334. *Influence of Substituents on the Additive Reactivity of Ethylene Derivatives. Part III. Further Experiments on the Addition of Bromine in Solution.*

By S. V. Anantakrishnan and Christopher K. Ingold.

In this paper we report an extension of the investigation commenced in Part I (Ingold and Ingold, J., **1931**, 2354) on the relative rates of addition of simple ethylene derivatives towards the electrophilic reagent, bromine. We have throughout standardised the catalytic conditions for this reaction by the method worked out in Part II (Anantakrishnan and Ingold, this vol., p. 984), a sufficient quantity of hydrogen bromide being added initially to cover up completely the autocatalysis of the reaction as well as any adventitious catalysis.

It was shown in Part I that the intrinsic effect of a given substituent on the reactivity of an ethylene bond towards a reagent such as bromine can be deduced only by reference to certain structural types. These may contain either just the single substituent under consideration or combinations of substituents subject to definite restrictions; for many combinations give rise to mutual effects which seriously distort, and may even invert, the separate effects of the groups. Theory, confirmed by observations as far as these have been extended, shows when it is possible for this to happen, and therefore indicates the structural types which may most profitably be studied.

Within such limits we have extended the work of Part I on the methyl and phenyl substituents, and on the combination of methyl groups. We have also studied the aldehydo-group and its combination with methyl. The experiments were carried out at − 78°, and, as heretofore, in methylene chloride solution with exclusion of light. The method was to allow two olefinic substances to compete for a deficit of bromine, and to calculate the ratio of the rate constants of the simultaneous reactions from the compositions of the mixtures of dibromides formed after absorption of the whole of the bromine. It was shown in Part II that the ratios thus obtained are insensitive to the concentrations of the reactants, to the concentration of the hydrogen bromide catalyst, and, within considerable limits, to the temperature. By means of a suitable set of such ratios it is possible to obtain " reduced rates," *i.e.*, rates of reaction for ethylene derivatives expressed as multiples or fractions of the rate for ethylene itself.

Table I summarises the competitions carried out in the previous parts and in this paper, together with the corresponding ratios of the rate constants and the calculated reduced rates. The italicised figures are based on the observational data in Table II on p. 1398.

Table I.

Expts. No.	X.	Y.	k_Y/k_X.	Reduced rate for Y.	Mean.
17—19	$CH_2{:}CH_2$	$CHPh{:}CH_2$	3·24	3·24	3·35
22—25	,,	,,	*3·43*	*3·43*	
28	$CHPh{:}CH_2$	$CHMe{:}CH_2$	*0·63*	0·63 × 3·35 = *2·10*	2·03
29	$CMe_2{:}CH_2$	,,	*0·35*	0·35 × 5·32 = *1·95*	
1—4	$CH_2{:}CH_2$	$CMe_2{:}CH_2$	5·5	5·5	5·53
20—21	,,	,,	*5·6*	*5·6*	
26—27	,,	$CMe_2{:}CHMe$	*10·4*	*10·4*	10·4
5	,,	$CMe_2{:}CMe_2$	13·6	13·6	14·0
6—8	$CMe_2{:}CH_2$	,,	2·54	2·54 × 5·53 = 14·1	
14—15	$CH_2{:}CH_2$	$CHBr{:}CH_2$	small	small	small
9—10	,,	$CO_2H{\cdot}CH{:}CH_2$	,,	,,	,,
11—13	$CHMe{:}CH_2$	$CO_2H{\cdot}CH{:}CHMe$	0·13	0·13 × 2·0 = *0·26*	0·26
30—32	$CH_2{:}CH_2$	$CHO{\cdot}CH{:}CH_2$	*1·5*	*1·5*	1·5
33	$CHMe{:}CH_2$	$CHO{\cdot}CH{:}CHMe$	*1·5*	1·5 × 2·0 = *3·0*	*3·0*

In spite of the new data, nothing need be added to the discussion in Part I of the effects caused by the groups Ph, Br, and CO_2H. The following remarks will therefore be confined to the effects of the substituents Me and CHO.

The methyl group releases electrons and therefore should facilitate the addition of electrophilic reagents such as bromine. Thus the reduced velocity for propylene should be greater than unity; it is in fact 2·0. The attack of the halogen should be initiated at that ethenoid carbon atom which is more remote from the methyl substituent, $\mathrm{Me}\!\rightarrow\!\mathrm{CH}\overset{\curvearrowright}{=}\mathrm{CH_2} \;.\;.\;.\;.\; \mathrm{Br}\overset{\curvearrowright}{—}\mathrm{Br}$; this also has been demonstrated (Ingold and Smith, J., 1931, 2742). As the methyl group is saturated and does not possess unshared electrons, the electron displacements which occur during addition are almost wholly confined to the double-bond electrons; and these displacements, which always start from nearly symmetrical positions with respect to the carbon nuclei, correspond to integral covalency changes. It is therefore to be expected that the polarisability of the ethenoid electrons, rather than their state of polarisation, will be the principal factor determining reactivity in ethylene derivatives containing only methyl (or higher alkyl) groups; and the greater is the number of electron-repelling methyl groups which are directly attached to the ethenoid centre the greater will be both the polarisability and the reactivity. A briefer way of expressing the same argument would be to assert that, as the methyl group is incapable of an electromeric effect, combinations of methyl substituents should show no inverted mutual influence (cf. Part I). A progressive accumulation in the number of methyl groups associated with an ethenoid link should therefore be accompanied by a progressive increase in the " reduced rate " of addition. This is what we find :

$\mathrm{CH_2{:}CH_2}$.	$\mathrm{CHMe{:}CH_2}$.	$\mathrm{CMe_2{:}CH_2}$.	$\mathrm{CMe_2{:}CHMe}$.	$\mathrm{CMe_2{:}CMe_2}$.
1·0	2·0	5·5	10·4	14·0

The data show, however, that the permanent state of polarisation of the ethenoid centre is not entirely without influence. The plot of the logarithm of the rate (to which, probably, the critical energy is approximately proportional) against the number of methyl groups gives a sigmoid curve, steepening so long as the structure is losing symmetry and flattening whilst symmetry is being restored. It is obvious from the ratios

$$\frac{k(\mathrm{CMe_2{:}CH_2})}{k(\mathrm{CH_2{:}CH_2})} = 5{\cdot}5 \qquad \frac{k(\mathrm{CMe_2{:}CHMe})}{k(\mathrm{CHMe{:}CH_2})} = 5{\cdot}2 \qquad \frac{k(\mathrm{CMe_2{:}CMe_2})}{k(\mathrm{CMe_2{:}CH_2})} = 2{\cdot}5$$

that the introduction of two methyl groups to give an unsymmetrical compound has a greater relative effect on the speed than when a symmetrical compound is the result of the change. The assumption due to Lucas (1925) of electron repulsion by alkyl groups attached to an ethenoid centre is, of course, entirely consistent with the data which have since accumulated on the dipole moments of olefins.

Discussing the proved deactivating effect of the carboxyl group in this reaction, and the possible effects of more powerfully electron-absorbing substituents such as ·CHO, Ingold and Ingold (*loc. cit.*) wrote : " Addition initiated by the attack of (δ-)Hal " [*i.e.*, the *negative* end of a polarised bromine molecule : $\cdot\mathrm{C}\overset{\curvearrowleft}{=}\mathrm{C} \;.\;.\;.\;.\; \mathrm{Br}\overset{\curvearrowleft}{—}\mathrm{Br}$] " would also be theoretically possible, provided that the intrinsically small reactivity of negative halogen could be overcome by the attachment of a sufficiently powerful electron-sink to the olefinic residue. It is not yet known whether any of the available groups (·CHO, ·COR, $\cdot\mathrm{NO_2}$) are in fact competent to cause this anticipated reversal of normal reactivity; the practical criterion which would reveal such an occurrence would be that the rate of addition would pass through a minimum as the efficacy of the electron-sink was progressively increased." It will be seen from Table I that we have carried out competitive experiments between ethylene and acraldehyde, and between propylene and crotonaldehyde. In each case it is found that the ·CHO group, instead of deactivating more powerfully than $\cdot\mathrm{CO_2H}$, actually increases the reaction rate quite appreciably. More complete evidence, is, of course, desirable, but it would appear *prima facie* that we here have under observation the enforced reversal of the functions of the reagent anticipated in the statement quoted above.

EXPERIMENTAL.

The methods have been described before and only the results need be given.* These are in Table II; and some data, obtained in the course of the experiments of Part II, which are as

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* The recorded b. p. (this vol., p. 986) of *as*.-dimethylethylene should read – 6·5°.

TABLE II.

Expt.	X.	Y.	x_0.	y_0/x_0.	$[Br_2]_0/x_0$.	$[HBr]_0/x_0$.	p_Y.	k_Y/k_X.
22	$CH_2{:}CH_2$	$CHPh{:}CH_2$	0·304	1·015	0·420	—	0·739	3·23
23	,,	,,	0·115	1·027	0·415	0·0032	0·765	3·50
24	,,	,,	0·308	0·973	0·380	0·0038	0·723	3·58
25	,,	,,	0·265	0·962	0·390	0·0078	0·741	3·40
28	$CHPh{:}CH_2$	$CHMe{:}CH_2$	0·099	0·990	0·398	0·0050	0·395	0·63
29	$CMe_2{:}CH_2$	,,	0·284	0·978	0·418	0·0045	0·275	0·35
20	$CH_2{:}CH_2$	$CMe_2{:}CH_2$	0·320	0·980	0·365	—	0·831	5·70
21	,,	,,	0·183	1·110	0·374	0·0027	0·840	5·50
26	,,	$CMe_2{:}CHMe$	0·318	1·055	0·303	0·0019	0·892	8·9
27	,,	,,	0·339	0·960	0·420	—	0·903	11·9
30	,,	$CHO{\cdot}CH{:}CH_2$	0·240	1·005	0·467	—	0·60	1·58
31	,,	,,	0·324	0·956	0·189	0·0072	0·56	1·32
32	,,	,,	0·289	0·963	0·288	0·0069	0·62	1·76
33	$CHMe{:}CH_2$	$CHO{\cdot}CH{:}CHMe$	0·238	1·000	0·482	0·0081	0·59	1·54

suitable as the new results for the calculation of relative rate constants, are included. The formula for this calculation is

$$k_Y/k_X = [\log y_0 - \log(y_0 - y)]/[\log x_0 - \log(x_0 - x)]$$

where x and y are the molar concentrations of X and Y, and the zero suffix refers to zero time. The initial concentration of bromine is given by $[Br]_0 = (x_0 - x) + (y_0 - y)$, and the molar proportion of YBr_2 in the mixture of bromides by

$$p_Y = (y_0 - y)/[(x_0 - x) + (y_0 - y)]$$

The figures (p_Y) for the aldehydes are only approximate. They were obtained by ultimate analysis after complete distillation of the mixed bromides at a low pressure with liquid air around the receiving bulb; and also by isolation of the ethylene bromide after fixation of the aldehydes either as semicarbazones or as 2 : 4-dinitrophenylhydrazones.

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