337. *The Kinetics of Halogen Addition. Part XVII. Acetylenic Compounds.*

By P. W. Robertson, W. E. Dasent, R. M. Milburn, and W. H. Oliver.

Rates of electrophilic halogen addition have been measured for stearolic acid, undecenolic acid, phenylacetylene, tolan, ethyl propylpropiolate, and 1-benzoyl-2-*o*-chlorophenylacetylene, and compared with those of the corresponding ethylenic compounds. The rate-ratio for ethylene to acetylene is increased by electron-repelling groups in the molecule, and reduced by electron-attracting groups, and in the above series varies from 50,000 to 23. A compound such as $Cl\cdot C_6H_4\cdot C{\vdots}C\cdot COPh$, containing a $-T,-I$ group, adds bromine by the nucleophilic mechanism, and the reaction is acid-catalysed in acetic acid solution.

In the course of the present series of investigations, various acetylenic compounds have been examined and sufficient material appears now to have accumulated to give a preliminary survey of this part of the work. There are certain differences between the acetylenic and ethylenic compounds that may help to elucidate the mechanism of halogen addition. The nature of this relatively complicated two-phase process is still imperfectly understood, in contrast with certain one-phase reactions such as nucleophilic substitution.

An acetylenic group has a greater electron-attractive power than an ethylenic group. For example, whereas phenylethylene has zero dipole moment, the value for phenylacetylene is 0·8 D. Reference to the related nitro-compounds ($PhNO_2$ 3·9, p-$NO_2\cdot C_6H_4\cdot C{\vdots}CH$ 3·6, p-$NO_2\cdot C_6H_4\cdot CH_3$ 4·4 D.) reveals that this moment acts in opposite directions in ethynyl and the electron-repelling methyl. This effect determines some of the chemical characteristics of acetylenic compounds, *i.e.*, their power of salt formation, the *meta*-nitration of phenylpropiolic acid, and the alkali fission of the compound $CH{\vdots}C\cdot CHO$, where the $CH{\vdots}C$ group behaves like the CCl_3 group. One such reaction that has been kinetically investigated is the rearrangement of the compounds $CHMe{:}CH\cdot CH(OH)\cdot C{\vdots}CH$ and $CHMe{:}CH\cdot CH(OH)\cdot CH{:}CH_2$ (Braude and Jones, *J.*, 1946, 128), the former reacting less rapidly than the latter by a factor of 3000. This reaction requires electron-accession at the reacting centre, namely the OH group, and is therefore retarded by the electron-attracting ethynyl group.

As electrophilic halogen addition requires electron-accession at the carbon atom which is attacked, it might be expected that acetylenes would be more reactive than the related ethylenes. But this is by no means the case. Some other more powerful effect must therefore operate to control the velocity of halogen addition to unsaturated compounds, and such a factor is related to the polarisability of the double and the triple bond. The position of the bands in the far ultra-violet spectra gives a measure of the relative energy required to shift an electron from the multiple linkage, and the ionisation potential is greater for acetylene than for ethylene (cf. Walsh, *Ann. Reports*, 1947, **44**, 35). The electrons in the π-bond of acetylene are held more tightly than those in the π-bond of ethylene, so that in the former case the electrons are less readily disengaged from their bonding orbitals to link with an approaching halogen molecule. It is found further that the reduction of ionisation potential is smaller in passing from acetylene to methylacetylene than from ethylene to propylene. That is, the π-electrons in an ethylene are rendered more mobile by a $+I,+T$ group than in an acetylene, and reversibly it might be expected that a $-I,-T,$ group in an ethylene might immobilise the electrons relatively more than in the corresponding acetylenic compound. If this is so, the difference in reactivity between ethylenes and acetylenes, for electrophilic halogen addition, should increase with electron-contributing groups and decrease with electron-withdrawing groups. The relative rates (at 25°) of the compounds named in the Table are in accord with this expectation. As the rates for the first four pairs of compounds, owing to widely varying reactivities, were measured at different concentrations, they are recalculated for the concentration M/1000 for the purposes of comparison. This assessment is made on the assumption that these reactions are similar to the previously examined bromine additions with mixed second- and third-order kinetics, and does not involve modification by a factor greater than two. The rates of bromine addition to the last two pairs of compounds are very slow in acetic acid solution and addition would be accompanied by nucleophilic reactions; measurements with these compounds were made under conditions which ensure that the comparison is for electrophilic halogen addition. The velocities shown in the Table and those subsequently quoted are second-order rate coefficients, k_2 (min.$^{-1}$ g.-mol.$^{-1}$ l.).

	Ethylenic compound.	Acetylenic compound.	Rate-ratio.
k_2, Br_2 (HOAc)	Oleic acid, $\sim 3 \times 10^4$	Stearolic acid, 0·65	50,000
k_2, Br_2 (HOAc)	Undecenoic acid, $1{\cdot}2 \times 10^3$	Undecenolic acid, 0·13	9,000
k_2, Br_2 (HOAc)	Styrene, $\sim 7 \times 10^3$	Phenylacetylene, 2·3	3,000
k_2, Br_2 (HOAc)	Stilbene, 11	Tolan, 0·042	250
k_2, Br_2 (HOAc, 50% H_2O)	Methyl *a*-ethylacrylate, 3·6	Methyl ethylpropiolate, 0·035	100
k_2, Cl_2 (HOAc–NaOAc) ...	1-Benzoyl-2-*o*-chlorophenylethylene, 1·8	1-Benzoyl-2-*o*-chlorophenylacetylene, 0·079	23

The rate given for oleic acid is that measured for methyl oleate, the substituent at the great distance from the ethylenic link being unlikely to cause any difference. Elaidic acid (*trans*) should have been preferably selected instead of oleic acid, as the other compounds in the list are *trans*-isomers. This would involve a reduction in rate by a factor of between two or three, giving a " rate ratio " of ~20,000. The value for undecenoic acid is in good agreement with the value for *n*-butylethylene, $k_2 = 1{\cdot}1 \times 10^3$. The rate for ethyl propiolate is as previously measured, and for methyl *a*-ethylacrylate is that of methyl crotonate multiplied by a factor of 1·5, the ratio of the two acids (*cf. J.*, 1945, 131; and preceding paper).

As shown in the Table, the ratio for related pairs of compound increases with the rates. Sufficient examples have not yet been collected to examine the relation between rate-ratio and constitution for the more slowly reacting compounds. There is the possibility, however, that when two electron-attracting groups are present the acetylene may add halogen more rapidly than the ethylene.

Phenylpropiolic and *o*-nitrophenylpropiolic acids have also been investigated, but the results for these substances are complicated by their ionisation in acetic acid. This is especially the case for acetylenedicarboxylic acid, which has an acid-strength comparable with that of sulphuric acid. The velocity of bromine addition to the unsaturated anion of this compound was determined, and the following comparison made for the sodium salts in water at 25°, in the presence of sodium acetate to combine with the liberated hydrogen bromide, using as reagent 0·01M-bromine, with 0·015M-potassium bromide. It is apparent that the difference in reactivity observed between acetylene and ethylene molecules persists in the unsaturated anions.

k_2	Fumarate ion, 200	Acetylenedicarboxylate ion, 2

Acetylenic compounds containing $-I,-T$ groups add bromine by a nucleophilic mechanism, which has the general characteristics already observed for the corresponding reactions of ethylenic compounds. This may be illustrated by reference to the rates of bromine addition to 1-benzoyl-2-*o*-chlorophenylacetylene (M/80-reactants in acetic acid at 25°) :

	M/40-NaOAc.	M/40-NaOAc + M/10-LiCl.	M/40-NaOAc + M/10-LiBr.	M/20-H_2SO_4.
k_2	0·0021	0·011	0·024	1·5

The considerable catalysis by lithium chloride and bromide, and the superiority of lithium bromide as a catalyst are indicative of the nucleophilic mechanism (cf. *J.*, 1949, 298), and the high rate in the presence of sulphuric acid shows that the acetylenic compound, like ethylenic compounds of this type (cf. *J.*, 1948, 982), adds bromine by an acid-catalysed nucleophilic reaction. Reference to the rate of chlorine addition ($k_2 = 0{\cdot}079$) shows that the bromine rate is lower by a factor of 35, the value being ~300 when both compounds react by the electrophilic mechanism. This relatively low rate of chlorine addition explains the difficulty in isolating the dichloro-addition product (Bickel, *J. Amer. Chem. Soc.*, 1948, **70**, 763), whereas bromine addition was found to take place readily, probably owing to the presence in the bromine of a trace of hydrogen bromide, which would cause a rapid nucleophilic reaction.

(*Added, May 5th,* 1950.) The expectation that an acetylene with two electron-attracting groups might add halogen by the electrophilic mechanism more rapidly than does the corresponding ethylene has been realised. Experiments by W. H. Oliver have shown that ethyl acetylenedicarboxylate (I) adds chlorine more rapidly than ethyl fumarate (II) by a factor of 60, the rates in acetic acid at 25° being for (I) $k_2 = 0{\cdot}0060$ and for (II) $k_2 = 0{\cdot}0001$. Measurements with ethyl maleate indicate that there was considerable *cis-trans* inversion on addition, but its rate should be about three times that of its *trans*-stereoisomer. That the relative reactivity becomes reversed for the ions of the corresponding acids is in accord with expectation, as CO_2^- repels electrons and should therefore make the p-electrons of an ethylene bond more mobile than the corresponding ethylene ion. P. W. R.

EXPERIMENTAL.

All the reactions were measured in acetic acid at 25°, with the technique previously described. The following compounds were used in this investigation: *o*-chlorobenzylideneacetophenone, m. p. 51·5°; 1-benzoyl-2-*o*-chlorophenylacetylene, m. p. 94°, prepared by the method of Bickel (*J. Amer. Chem. Soc.*, 1946, **68**, 866; 1947, **69**, 74); phenylacetylene, Eastman Kodak Co., b. p. 143°/760 mm.; tolan (prepared from stilbene), m. p. 61°; acetylenedicarboxylic acid (prepared from fumaric acid), m. p. 175—177° (decomp.); stearolic acid (prepared from methyl oleate), m. p. 46·5° (Found: equiv., 280. Calc.: equiv., 280); undecenolic acid, m. p. 41·5° (Found: equiv., 182. Calc.: equiv., 182); undecenoic acid, fraction b. p. 112—118°/1 mm., recrystallised from light petroleum, m. p. 24·0°; methyl oleate (Found: equiv., 295; I value, 85. Calc.: equiv., 296; I value, 86).

Herewith are details of a typical rate determination:

$$\text{M}/80\text{-}o\text{-Cl}\cdot C_6H_4\cdot C\vdots C\cdot \text{COPh} + \text{M}/80\text{-}Br_2 + \text{M}/40\text{-NaOAc} + \text{M}/10\text{-LiBr}$$

in HOAc at 25°; 1-ml. samples titrated with N/80-$Na_2S_2O_3$.

Time (mins.)	0	520	1510	2500;	0	970	1950	3000
Titre (ml.)	2·02	1·71	1·40	1·16;	2·01	1·56	1·27	1·06

From the combined % change–time curve the following second-order coefficients were obtained:

x	10	20	30	40	50
k_2	0·025	0·025	0·025	0·024	0·023

Herewith are details for M/80-*o*-Cl·C_6H_4·C⋮C·COPh + M/80-Br_2 + M/20-H_2SO_4:

Time (mins.)	0	8	25	50;	0	15	30	40
Titre (ml.)	1·99	1·79	1·21	0·64;	2·01	1·55	1·06	0·84

From the combined curve we obtained second-order coefficients showing autocatalysis:

x	10	20	30	40	50	60
k_2	1·2	1·5	1·7	2·0	2·4	2·9

The following are additional results for this compound, expressed as times (minutes) for x% halogen absorption at 25° in acetic acid: M/80-*o*-Cl·C_6H_4·C⋮C·COPh: + M/80-Cl_2 + M/40-NaOAc, $x = 20$, $t = 252$; + M/80-Br_2 + M/40-NaOAc, $x = 10$, $t = 4200$; + M/80-Br_2 + M/10-LiCl, $x = 20$, $t = 1780$. M/80-*o*-Cl·C_6H_4·CH:CH·COPh + M/80-Cl_2 + M/80-NaOAc, $x = 20$, $t = 11{\cdot}0$.

Herewith are the third-order rate coefficients for M/80-tolan + M/80-Br_2 in acetic acid at 25°:

x (% Br_2 absorption)	10	20	30	40	50
k_3	8·2	7·5	7·7	8·0	7·7

Details for this compound (M/80-reactants) are: $x = 20$, $t = 240$; +M/20-LiCl, $t = 120$. For phenylacetylene, $x = 20$, $t = 6{\cdot}0$; +M/20-LiCl, $x = 20$, $t = 3{\cdot}3$. These measurements with lithium chloride show that its catalytic effect is very similar to that for ethylenic compounds that give the normal electrophilic reaction (cf. Table I, *J.*, 1949, 295).

M/1000-Methyl oleate + M/1000-Br_2, $x = 50$, $t = 0{\cdot}03$. M/1000-Undecenoic acid + M/1000-Br_2, $x = 50$, $t = 0{\cdot}91$. M/80-Stearolic acid + M/80-Br_2, $x = 20$, $t = 15$. M/80-Undecenolic acid + M/80-Br_2, $x = 20$, $t = 80$.

VICTORIA UNIVERSITY COLLEGE, WELLINGTON, N.Z.

[*Received, March* **16*th*, 1950**.]