

179. *The Kinetics of Halogen Addition to Unsaturated Compounds.*  
*Part XXII.\* Alkyl- and Halogenoalkyl-ethylenes.*

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The rates of bromine addition to the following ethylenic hydrocarbons in acetic acid solution have been measured: *n*-butyl-, *tert.*-butyl-, *neopentyl*-, and 1-ethyl-1-methyl-ethylene, cyclopentene, cyclohexene, camphene, and  $\alpha$ -methylstyrene. Compounds of the type  $\text{CRR}'\text{CH}_2$  and  $\text{CHR}\cdot\text{CHR}'$  ( $\text{R} = n$ -alkyl), including the cycloalkenes, react more rapidly than do  $\text{CHR}\cdot\text{CH}_2$  by a factor of 30—40. *tert.*-Butylethylene is slightly less reactive than *n*-butylethylene, and *neopentylethylene* is some ten times less reactive still. The rate for allyl fluoride shows that the order in the series, fluoride > chloride > bromide, is contrary to that expected from consideration of the inductive effects of the halogens. The theories relating to these various reactions are discussed.

KINETIC investigations of addition of bromine to ethylenic hydrocarbons involve certain difficulties. Since the lower members are gases at ordinary temperatures and react very rapidly with bromine in acetic acid, modifications of the usual technique are necessary. The purity of the higher liquid homologues must be specially checked, as the methods of preparation frequently give mixtures of isomers.

#### EXPERIMENTAL

We are indebted to the American Petroleum Institute Research Project 45, a function of the Ohio State University Research Foundation, Columbus, Ohio, U.S.A., for a gift of purified samples of *n*-butylethylene (hex-1-ene) (b. p.  $63.5^\circ/760$  mm.,  $d_4^{20}$  0.6733,  $n_D^{20}$  1.3880), *tert.*-butylethylene (3 : 3-dimethylbut-1-ene) (b. p.  $41.2^\circ/760$  mm.,  $d_4^{20}$  0.6530,  $n_D^{20}$  1.3760), and 1-ethyl-1-methylethylene (2-methylbut-1-ene) (b. p.  $31.1^\circ/760$  mm.,  $d_4^{20}$  0.6584,  $n_D^{20}$  1.3778). Other compounds used in this investigation included *neopentylethylene* (4 : 4-dimethylpent-1-ene),<sup>†</sup> b. p.  $71.9^\circ/760$  mm.,  $n_D^{25}$  1.3909, allyl fluoride (prepared by Meslans's method, *Compt. rend.*, 1890, 111, 882; evaporated through a calcium chloride tube from a mixture of powdered silver nitrate and mercurous fluoride into acetic acid, and standardised by bromine addition, and by reaction with hypochlorous acid acidified with hydrochloric acid),<sup>†</sup>  $\alpha$ -methylstyrene, b. p.  $160^\circ/755$  mm., cyclohexene, b. p.  $81.6$ — $82.6^\circ/750$  mm., and cyclopentene, b. p.  $43.4^\circ/750$  mm.

The solvents and methods were as previously described (cf. *J.*, 1947, 630), and the results, except where otherwise stated, refer to reactions in acetic acid at  $25^\circ$ . The rapidly reacting compounds were examined at  $M/1000$ -concentration, at which the reaction proceeds by second-order kinetics ( $-\text{d}[\text{Br}_2]/\text{d}t = k[\text{A}][\text{Br}_2]$ ), with only a small incursion of the third-order mechanism (*J.*, 1939, 1515). The bromine solution was contained in a tube with a fragile bulb, which was broken in a solution of the other reactant, with rapid agitation of the mixture by the broken tube. The reaction was stopped at about  $x = 50\%$  absorption of bromine by rapid addition of potassium iodide solution, the time being measured by a second observer with a stop-watch. Five or six measurements were made at approximately the same time interval, and the bimolecular rate coefficient ( $k_2$ , l. mole<sup>-1</sup> min.<sup>-1</sup>) was estimated from the average of these measurements. Independent observers, using slightly different techniques for preparing the solutions of the hydrocarbons, obtained the following values of  $k_2 \times 10^{-3}$ : 1.0, 1.1 for *n*-butylethylene; 0.74, 0.65 for *tert.*-butylethylene. The influence of lithium chloride and lithium bromide on the rate of addition to *tert.*-butylethylene was examined. With  $M/1000$ -reactants and  $M/100$ -lithium chloride, the rate was increased by a factor of 2.7; with  $M/100$ -lithium bromide, the rate was reduced by a factor of 1.7. The acceleration with added lithium chloride is probably a salt effect, which is obscured, when lithium bromide is added instead, by the removal of bromine as the less reactive lithium tribromide.

\* Part XXI, *J.*, 1950, 2838.

† For the preparation and rate measurements on these two compounds, we are indebted to Professor E. D. Hughes, D.Sc., F.R.S., and his co-workers.

The rates for the still more rapidly reacting compounds are less accurate, as the times for 50% reaction are very small, and the agreement between the results of separate observers is less good. The following are average times (minutes) for 50% reaction, with  $m/1000$ -reactants: 1-ethyl-1-methylethylene, 0.030; cyclohexene, 0.036; cyclopentene, 0.025;  $\alpha$ -methylstyrene, 0.036.

The following are the results for the more slowly reacting compounds.

0.0017 $m$ -*neo*Pentylethylene + 0.0010 $m$ -bromine:  $x = 20$ ,  $t = 1.1$ ;  $x = 50$ ,  $t = 3.7$ .

$m/80$ -Allyl fluoride +  $m/80$ -bromine;  $x = 10$ ,  $t = 2.4$ ;  $x = 20$ ,  $t = 6.8$ ;  $x = 50$ ,  $t = 30.8$ ;  
+  $m/25$ -LiCl,  $x = 20$ ,  $t = 1.5$ .

The earlier value for allyl chloride was confirmed.

#### DISCUSSION

(a) *Compounds* CHR:CH<sub>2</sub>.—The following results were obtained:

Compound:	Bu <sup>n</sup> ·CH:CH <sub>2</sub>	Bu <sup>t</sup> ·CH:CH <sub>2</sub>	Bu <sup>t</sup> ·CH <sub>2</sub> ·CH:CH <sub>2</sub>
10 <sup>-3</sup> $k_2$ .....	1.05	0.70	0.10

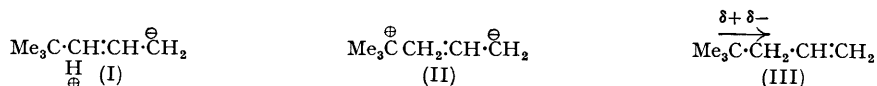
Berliner and Berliner (*J. Amer. Chem. Soc.*, 1950, **72**, 222) have recorded corresponding relative rates for bromination of alkylbenzenes, and have made plausible estimates of the ratios of *ortho*- to *para*-substitution, from which may be derived the following relative rates of *para*-substitution: PhBu<sup>n</sup>, 1.0; PhBu<sup>t</sup>, 0.42; Ph·CH<sub>2</sub>Bu<sup>t</sup>, 0.35.

Alkyl groups favour electrophilic substitution by an inductive effect ( $+I$ ; Bu<sup>t</sup> > Bu<sup>n</sup> > Me), and by hyperconjugation ( $+T$ ; Me > Bu<sup>n</sup> > Bu<sup>t</sup>). The decrease in the rate of bromine substitution from toluene to *tert.*-butylbenzene was interpreted by de la Mare and Robertson (*J.*, 1943, 279), and by Berliner and Berliner (*J. Amer. Chem. Soc.*, 1949, **71**, 1195), as a manifestation of decreasing hyperconjugation, for which the increasing inductive effect does not completely compensate. The rates of bromine addition to *n*-butyl- and *tert.*-butyl-ethylene are more nearly equal. This may be explained by the hypothesis that the inductive effect, being electrostatic in origin, is more effective in the ethylenic than in the *para*-position of the aromatic system, since in the former the substituent is nearer to the point of electrophilic attack. Similarly was explained the observation (*J.*, 1950, 1624) that the order of rates for substitution, PhMe > PhEt, becomes reversed with respect to the two alkyl groups for addition, in the example, CH<sub>3</sub>Et:CH·CO<sub>2</sub>H > CHMe:CH·CO<sub>2</sub>H.

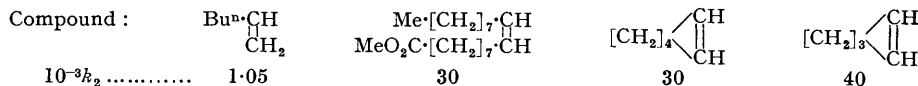
As electrophilic addition is a two-stage process resulting in *trans*-addition with inversion, there exists the possibility of steric hindrance in the second phase of the reaction. In the case of *tert.*-butylethylene, there is involved a *neopentyl*-like structure, Me<sub>3</sub>C·CH·CH<sub>2</sub>Br, which should be especially favourable for causing steric hindrance to the approach of the nucleophilic reagent required for completion of the addition. The observed rate of bromination of this compound, however, is as predicted from comparison with *n*-butylethylene, for which steric hindrance would not be expected. Similarly, the results for the *cycloalkenes*, described later in this communication, and for certain other compounds (cf. *J.*, 1950, 1624), support the conclusion that this type of steric hindrance does not operate, or is of very minor importance, in halogen addition.

The *neopentyl* group, as indicated by the rates of bromine addition to *neopentyl*ethylene and of bromination of *neopentyl*benzene, is characterised by a low power of electron-release, in comparison with a group such as *n*-butyl. As the inductive effects of such groups would be expected to be similar, the cause of the difference would appear to lie in a variation in the tautomeric effect. The low rates for the *neopentyl*-substituted compounds are remarkable; it might have been expected, for example, that the facilitation of the reaction by the hyperconjugative structure (I) would be augmented by contribution from structure (II). However, it seems possible that the inductive influence of the *tert.*-butyl group may, by transference of a fractional charge to the adjacent carbon atom, as illustrated in (III), tend to be unfavourable to the development of structure (I), and in this way may reduce the effectiveness of the *neopentyl* group in promoting reaction by mechanisms favoured by this type of structure. In *neopentyl*benzene, owing to the relatively greater distribution of charge in the aromatic ring, the effect may be less, as is shown in the smaller

spread of relative rates. In the allyl halides, as is discussed in a later section, the inductive influence of the halogen substituent acts in the opposite direction.

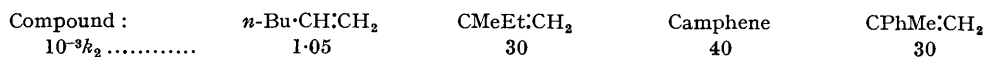


(b) *Compounds CHR:CHR'*.—The following rates of bromine addition have been measured:



In methyl oleate (*J.*, 1950, 1628), the carboxymethyl group is too far away from the ethylenic system to have an appreciable effect on the rate of reaction, and this compound may therefore be considered analogous to a *cis*-1 : 2-dialkylethylene, in which the second substituent increases the reactivity by a factor of about thirty. The values for *cyclopentene* and *cyclohexene* show that cyclic structures have no special influence on the rate of bromine addition. This result would be expected only if the second phase of the reaction were not rate-determining. These compounds, therefore, provide further evidence that steric hindrance of this type is not a controlling factor in halogen addition.

(c) *Compounds CRR':CH<sub>2</sub>*.—The following are some further comparisons of reactivity:



An ethyl group does not differ greatly from a *n*-butyl group in its influence on the reactivity, and the methyl group in ethylmethylethylene is seen to increase the rate of bromine addition by a factor of about thirty. The ratio of rates of bromine addition in methylene chloride as solvent, with hydrogen bromide as catalyst, has been recorded by the competition method for the compounds  $\text{CHMe}\cdot\text{CH}_2$  and  $\text{CMe}_2\cdot\text{CH}_2$  as 1 : 2 (Ingold and Ingold, *J.*, 1931, 2354). Direct measurements of bromine addition in chloroform solution with *m*/1000-olefin, *m*/2000-bromine, and added *m*/100-hydrogen bromide, at 25°, gave the values for  $k_2$ ,  $n\text{-Bu}\cdot\overset{\text{H}}{\text{C}}\text{H}\cdot\text{CH}_2$  20, and  $\text{CMeEt}\cdot\text{CH}_2$  500. The relative reactivity (ratio of rates, 1 : 29 in acetic acid, 1 : 25 in chloroform with hydrogen bromide as catalyst) is little affected by the change in conditions. This comparison confirms the previous discovery (de la Mare, Scott, and Robertson, *J.*, 1945, 509), that the kinetic rate ratio may in certain cases considerably exceed that found by the competitive method.

Bromine addition to camphene involves molecular rearrangement to form the 1 : 3-dibromo-derivative. Such a change need not necessarily influence the rate of bromine addition, since the rearrangement may occur in a stage of the reaction which is not rate-determining. In fact, camphene reacts at a rate almost the same as that of other hydrocarbons of the type  $\text{CR}_2\cdot\text{CH}_2$ .

A phenylalkylethylene is included for comparison with the dialkylethylenes. The phenyl group, compared with ethyl by reference to such compounds as  $\text{CHPh}\cdot\overset{\text{H}}{\text{C}}\text{H}\cdot\text{CO}_2\text{H}$  and  $\text{CHEt}\cdot\overset{\text{H}}{\text{C}}\text{H}\cdot\text{CO}_2\text{H}$ , increases the rate of bromine addition by a factor of about seven. The relatively small effect of the former group in the comparison of ethylmethylethylene with  $\alpha$ -methylstyrene suggests that the phenyl group is prevented by the methyl from rotating into the position most favourable for conjugation with the ethylene link. The ionisation potential of  $\alpha$ -methylstyrene, compared with that of styrene, is explained similarly by Walsh (*Ann. Reports*, 1947, 44, 34).

(d) *Halogenoalkylethylenes*.—In previous papers (*J.*, 1944, 131; 1947, 630; 1950, 812), there has been discussed the unexpected order of reactivity, *viz.*,  $\text{CH}_2\text{Cl}\cdot\overset{\text{H}}{\text{C}}\text{H}\cdot\text{CH}_2 > \text{CH}_2\text{Br}\cdot\overset{\text{H}}{\text{C}}\text{H}\cdot\text{CH}_2$ , found for third-order bromine addition in acetic acid both with and without added hydrogen bromide ( $-\text{d}[\text{Br}_2]/\text{d}t = k[\text{A}][\text{Br}_2]^2$  or  $k[\text{A}][\text{Br}_2][\text{Br}^-]$ ; products dibromide and bromoacetate\*), for halide-ion-catalysed bromine addition ( $-\text{d}[\text{Br}_2]/\text{d}t = k[\text{A}][\text{Br}_2][\text{Cl}^-]$ ; products dibromide and bromochloride\*), and for third-order addition in chlorobenzene

\* Cf., e.g., Nozaki and Ogg, *J. Amer. Chem. Soc.*, 1942, 64, 697.

( $-\text{d}[\text{Br}_2]/\text{d}t = k[\text{A}][\text{Br}_2]^2$ ; products dibromide). The same order was found for the chlorination of the benzyl halides, *i.e.*,  $\text{Ph}\cdot\text{CH}_2\text{Cl} > \text{Ph}\cdot\text{CH}_2\text{Br}$ . We consider, therefore, that the sequence  $\text{CH}_2\text{Cl} > \text{CH}_2\text{Br}$  represents the true order of effectiveness of these groups in their influence on electrophilic reactions of halogens, in view of the appearance of this order under so many diverse conditions of reaction, solvent, and catalyst. It was nevertheless considered of interest to extend the series to include allyl fluoride, and the following are the rates of bromine addition in acetic acid solution at  $25^\circ$ :

	$\text{CH}_2\text{F}\cdot\text{CH}\cdot\text{CH}_2$	$\text{CH}_2\text{Cl}\cdot\text{CH}\cdot\text{CH}_2$	$\text{CH}_2\text{Br}\cdot\text{CH}\cdot\text{CH}_2$
Rate (as $k_2$ , $x = 20$ , $M/80$ ) .....	2.9	1.6	1.0

The same order was found in the presence of lithium chloride as catalyst.

Two modes of reaction are possible for these compounds, depending on the two possible positions for electrophilic attack:



The contribution of the second process in the total reaction has been calculated (*J.*, 1950, 814) to be 12%, approximately the same as the value found for *meta*-substitution in benzyl chloride, in which the aromatic ring is affected by similar electronic drifts (*cf.* Ingold and Shaw, *J.*, 1949, 975). The relative rate order shown above for the allyl halides is therefore chiefly due to the operation of the mechanism (A), and the effect of mechanism (B) is merely to reduce slightly the spacing of the series.

The allyl halides add bromine considerably less rapidly than does propylene, the rate factor being greater than  $10^3$ , as must be expected in view of the powerful electron-withdrawing influence ( $-I$ ) of halogen substituents. This influence, however, decreases in the order  $\text{F} > \text{Cl} > \text{Br}$ , and thus, on the basis only of the inductive effect, the reactivities of these compounds would be expected to fall in a sequence opposite to that observed. The electron-donating properties ( $+T$ ) of the halogens ( $\text{F} > \text{Cl} > \text{Br}$ ; *cf.* de la Mare and Robertson, *J.*, 1948, 100) cannot reasonably be invoked to explain the present results, since in the allyl compounds the halogen substituent is not conjugated with the double linking; nor does carbon-halogen hyperconjugation (*cf.* de la Mare, Hughes, and Ingold, *J.*, 1948, 17) appear to give a satisfactory explanation, as this effect would here be expected to augment the inductive effect.

It is possible to describe the relative reactivities of these compounds by the postulate that the extent of hyperconjugation from the C-H bonds of a group  $\text{CH}_2\text{X}$  is altered by X in such a way as to give the order of electron release  $\text{CH}_2\text{F} > \text{CH}_2\text{Cl} > \text{CH}_2\text{Br}$ . It is suggested that the loosening of the carbon-hydrogen electrons required for hyperconjugation is determined by the inductive effect of the group X. A similar order of reactivity for aromatic substitution should be expected for the series  $\text{Ph}\cdot\text{CH}_2\text{X}$ , and has been found for the chloride and bromide.

Finally, reference is made to the compound  $(\text{CH}_2\text{Cl})_2\text{C}\cdot\text{CH}_2$ , as the earlier theoretical explanation (*J.*, 1947, 630) of its behaviour must be modified in the light of later developments. By reference to the reactivities of ethylene and allyl chloride (*J.*, 1950, 812), the following relative rates of bromine addition may be assessed:

$\text{CH}_2\cdot\text{CH}_2$	$\text{CH}_2\text{Cl}\cdot\text{CH}\cdot\text{CH}_2$	$(\text{CH}_2\text{Cl})_2\text{C}\cdot\text{CH}_2$
1	0.019	0.00024

The reactivity of the bischloromethyl compound is thus of the expected low order and is not attributable to the influence of steric hindrance. Likewise, the large catalytic influence of lithium chloride on the rate of bromine addition to this compound (reactants  $M/80$ ,  $+M/20$ -lithium chloride, 22-fold acceleration compared with the value of 6.3 for allyl chloride) may be explained without reference to the operation of steric influences. The compound  $(\text{CH}_2\text{Cl})_2\text{C}\cdot\text{CH}_2$  belongs to the general class of compounds,  $\text{CHR}\cdot\text{CH}_2$ , containing a group R with a ( $+T$ ,  $-I$ ) characteristic (*J.*, 1949, 298). This classification may be extended

to include compounds of the class  $\text{CR}_2\text{:CH}_2$ , with two such groups attached to the same carbon atom, for which compounds it is not unreasonable to expect an especially large catalytic effect.

We are indebted to Professor E. D. Hughes, D.Sc., F.R.S., for valuable discussion of this manuscript, and for permission to refer to unpublished measurements on allyl fluoride and *neo*-pentylethylene, made in collaboration with P. B. D. de la Mare, M.Sc., Ph.D., and C. A. Vernon, B.Sc., to whom we are also greatly indebted.

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