The Effect of 2-Halogeno-substituents on the Rates of Bromination of Olefins

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Second-order rate coefficients have been determined for the reaction of bromine with $CH_2{=}C(X)CH_2Cl$ for X = H, F, Cl, and Br, in both trifluoroacetic acid and 50% methanol–water. In both solvents there was a large decrease in the rate coefficient for X = F, Cl, and Br compared with that for X = H. The fluoro-olefin however reacted considerably faster than did the chloro- and bromo-olefin, resulting in the reactivity order H $\gg$ F > Cl $\sim$ Br. These substituent effects are compared with those obtained for the addition of trifluoroacetic acid to 2-halogenopropenes (the only other known case of the kinetic effect of vinyl halogen substituents in addition reactions) and more generally with those found in electrophilic aromatic substitution. The results are discussed in terms of the relative importance of bridged bromonium ion structures and classical carbonium ion structures in the transition states of electrophilic additions to olefins.

THE kinetic effect of substituent groups is a widely used technique in the elucidation of reaction mechanisms. Halogen substituents have been particularly useful probes since they show both the $-I$ inductive and the $+M$ resonance effects, which, of course, affect the electronic movements within a molecule in opposing directions. Either the $-I$ or the $+M$ effect can dominate depending upon the position of the substituent halogen, and upon the selectivity of the reagent; thus it is possible to rationalise the relative rates of reaction and also for electrophilic aromatic substitution and electrophilic addition the nature of the orientation as well. The position of fluorine is particularly interesting since it can act as an overall electron-attracting or electron-releasing substituent with respect to hydrogen. This is demonstrated by the observed partial rate factors, which for a fluorine atom substituted *para* to the position of attack in electrophilic aromatic substitution have the values 0·77 for nitration,[1] *ca.* 3·9 for chlorination,[2] and 1·31 for acetylation.[3] There are many other examples which show that although all halogen substituents lead to overall deactivation (*i.e.* the rate coefficients relative to those of the unsubstituted compounds are <1), fluorine substitution can, for certain reagents of high selectivity, specifically activate the *para*-position towards electrophilic attack.

In solvolyses, activation by a *para*-fluoro-substituent has often been observed; for example, in the solvolysis of 1-methyl-1-phenylethyl chlorides, the rate is increased two-fold by a *para*-fluoro-substituent.[4] This is the basis of the negative value of $-0{\cdot}073$ for the σ^+ value for a *para*-fluoro-substituent for reaction where the resonance contribution from substituents is of primary importance. Similarly the rate coefficient for the hydrolysis of diphenylmethyl chloride is almost doubled by the introduction of one *para*-fluoro-substituent;[5] a *para*-chloro-substituent in the same system reduces the rate coefficient by about one-third. These rate changes have been shown to arise entirely from changes in the activation energies. Both α-fluoro- and α-chloro-substituents act as overall donors in S_N reactions where the substituents are now directly attached to the reaction centre,[6] and so the resonance effects are presumably dominant. However, the effect of these substituents on the rate is complicated by the entropy changes which accompany the changes in the activation energy.

Very little kinetic work has been reported on the effect of α-halogen-substitution (particularly fluorine) on the reactivity of olefinic compounds towards electrophilic reagents. There are examples of large deactivations by α-chloro-substituents, *viz.* 3,3-dichloropropene is *ca.* 600 times more reactive than 1,3,3-trichloropropene towards chlorine addition in acetic acid,[7] whilst allyl chloride is *ca.* 500 times more reactive than 2,3-dichloropropene in its acid-catalysed reaction with hypochlorous acid.[8] However, as far as the authors are aware, the only quantitative work describing the effect of α-fluorine substitution on the reactivity of olefins towards electrophilic addition is that of Peterson and his co-workers[9] who determined the rate coefficients for the addition of trifluoroacetic acid to 2-halogenopropenes. Their results are given in Table 1. It is clear that whereas both chlorine and bromine substitution reduces the rate coefficient, 2-fluoro-substitution leads to substantial activation, presumably by a stabilisation of the transition state leading

TABLE 1

First-order rate coefficients for the reaction of trifluoroacetic acid with 2-substituted propenes at 25°

Substrate	$10^5\,k_1/s^{-1}$	Relative rate coefficients
Propene	4·81	1
2-Fluoropropene	340	71
2-Chloropropene	1·70	0·35
2-Bromopropene	0·395	0·082

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[1] J. R. Knowles, R. O. C. Norman, and G. K. Radda, *J. Chem. Soc.*, 1960, 4885.

[2] L. M. Stock and F. W. Baker, *J. Amer. Chem. Soc.*, 1962, **84**, 1661.

[3] H. C. Brown and G. Marino, *J. Amer. Chem. Soc.*, 1959, **81**, 5929; 1962, **84**, 1658.

[4] Y. Okamoto and H. C. Brown, *J. Org. Chem.*, 1957, **22**, 485; *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[5] G. Kohnstam, *J. Chem. Soc.*, 1960, 2066.

[6] B. Bensley and G. Kohnstam, *J. Chem. Soc.*, 1956, 286; G. Kohnstam, D. Routledge, and D. L. H. Williams, *Chem. Comm.*, 1966, 113; S. C. J. Olivier and A. P. Weber, *Rec. Trav. chim.*, 1934, **53**, 869.

[7] P. B. D. de la Mare and R. Bolton, 'Electrophilic Additions to Unsaturated Systems,' Elsevier, Amsterdam, 1966, p. 85.

[8] P. B. D. de la Mare and J. G. Pritchard, *J. Chem. Soc.*, 1954, 3910; D. L. H. Williams, *J. Chem. Soc.* (*B*), 1969, 421.

[9] P. E. Peterson, R. J. Bopp, and M. M. Ajo, *J. Amer. Chem. Soc.*, 1970, **92**, 2834.

towards carbonium ion formation, by contribution of a structure where the positive charge is now localised on the fluorine atom, *i.e.* the resonance effect of the fluorine atom controls the rate of reaction. In order to establish whether this activation by fluorine attached directly to the double bond occurs generally in electrophilic addition we have determined the rate coefficients for the bromination of $CH_2{=}C(X)CH_2Cl$ for $X = H$, F, Cl, and Br, in two solvent systems.

EXPERIMENTAL

Preparation of Materials.—Commercial samples of allyl chloride, 2,3-dichloropropene, and 2-bromo-3-chloropropene were distilled and further purified by preparative g.l.c. prior to their use in the kinetic runs. 2-Fluoro-3-chloropropene was prepared by allylic chlorination of 2-fluoropropene as described by Moore and his co-workers.[10] It was also purified by g.l.c. Methanol was dried with magnesium and distilled from bromine immediately before use. Trifluoroacetic acid was refluxed with bromine and fractionated.[11] Water was distilled from potassium permanganate. Sodium bromide was recrystallised from water and dried.

Kinetic Measurements.—Rate coefficients were obtained by following the change in the electrode potential of the Pt, Br_2–Br^- electrode relative to that of a glass electrode.[12] Bromine was produced electrolytically directly in the reaction vessel and its concentration was usually in the range 1—2 × 10^{-4}M. The olefin, which was added from a weighed syringe, was at least in a 20-fold excess over the bromine. Good straight lines were obtained on a recorder for the e.m.f. *vs.* time plot over 60 mV which corresponded to 99% reaction. The second-order rate coefficient k_2, was obtained from the expression (1) where *a* and *b* are the

$$k_2 = \frac{-4{\cdot}692}{(a - b)} \cdot \frac{dE}{dt} \qquad (1)$$

initial concentration of the olefin and the bromine respectively and *E* and *t* are in mV and seconds. Runs were carried out in the presence of sodium bromide at 25° using a total reaction volume of 75 or 100 ml. The rate coefficients (Table 2) represent the mean value of at least three determinations.

Product Analyses.—Small quantities of bromine were added to a solution of the olefin in 50% methanol–water, over a period of time so that at no time did the bromine concentration exceed that used in the kinetic experiments. When reaction was complete the solvent was removed, water was added to the mixture, and the whole was extracted with ether. After drying and removal of the solvent the remaining liquid was examined by analytical g.l.c. The product from allyl chloride was a mixture of 1-bromo-3-chloropropan-2-ol (30%) and 2-bromo-3-chloropropanol (70%). The mixture was separated on g.l.c. and the secondary alcohol was identified by its retention time compared with that of a commercial sample. The product mixture had an i.r. spectrum identical with that of the product mixture from hypobromous acid and allyl chloride in water.[13] The main product (at least 70%) from all three 2-halogeno-olefins was 1-bromo-3-chloroacetone. This was identified by its retention time on g.l.c. compared with that of a sample prepared from the oxidation of 1-bromo-3-chloropropan-2-ol with chromic acid. Further, the 2,4-dinitrophenylhydrazones from all three reaction mixtures and from the authentic sample were identical, as shown by their i.r. spectra.

RESULTS AND DISCUSSION

The observed second-order rate coefficients, k_2, for the reaction of bromine with the olefins $CH_2{=}C(X)CH_2Cl$ are given in Table 2. These values are composite rate coefficients which can be analysed in terms of two concurrent reactions involving the bromine molecule Br_2 and the tribromide anion Br_3^-. In this work we have not determined the individual rate coefficients since it has been shown that, although there is some uncertainty regarding the exact role of the tribromide anion,[14] the composite rate coefficient can be used successfully to correlate reactivity with molecular structure.[15] We feel justified therefore in using the observed k_2 values directly in this work in the comparison of the substituent effects of the halogens. In some of our other work concerning substituent effects in bromination, including neighbouring group participation,[16] we have found that the composite rate coefficients parallel those for the reactions involving the bromine molecule alone.

TABLE 2

Values of k_2 for the bromination of $CH_2{=}C(X)CH_2Cl$ at 25°

X	k_2/l mol^{-1} s^{-1} in 50% MeOH–H_2O [a]	k_2/l mol^{-1} s^{-1} in CF_3CO_2H [b]
H	1440 ± 40	1020 ± 20
F	5·3 ± 0·3	0·56 ± 0·03
Cl	0·27 ± 0·01	0·11 ± 0·005
Br	0·34 ± 0·01	

[a] In the presence of 0·2M-NaBr. [b] In the presence of 0·01M-NaBr.

It is evident from Table 2 that all the halogens when substituted in the 2-position substantially deactivate the olefin in its reaction with bromine. This occurs in both solvent systems, 50% methanol–water and trifluoroacetic acid, thus indicating that the electron-withdrawing, inductive effect of the halogens is the principal factor which determines the reactivity of these 2-halogeno-olefins. If the inductive effect were the sole factor however, then one would expect a reactivity sequence $X = H \gg Br > Cl > F$ since it is generally accepted that the strength of the inductive effect decreases from fluorine to bromine. Our results, however, show that the 2-fluoro-olefin is considerably more reactive than both the 2-chloro- and 2-bromo-olefins; this is consistent with the interpretation that superimposed upon the inductive effect we have a contribution from the electron-

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[10] L. O. Moore, J. P. Henry, and J. W. Clark, *J. Org. Chem.*, 1970, **35**, 4201.

[11] H. C. Brown and R. A. Wirkkala, *J. Amer. Chem. Soc.*, 1966, **88**, 1447.

[12] J. R. Atkinson and R. P. Bell, *J. Chem. Soc.*, 1963, 3260.

[13] P. B. D. de la Mare, P. G. Naylor, and D. L. H. Williams, *J. Chem. Soc.*, 1962, 443; C. A. Clarke and D. L. H. Williams, *ibid.*, 1966, 1126.

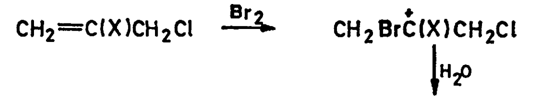
[14] J. E. Dubois and X. Q. Huynh, *Bull. Soc. chim. France*, 1968, 1436.

[15] J. E. Dubois and G. Mouvier, *Tetrahedron Letters*, 1963, **20**, 1325, and later papers.

[16] D. L. H. Williams, E. Bienvenüe-Goetz, and J. E. Dubois, *J. Chem. Soc.* (*B*), 1969, 517.

releasing, resonance effect which decreases in the order $F > Cl > Br$. A combination of these two effects (although with the $-I$ effect dominant) would then result in the observed order of reactivity. This explanation is generally used[17] to account for the reactivity of the halogenobenzenes in electrophilic aromatic substitutions. In all instances quoted the overall reactivity order is $X = H > F > Cl \sim Br$, *i.e.* the same order as we have observed in the bromination of olefins, although in our work, the overall deactivations by the halogen substituents are much greater than are those observed in the aromatic substitutions. The main point of similarity however is that the fluoro-substrate is significantly more reactive, in all cases than are both the chloro- and bromo-compounds.

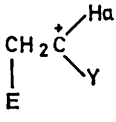
The analogy between electrophilic aromatic substitution and electrophilic addition to olefins extends also to the question of the orientation of the products. Halogen substituents in general lead to deactivation and *ortho–para* substitution, although analysis of the partial rate factors shows that fluorine can act as an overall donor of electrons. The reactivity is controlled by the $-I$ effect whereas the orientation of the products is governed by the $+M$ resonance effect. The same appears to be true for the addition to olefins. The products from the reaction of allyl chloride ($X = H$) and bromine in 50% methanol–water were found to be the mixed bromochloropropanols with the anti-Markownikoff product predominating as is the case in the addition of hypobromous acid, and also hypochlorous acid to allyl chloride and allyl bromide.[8,13] When $X =$ halogen the main product was that corresponding to Markownikoff addition, *i.e.* the 1-bromo product, in this case 1-bromo-3-chloroacetone (see Scheme). This reversal of the mode of addition by 2-halogeno-substituents has been observed previously, *e.g.* a 2-chloro-substituent reversed the orientation of the addition product obtained from allyl chloride and hypochlorous acid,[8] where the ratio of Markownikoff : anti-Markownikoff products changed from 30 : 70 to 98 : 2.



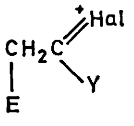
SCHEME

A further point remains to be discussed, *viz.* the apparent discrepancy between our results for bromination and those obtained by Peterson and his co-workers[9] for the addition of trifluoroacetic acid where a substantial activation by a 2-fluoro-substituent was observed (Table 2). We believe this can be resolved by a consideration of the detailed nature of the transition states involved.

If the transition state for electrophilic addition (of E^+) to an olefin $CH_2{=}C(Hal)Y$ approximates to the structure of the classical carbonium ion (I), then it is possible to predict the reactivity sequence $F > Cl > Br > H$ for 2-halogeno-substituents in the olefin. This is the order expected from the conjugative effect of the substituents and reflects their ability to stabilise such an ion by substantial contribution from structure (II). Stabilisation



(I)



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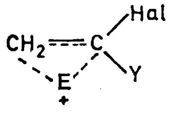

(III)

would thus be expected for *all* the halogens, as is observed in the S_N1 solvolyses of α-halogeno-halides.[6] Non-empirical LCAO–MO–SCF calculations have confirmed this order of stability $H < Cl < F$ for the classical halogen substituted ethyl cations[18] ($E = H$, $Y = H$). Our kinetic results therefore suggest that the transition state for electrophilic addition of bromine cannot be adequately represented by the classical carbonium ion (I). An alternative view is that the transition state resembles more closely the bridged ion (III). Here the effect of 2-halogeno-substitution would be expected to be one of destabilisation by the $-I$ effect of the substituents thus predicting a reactivity sequence $H > Cl > F$, *i.e.* deactivation by *all* the halogen substituents. Our bromination results are more in accord with this view. However, although we observe considerable deactivation by all the substituents relative to hydrogen, the 2-fluoro-olefin is considerably more reactive than the 2-chloro- and 2-bromo-olefins. This suggests that, although we write the transition state as structure (III), there must be a significant contribution, in the case of the halogeno-olefins, from structure (II), sufficient in fact to reverse the positions of F and Cl in the reactivity sequence. When $E = H$ however, as in the addition of trifluoroacetic acid,[9] it might be expected that the contributions from (II) are relatively greater since it is reasonable to expect that a bridged structure such as (III) would be less stable for $E = H$ than for $E = Br$. Again calculations support this view.[19] We can thus account for the different 2-halogeno-substituent effects found by us and by Peterson and his co-workers[9] in terms of the detailed structures of the two transition states involved.

It seems likely from our kinetic and product analysis results that the actual *intermediate* formed from allyl chloride and bromine is the bromonium ion, since both possible products of the ring-opening with the solvent are found. Many authors consider the bromonium ion to be a fully developed three-membered ring (IV)[20] whereas others[21] prefer the form (V) where the bromine

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[17] P. B. D. de la Mare and J. H. Ridd, 'Aromatic Substitution,' Butterworths, London, 1959, pp. 84—85.

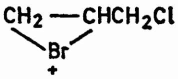
[18] D. T. Clark and D. M. J. Lilley, in the press.

[19] D. T. Clark, XXIII International Congress of Pure and Applied Chemistry, Butterworths, London, 1971, vol. I, p. 33.

[20] E. S. Gould, 'Mechanism and Structure in Organic Chemistry,' Holt, New York, 1959, p. 523; J. G. Traynham, *J. Chem. Educ.*, 1963, 392.

[21] Ref. 7, p. 116.

is fully attached to carbon atom 1 whilst there is additionally an electrostatic ion–dipole interaction between the bromine and carbon atom 2. The fact that the main addition product is that resulting from Markownikoff addition for the 2-halogeno-olefin suggests that the *intermediate* here is of the classical open chain form (VI), no doubt stabilised over the bromonium ion structure by the conjugative electron release from the halogen substituents. It would be difficult to envisage on steric grounds, particularly for the 2-chloro- and 2-bromo-olefins, the ring-opening of a bromonium ion exclusively by attack of the solvent at the crowded carbon atom 2.



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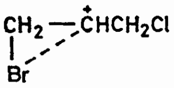

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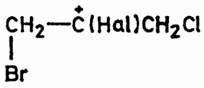

(VI)

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