x = 20$, $t = 1060$; $+ [\text{HBr}]$, $x = 20$, $t = 12$.

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