The Kinetics and Mechanisms of Nucleophilic Displacements in Allylic Systems. Part V. Reactivities of Allylic Halides by the* S_N1 *Mechanism of Hydrolysis.*

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Rates of hydrolysis of a number of allylic chlorides in aqueous formic acid and in aqueous ethanol have been measured. In slightly aqueous formic acid the reactions proceed by the unimolecular mechanism; in aqueous ethanol some of the reactions are bimolecular. The unimolecular reactivity of allyl chloride is found to be greater, by a factor of about 25, than that of *n*-propyl chloride. Methyl and *tert.*-butyl groups in the 1- and the 3-position of allyl chloride enormously increase the rate of unimolecular hydrolysis. The theoretical significance of these results is discussed.

Previous papers (Parts I—IV *) have been concerned with bimolecular substitution with anionotropic rearrangement (S_N2'). As a further step in the study of nucleophilic displacement of chlorine in allylic chlorides, the present paper reports an investigation of the kinetics of the unimolecular (S_N1) process in these and related compounds.

Several investigations, mostly of solvolytic reactions in highly aqueous solvents, have provided evidence for the occurrence of the S_N1 mechanism in the reactions of some of the compounds studied. For example, the rate of hydrolysis of 1-methylallyl chloride in 50% aqueous ethanol was found by Young and Andrews (*J. Amer. Chem. Soc.*, 1944, **66**, 421) to be substantially unaffected by addition of hydroxyl ions: the reaction is therefore unimolecular. On the other hand, the hydrolyses of allyl chloride and 1 : 3-dichloroprop-1-ene in 50% aqueous ethanol (Andrews and Kepner, *ibid.*, 1948, **70**, 3456) and of allyl chloride, 2-methylallyl chloride, and 1 : 3-dichloroprop-1-ene in 50% aqueous dioxan (Pourrat and Schmitz, *Bull. Soc. chim.*, 1952, 505; Kirrmann, Schmitz, and Saito, *ibid.*, 1952, 515) are to a large extent bimolecular, since in these cases addition of hydroxyl ion produced a typically large acceleration in rate and led to purely second-order kinetics. 3-Methylallyl (but-2-enyl) chloride provides an intermediate type of behaviour; its rate of hydrolysis in 50% aqueous ethanol was found by Young and Andrews (*loc. cit.*) to be appreciably increased by the addition of hydroxyl ions, and they concluded that its solvolysis was partly bimolecular.

Oae and Werf recently (*J. Amer. Chem. Soc.*, 1953, **75**, 2724) studied the reactions between some allylic chlorides and silver nitrate in ethanol solution. The relative reactivities obtained are similar to those found in the present investigation for the solvolytic reactions in aqueous ethanol, where, as indicated by previous work and further substantiated by the results discussed later in this paper, hydrolysis proceeds by the unimolecular mechanism only with those allylic compounds having especially favourable structures. Oae and Werf found that the reactions with silver nitrate were of first order with respect to both organic chloride and silver nitrate. The products were identified only for the isomeric 1 : 3- and 3 : 3-dichloroprop-1-enes, and in each case it was only 3-chloroprop-2-enyl nitrate. In view of this result, it is not likely that the reaction of 1 : 3-dichloroprop-1-ene proceeds *via* a carbonium-ion intermediate, since in these circumstances ethers as well as nitrates would be expected. Furthermore, it has been shown by de la Mare and Vernon (*Research*, in the press) that, whereas bimolecular substitution in 1 : 3-dichloroprop-1-ene gives rise to unrearranged products, yet in unimolecular substitution derivatives of acraldehyde arising from anionotropic rearrangement are also found. It therefore seems probable that the silver nitrate reactions are mechanistically complex and should not be regarded as of simple S_N1 type.

To isolate the unimolecular mechanism for a series of allylic chlorides, including compounds with no especially facilitating structural feature, a solvent less favourable than

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* Parts I—III, *J.*, 1952, 3326, 3331, 3628; Part IV, *J.*, 1953, 3555.

aqueous ethanol or dioxan for the competing bimolecular process must be used. Such a solvent is slightly aqueous formic acid in which a low concentration of the nucleophilic reagent (water) is combined with a high ionising power. Since in this solvent even methyl and ethyl bromide are hydrolysed by the unimolecular mechanism, at least to a sufficient extent to give the characteristic rate sequence Me $<$ Et $<$ Pr^i (Bateman and Hughes, *J.*, 1940, 945), it is to be expected that in the more favourable case of the allylic chlorides similar mechanistic behaviour will be found.

Rates of hydrolysis of a number of compounds in formic acid containing 0·5% of water (hereafter called 0·5% aqueous formic acid) have therefore been measured, and the effect of increasing the water content of the solvent to 10% has also been determined. The reactions in 0·5% aqueous formic acid were found to be reversible, the value of the first-order rate coefficient (k_1) decreasing after about 10% reaction had occurred. The initial value of k_1, found by graphical extrapolation, or as the mean of values taken within the first 10% of reaction, was taken as the rate of the forward process. The results are given in Table 1.

TABLE 1. *Kinetic data for hydrolyses in aqueous formic acid.**

		0·5% of water			10% of water
Compound	Temp.	10^3k_1	E_A	log B	10^3k_1
$CH_2{:}CH{\cdot}CH_2Cl$	100°	0·762	24·8	11·48	—
$CH_3{\cdot}CH_2{\cdot}CH_2Cl$	100	*ca.* 0·029	—	—	—
$CH_2{:}C(CH_3){\cdot}CH_2Cl$	100	0·358	—	—	—
trans-$CHCl{:}CH{\cdot}CH_2Cl$	100	2·14 †	24·4	11·60	3·49 †
cis-$CHCl{:}CH{\cdot}CH_2Cl$	100	1·48 †	—	—	—
$CH_2{:}CH{\cdot}CHCl_2$	44·6	0·142 †	23·6	12·44	0·234 †
$CH_2{:}CH{\cdot}CHCl{\cdot}CH_3$	44·6	12·3	22·1	13·39	18·1
$CH_3{\cdot}CH{:}CH{\cdot}CH_2Cl$	44·6	7·7	22·6	13·59	10·5
$CH_2{:}CH{\cdot}CHBu^tCl$	44·6	5·46	—	—	—
$CHBu^t{:}CH{\cdot}CH_2Cl$	44·6	4·90	—	—	—

* Values of k_1 are expressed in $min.^{-1}$, E_A in kcal./mole.
† Calc. on the assumption that one chloride ion per mole is released.

Rate measurements on cinnamyl chloride and 1 : 1- and 3 : 3-dimethylallyl chloride could not be made in formic acid solvents, partly because the rates were inconveniently rapid even at the lowest temperature at which the solvent was liquid (*ca.* 8·0°) and partly because potentiometric titration of chloride ions could not be satisfactorily carried out in the presence of the unchanged materials. Rate measurements were, however, possible in 50% aqueous ethanol as solvent, and for comparison purposes similar measurements were made on the other compounds in the series. The results are given in Table 2.

TABLE 2. *Kinetic data for hydrolyses in 50% aqueous ethanol.*

Compound	Temp.	10^3k_1 *	E_A	log B	KOH (M)	10^3k_1	10^2k_2
$CH_2{:}CH{\cdot}CH_2Cl$	44·6°	0·101	20·4	10·08	0·1698	2·50 †	1·68
$CH_3{\cdot}CH_2{\cdot}CH_2Cl$	101·6	0·58	—	—	0·5329	18·6 †	3·55
$CH_2{:}C(CH_3){\cdot}CH_2Cl$	44·6	0·154	—	—	0·1552	2·56 †	1·78
trans-$CHCl{:}CH{\cdot}CH_2Cl$	44·6	0·099	21·0	10·48	0·1584	3·87 †	2·56
cis-$CHCl{:}CH{\cdot}CH_2Cl$	44·6	0·099	20·5	10·07	0·1622	5·81 †	3·52
$CH_2{:}CH{\cdot}CHCl_2$	64·0	1·13	23·5	12·34	0·1508	1·41	—
$CH_2{:}CH{\cdot}CHCl{\cdot}CH_3$	44·6	8·23	21·0	12·73	0·1165	8·77	—
$CH_3{\cdot}CH{:}CH{\cdot}CH_2Cl$	44·6	9·22	22·3	13·34	0·1960	20·0	—
$CHPh{:}CH{\cdot}CH_2Cl$	0	3·31	21·0	14·38	0·0150	3·47	—
$(CH_3)_2C{:}CH{\cdot}CH_2Cl$	0	93·0	—	—	0·1010	*ca.* 95·0	—
$CH_2{:}CH{\cdot}C(CH_3)_2Cl$	0	*ca.* 500	—	—	—	—	—

* In absence of KOH.
† Initial values of k_1 and E_A are in the same units as in Table 1; k_2 is in l. $mole^{-1}$ $min.^{-1}$.

Discussion of Results.—(a) *Mechanisms.* The unimolecular mechanism of nucleophilic displacement is characterised by a non-dependence of reaction rate on the concentration of the nucleophilic reagent. The simplest use of this criterion for reactions in aqueous solvents would be to expect that for a unimolecular reaction variation of the water content of the solvent would produce no change of rate. This test has been used to interpret experiments in aqueous formic acid where the ionising power of the solvent is not greatly dependent on the water content (Bateman and Hughes, *J.*, 1937, 1187). On the other hand, in aqueous ethanol, where a change in the water content produces a large "solvent effect," the criterion for unimolecularity must be differently applied. In this case the test is that, if a powerful base (*e.g.*, hydroxyl ion) causes no increase in rate, then the much more weakly basic solvent cannot be functioning as a reagent in the rate-determining stage, and the reaction must be unimolecular (Hughes, *Trans. Faraday Soc.*, 1941, **37**, 612).

On this basis the solvolytic reactions of allyl chloride, 2-methylallyl chloride, and 1 : 3-dichloroprop-1-ene in 50% aqueous ethanol are largely and perhaps entirely bimolecular, since in each case the addition of hydroxyl ions produced a large acceleration in rate similar to that found for *n*-propyl chloride. By the same criterion, the reactions of 3 : 3-dimethyl- and 1-methyl-allyl chloride are, on the other hand, nearly purely unimolecular. Incursion of a bimolecular component is apparent in the reactions of cinnamyl chloride, 3 : 3-dichloroprop-1-ene, and 3-methylallyl chloride, but except with the last compound the effect is probably comparatively small. The solvolysis of the tertiary halide, 1 : 1-dimethylallyl chloride, although too rapid for accurate assessment of the effect of added hydroxyl ions, must, for structural reasons, be purely unimolecular.*

From the results in formic acid solvents, it was found that increase of the water content of the solvent from 0·5 to 10% slightly increased the rate of solvolysis for all the compounds. In this connection, consideration should be given to the possibility of a "solvent effect" or the incursion of bimolecular reactions. The hydrolysis of *tert.*-butyl chloride in aqueous formic acid is unquestionably unimolecular, and its rate is independent of the water content over a range of 0·5—10% (Bateman and Hughes, *loc. cit.*). On the other hand, the increase in rate observed in the present instance is about the same for compounds having widely different bimolecular reactivities, and is shown, for example, by 1-methylallyl chloride, whose hydrolysis is unimolecular in 50% aqueous ethanol. We may, however, assume that the reactions in the less aqueous formic acid solvent are substantially unimolecular for the following reason. 1-Methylallyl chloride and 3 : 3-dichloroprop-1-ene are hydrolysed largely by the unimolecular mechanism in 50% aqueous ethanol, a solvent known from Bateman and Hughes's work (*loc. cit.*) to be less favourable for this mechanism than formic acid. Also, it has been previously noticed by these authors that, when the unimolecular mechanism operates in both solvents, there is a rough equality of rates. Tables 1 and 2 show that this equality of rate (and also of activation energy) holds approximately for those compounds whose hydrolysis in aqueous ethanol is unimolecular. For the other compounds the rates in 0·5% aqueous formic acid are much slower, and the activation energies larger, indicating a difference of behaviour in the two solvents. It is probable that the reactions of the less reactive compound are not entirely unimolecular in formic acid but are sufficiently so to enable valid structural comparisons to be made.

(b) *Structural comparisons.* The Table on p. 426 shows the relative rates of unimolecular hydrolysis at 44·6° of a number of compounds in 0·5% aqueous formic acid.

Comparison of the unimolecular reactivities of allyl and *n*-propyl chlorides shows that the allylic compound is the more reactive, as indeed it should be, but the ratio of the rates (*ca.* 25) is surprisingly small. In terms of the qualitative electronic theory, this might be interpreted as opposition of the inductive effect, $CH_2{=}CH{\leftarrow}CH_2{\leftarrow}Cl$, to electron release $CH_2{=}CH{-}CH_2{-}Cl$. Nevertheless, the resonance energy of the allyl radical is about 18 kcal., and a similar stabilisation in the ion, leading to a large rate difference between allyl and *n*-propyl chlorides, might have been expected. The observed ratio of rates corresponds, identity of the *B* factors being assumed, to a difference in activation energy of about 2·4 kcal. Using A. G. Evans and Hamann's value (*Trans. Faraday Soc.*,

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* The solvolysis of this compound in absolute ethanol is unaffected by added sodium ethoxide, and is therefore unimolecular. The reaction in 50% aqueous ethanol is very much faster, as would be expected for a unimolecular reaction. In aqueous ethanol, however, the first-order rate coefficient decreases as the reaction proceeds. A similar effect in glacial acetic acid has been shown by Young, Winstein, and Goering (*J. Amer. Chem. Soc.*, 1951, **73**, 1958) to be due to simultaneous solvolysis and rearrangement to 3 : 3-dimethylallyl chloride.

1951, **47**, 25) for the solvolysis at 25° of allyl chloride in slightly aqueous formic acid, and other published data, Franklin and Lumpkin (*J. Chem. Phys.*, 1951, **19**, 1073) computed that the S_N1 reactivities of allyl and *n*-propyl chloride in aqueous formic acid do not differ by a large factor. They drew attention to this as relevant to their observation that the appearance potential of the allyl ion from allyl chloride is the same, within the experimental error, as that of the *n*-propyl ion from *n*-propyl chloride (Stevenson and Hipple, *J. Amer. Chem. Soc.*, 1942, **64**, 2766). Their conclusion was that the resonance energy of the allyl ion is small. Such a conclusion is not at variance with the present results, which show that the allyl double bond produces a small but significant enhancement of unimolecular reactivity.

$\mathrm{CH_2{:}CH{\cdot}CH_2Cl}$ 1·00	$\mathrm{CH_2{:}C(CH_3){\cdot}CH_2Cl}$ *ca.* 0·5 *	$\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2Cl}$ *ca.* 0·04 *	*trans*-$\mathrm{CHCl{:}CH{\cdot}CH_2Cl}$ 3·09
cis-$\mathrm{CHCl{:}CH{\cdot}CH_2Cl}$ *ca.* 2·1 *	$\mathrm{CH_2{:}CH{\cdot}CHCl_2}$ $6{\cdot}54 \times 10$	$\mathrm{CH_2{:}CH{\cdot}CHCl{\cdot}CH_3}$ $5{\cdot}67 \times 10^3$	
$\mathrm{CH_3{\cdot}CH{:}CH{\cdot}CH_2Cl}$ $3{\cdot}55 \times 10^3$	$\mathrm{CH_2{:}CH{\cdot}CHBu^tCl}$ $2{\cdot}52 \times 10^3$	$\mathrm{CHBu^t{:}CH{\cdot}CH_2Cl}$ $2{\cdot}26 \times 10^3$	
$\mathrm{CHPh{:}CH{\cdot}CH_2Cl}$ *ca.* 5×10^5 †	$\mathrm{(CH_3)_2C{:}CH{\cdot}CH_2Cl}$ *ca.* $1{\cdot}5 \times 10^7$ †	$\mathrm{CH_2{:}CH{\cdot}C(CH_3)_2Cl}$ *ca.* 8×10^7 †	

* These are actually the relative rates observed at 100°. The true values at 44·6° are probably not very different.

† These values have been found by comparing the rates in 50% aqueous ethanol at 0° with the rate for 1-methylallyl chloride under the same conditions. The factors so obtained were multiplied by the rate of solvolysis of 1-methylallyl chloride, relative to allyl chloride in 0·5% aqueous formic acid at 44·6°. The relative rates found in this way will be strictly correct only if the changes of solvent and temperature are without effect. This, of course, will not be the case, but the error is unlikely to be large.

Substitution by an α-chlorine atom in allyl chloride is seen to increase the rate of hydrolysis in 0·5% aqueous formic acid, owing partly to a decrease in activation energy and partly to an increase in the *B* factor.* Similar increases in rate with α-halogen substitution have been found in the hydrolysis of benzyl halides in highly aqueous solvents, although under these conditions the reaction of the unsubstituted compound was not entirely unimolecular, and substitution by the second halogen increased the activation energy (Olivier and Weber, *Rec. Trav. chim.*, 1934, **53**, 869; Hine and Lee, *J. Amer. Chem. Soc.*, 1951, **73**, 22). Hughes (*Trans. Faraday Soc.*, 1941, **37**, 603) has stated that α-halogen atoms enhance unimolecular reactivity by their electron-releasing properties, presumably giving increased stabilisation to the carbonium ion formed. In the same way, a chlorine atom in the 3-position of allyl chloride produces a similar, though smaller, enhancement of reactivity.

Methyl groups in either the 1- or the 3-position produce large increases in unimolecular reactivity, the effect of a second group being similar in magnitude to that of the first. Thus 1 : 1- and 3 : 3-dimethylallyl chloride † are more reactive than the unsubstituted compound by a factor of about 10^7—10^8. A phenyl group in the 3-position produces an effect intermediate in magnitude between those of one and two methyl groups. A methyl group in the 2-position is without significant effect.

It is noteworthy that the expected order of reactivity, 3- > 1-methylallyl chloride, is actually found under unimolecular conditions, whereas for the solvolysis in aqueous ethanol (Young and Andrews, *loc. cit.*) and the reaction with ethanolic silver nitrate (Oae and Werf, *loc. cit.*) the reverse order is obtained.

Two major points of interest emerge when comparison is made of the effects produced by methyl and *tert.*-butyl groups; first, the increase in rate is much the same for substitution of a given group in either the 1- or the 3-position, and secondly, for each position of substitution the order of electron release is $\mathrm{Me} > \mathrm{Bu^t} \gg \mathrm{H}$. This so-called

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* This simultaneous operation of effects appears to be general among unimolecular reactions in solution.

† This result shows that the reactivity of the tertiary compound is not due to steric acceleration, since the methyl groups have roughly the same effect when in a position removed from the reaction centre.

" hyperconjugation order " is to be expected in $S_{\mathrm{N}}1$ reactions because of their strongly electron-demanding nature (Bevan, Hughes, and Ingold, *Nature*, 1953, **171**, 301), and has been previously observed in the solvolyses of *p*-alkyldiphenylmethyl chlorides (Hughes, Ingold, and Taher, *J.*, 1940, 949). Owing no doubt to the proximity of the electron-releasing groups to the reaction centre, the rate factors observed in the present case are, however, considerably larger than any previously reported.

Hyperconjugation, as it is usually considered (cf. Baker, " Hyperconjugation," Oxford Univ. Press, 1952), arises from the intervention in the reaction process of the σ electrons of the C–H bonds of the methyl groups and may be represented by $\mathrm{H}\overset{\curvearrowright}{—\mathrm{C}}—$. Although there is no formal need in the present case to postulate a similar intervention of the σ electrons of the C–C bonds in the *tert.*-butyl group, it is nevertheless tempting to do so, since the electron-releasing power of the *tert.*-butyl group is apparently relayed through the allyl chain, exactly as with the methyl group, without appreciable loss. Thus the rate of hydrolysis of 3-*tert.*-butylallyl chloride is not much less than that of the 1-substituted compound. The postulation of the operation of C–C hyperconjugation, made by Berliner and Bondhus (*J. Amer. Chem. Soc.*, 1948, **70**, 854) for the case of electrophilic halogen substitution in *tert.*-butylbenzene, seems plausible in reactions which create a strong electron demand, and therefore draw forth all possible forms of electron release.

EXPERIMENTAL

(a) *Materials.*—Allyl chloride, 2-methylallyl chloride, *n*-propyl chloride, and cinnamyl chloride were prepared from commercial samples, which were washed with aqueous sodium hydrogen carbonate, dried ($CaCl_2$), and fractionated. The products had, respectively : b. p. 44·7—44·8°/760 mm., n_{D}^{25} 1·4116, hydrolysable Cl 46·3% (Calc. for C_3H_5Cl : Cl, 46·3%) ; b. p. 72·1—72·2°/760 mm., n_{D}^{25} 1·4244, hydrolysable Cl 39·1% (Calc. for C_4H_7Cl : Cl, 39·2%) ; b. p. 47·1°/781 mm., n_{D}^{25} 1·3850 ; b. p. 95—96°/3 mm., hydrolysable Cl 23·3% (Calc. for C_9H_9Cl : Cl, 23·3%). *cis*- and *trans*-1 : 3-Dichloroprop-1-ene and 3 : 3-dichloroprop-1-ene were prepared as described in Part I (*loc. cit.*).

Samples of 1- and 3-*tert.*-butylallyl chloride were kindly given by Dr. P. C. Merriman and had, respectively : b. p. 53·5—54·7°/58 mm., n_{D}^{25} 1·4348 (Found : C, 63·8 ; H, 10·0 ; Cl, 26·4. Calc. for $C_7H_{13}Cl$: C, 63·4 ; H, 9·8 ; Cl, 26·8%) ; b. p. 63·4—63·6°/58 mm., n_{D}^{95} 1·4390 (Found : C, 63·3 ; H, 10·0 ; Cl, 26·3. Calc. for $C_7H_{13}Cl$: C, 63·4 ; H, 9·8 ; Cl, 26·8%).

1 : 1- and 3 : 3-Dimethylallyl chloride were prepared by Ultée's method (*J.*, 1948, 530), and had, respectively : b. p. 28·0—29·5°/120 mm., n_{D}^{25} 1·4170, n_{D}^{20} 1·4197 ; b. p. 58—59°/120 mm., n_{D}^{25} 1·4477, n_{D}^{20} 1·4492 (Found : C, 57·4 ; H, 8·7 ; Cl, 33·2. Calc. for C_5H_9Cl : C, 57·4 ; H, 8·6 ; Cl, 34·0%).

1- and 3-Methylallyl chloride were obtained by the action of thionyl chloride on crotyl alcohol. Cautious dropwise addition of crotonaldehyde (200 g.) to a stirred suspension of lithium aluminium hydride (36 g.) in dry ether gave, after working up in the usual way, crotyl alcohol (120 g., 58%), b. p. 120—122°/760 mm. The alcohol (116 g.) was cooled to 0° and thionyl chloride (195 g.) added dropwise during 2 hr. Next morning, the product was washed with aqueous sodium hydrogen carbonate until no further reaction was observed, and dried ($CaCl_2$). Fractionation yielded 1-methylallyl chloride (33 g.), b. p. 63·6—63·9°/760 mm., n_{D}^{25} 1·4125, hydrolysable Cl 39·2% (Calc. for C_4H_7Cl : Cl, 39·2%) ; an intermediate fraction (10 g.), b. p. 63·9—84·1°/760 mm. ; 3-methylallyl chloride (39 g.), b. p. 84·1—84·4°/760 mm., n_{D}^{25} 1·4325, hydrolysable Cl 39·2%. Chlorination of crotyl alcohol under these conditions therefore gives the isomeric 1- and 3-chlorides in the ratio 1 : 1·16, and with a combined yield of 57%.

Anhydrous formic acid, obtained by careful fractionation of the commercial 98—100% acid, had b. p. 101°/760 mm., m. p. 8·30°. Aqueous formic acid solvents were prepared by adding a known weight of water to a known weight of anhydrous acid.

Ethanol was dried by refluxing it with sodium ethoxide and ethyl phthalate and then distilled (Manske, *J. Amer. Chem. Soc.*, 1931, **53**, 1106). Aqueous ethanol solvents were prepared by mixing known volumes of water and dry ethanol.

(b) *Rate Measurements.*—Thermostats were of conventional design and were constant in temperature to within ±0·03°. Kinetic experiments with formic acid solvents were carried out as follows : a known quantity of organic chloride was dissolved in the medium, and the solution made up to 100 c.c. at room temperature. Portions of the solution (*ca.* 5·0 c.c.) were sealed, leaving little free space, in stout Pyrex tubes. These were heated in a thermostat,* removed at appropriate intervals, cooled in alcohol–carbon dioxide, and broken under 100 c.c. of ethanol.† The amount of chloride ions produced was determined by potentiometric titration with 0·01N-silver nitrate. The extent of reaction in the time required for the tubes to reach the temperature of the thermostat was determined from blanks. First-order rate coefficients were calculated from the formula $k_1 = (2{\cdot}303/t) \log a/(a - x)$, where a is the initial concentration of organic chloride and x is the amount which has reacted at time t. When the value of k_1 decreased as the reaction proceeded, the initial value was found by graphical extrapolation.

Details for typical runs with 3-methylallyl chloride at 44·6° are given below, titres referring to c.c. of 0·01N-silver nitrate :

0·5% Aqueous formic acid

t (min.)	Titre	10^3k_1 (min.$^{-1}$)	t (min.)	Titre	10^3k_1 (min.$^{-1}$)
0	6·58	—	25	11·88	6·17
8	8·60	6·99	30	12·60	5·91
12	9·40	6·53	35	13·22	5·65
16	10·30	6·62	40	13·90	5·50
20	11·04	6·41	50	14·70	4·88

[RCl] = 0·084M, 5·17-c.c. portions,
k_1 (initial) = $7{\cdot}50 \times 10^{-3}$.

10% Aqueous formic acid

t (min.)	Titre	10^3k_1 (min.$^{-1}$)	t (min.)	Titre	10^3k_1 (min.$^{-1}$)
0	7·90	—	21	14·90	10·3
4	9·38	10·4	26	16·55	10·5
8	10·80	10·5	31	17·87	10·4
12	12·28	10·5	36	19·35	10·6
16	13·53	10·5	46	21·85	10·6

[RCl] = 0·0852M, 5·17-c.c. portions,
k_1 (mean) = $10{\cdot}5 \times 10^{-3}$.

Kinetic experiments in aqueous ethanol at temperatures above 40° were also carried out by the sealed-tube method. The tubes were broken under 100 c.c. of ethanol, and the resulting solutions were titrated with standard alkali (or acid, if the reaction mixture contained alkali), lacmoid being used as indicator. At lower temperatures a different procedure was used : a suitable quantity of organic halide was added to the solvent contained in a stoppered flask in a thermostat. After shaking, aliquot parts of the solution were removed by pipette at appropriate times and run into 100 c.c. of ethanol. The resulting solution was then titrated as previously described. The initial concentration of the organic halide was calculated from the titre obtained after complete reaction.

For the very reactive 1 : 1- and 3 : 3-dimethylallyl chlorides it was necessary to cool the ethanol used to quench the reaction and to titrate with standard alkali (or acid) made up in absolute ethanol.

Details for a typical run with cinnamyl chloride (0·0123M, 20-c.c. portions of solution) in 50% aqueous ethanol at 25·8° are as follows, the titres referring to 0·0324N-sodium ethoxide :

t (min.)	0	2·09	4·67	6·59	8·83	11·10	13·72	16·25	18·93	21·63	25	33	∞
Titre	1·26	2·60	3·78	4·80	5·60	6·25	6·81	7·29	7·51	7·90	8·19	8·50	8·88
10^2k_1 (min.$^{-1}$)	—	9·3	9·3	9·5	9·6	9·0	9·7	9·7	9·2	9·7	9·8	9·3	—

k_1 (mean) = $9{\cdot}5 \times 10^{-2}$.

Values of Arrhenius parameters were obtained by graphical means from measurements of rate coefficients at three different temperatures, usually spaced at 10° intervals; *e.g.*, mean values of first-order rate coefficients ($\times 10^3$, min.$^{-1}$) for 3-methylallyl chloride in 0·5% aqueous formic acid were : 44·6°, 7·50, 7·50, 8·10; 35·1°, 2·46; 25·1°, 0·735.

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* At the higher temperatures considerable pressure developed in the tubes, owing to formation of carbon monoxide from formic acid. For example, tubes containing 0·5% aqueous formic acid mostly exploded after 3 hr.' heating at 100°. It was found best to cool the tubes in alcohol–carbon dioxide at −80°, thereby completely freezing the liquid contents, and then to release the pressure by cautiously applying a small blowpipe flame to the tip of the tube.

† Ethanol was used as the titration medium, in order to prevent further hydrolysis of the organic chloride during titration.