The Kinetics and Mechanisms of Nucleophilic Displacements in Allylic Systems. Part VI. Solvolysis and the accompanying Rearrangement of* 1 : 1- *and of* 3 : 3-*Dimethylallyl Chloride.*

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The kinetics of the solvolysis of 1 : 1- and of 3 : 3-dimethylallyl chloride have been examined in ethanol and in aqueous ethanol, both with and without added chloride or ethoxide ions. The products recoverable from partial reaction of the former compound in 75% ethanol in the presence of $^{36}Cl^-$ include 1 : 1-dimethylallyl [^{36}Cl]chloride and 3 : 3-dimethylallyl [^{36}Cl]chloride. Similarly, 1 : 1-dimethylallyl [^{36}Cl]chloride can be identified in the products of partial solvolysis of 3 : 3-dimethylallyl chloride in the presence of $^{36}Cl^-$. These results are interpreted as evidence that solvolysis of these compounds in aqueous alcohol is accompanied by both (*a*) intramolecular rearrangement (S_Ni'; " internal return ") and (*b*) unimolecular rearrangement (S_N1').

IN Part IV (*J.*, 1953, 3555), the second-order reaction of 1 : 1-dimethylallyl chloride with sodium thiophenoxide in ethanol, giving 3 : 3-dimethylallyl phenyl sulphide, was interpreted as a bimolecular nucleophilic displacement with anionotropic rearrangement (S_N2'). The structure and reactions of 1 : 1-dimethylallyl chloride (cf. Ultée, *Rec. Trav. chim.*, 1949, **68**, 483) make it clear, however, that both this compound and its allylic isomer are favourably disposed to unimolecular (S_N1) reactions in which ionisation, giving a mesomeric carbonium ion, is the rate-determining step; rate-comparisons supporting this view were presented in Part V (Vernon, *J.*, 1954, 423).

Young, Winstein, and Goering (*J. Amer. Chem. Soc.*, 1951, **73**, 1958) examined in detail the solvolysis of 1 : 1- and of 3 : 3-dimethylallyl chloride in glacial acetic acid, and observed that solvolysis of the former chloride is accompanied by rearrangement to the latter. The rates of the rearrangement and of the solvolyses were unaffected by added chloride ions (0·024M). It was deduced that the rearrangement is essentially intramolecular, in that the migrating chlorine atoms do not become kinetically equivalent to the chloride ions of the environment. They concluded that the migration involved an incipient formation of an ion-pair which collapsed to give the isomeric chloride more rapidly than it reacted to give products of solvolysis.

The present results extend our knowledge of the reactions of these compounds in ethanol and aqueous ethanol and show that both S_N1' and S_Ni' rearrangements can occur in this system.

EXPERIMENTAL

Materials and methods. The methods described in Parts IV and V (*locc. cit.*) were used for the preparation of 1 : 1- and 3 : 3-dimethylallyl chloride; their refractive indices were checked

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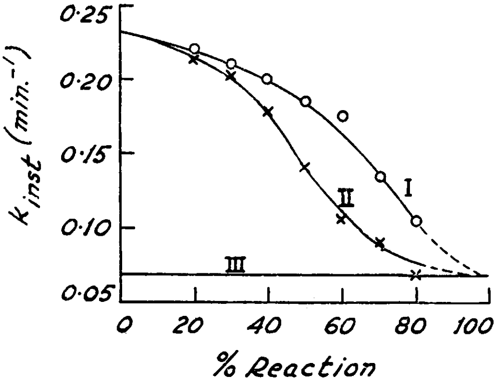
* Part V, *J.*, 1954, 423.

before use. Solvents and general methods were as described in earlier parts. Sodium [^{36}Cl]chloride was supplied by the Atomic Energy Research Establishment, Harwell; it was distilled with dilute sulphuric acid, the first few ml. of distillate being rejected. The resulting solution of [^{36}Cl]hydrochloric acid was converted as required into lithium [^{36}Cl]chloride. Radioactivity was measured with a counter made by Twentieth Century Electronics Ltd. for counting of liquid samples, with standard amplifying and recording equipment.

*Kinetic measurements in 75% ethanol.** The following are the results for the solvolysis of 1 : 1-dimethylallyl chloride at 25·0°. At intervals, samples (5·0 ml.) were titrated in cooled ethanol with 0·0119N-sodium hydroxide, lacmoid being used as indicator. The stability of the end-points proved that the reaction was stopped instantaneously by this procedure. If the reaction is quenched with water, as was done by Hatch and Gerhardt (*J. Amer. Chem. Soc.*, 1949, **71**, 1677) and by Hatch and Journeay (*ibid.*, 1953, **75**, 3712), who used the method of Tamele, Ott, Marple, and Hearne (*Ind. Eng. Chem.*, 1941, **33**, 115) in studying the reactions of ethoxide ion in ethanol with 3 : 3-dimethallyl chloride and with 2 : 3 : 3-trimethylallyl chloride, further rapid hydrolysis results, as would be expected, and this is therefore an unsuitable method for these compounds.



Instantaneous rate coefficients ($k_{inst.}$) *for solvolyses in* 75% *ethanol at* 25°.

I = 1 : 1-Dimethylallyl chloride.
II = 1 : 1-Dimethylallyl chloride + lithium chloride (0·98M).
III = 3 : 3-Dimethylallyl chloride (mean k_1).

In the Figure are shown (circles) the instantaneous rate-coefficients, $k_{inst.} = (dx/dt)/(a - x)$, obtained by drawing, at intervals of 10% reaction, tangents to the curve of % reaction (x) against time (t). Similar results are also shown (crosses) for reaction under identical conditions, in the presence of added 0·98N-lithium chloride. The reactions are very fast, and it is difficult to estimate instantaneous rate-coefficients with precision, so that the observed scatter is not unexpected, but it is clear that the coefficients begin to decrease at an earlier point in the reaction when lithium chloride is present.

Time (min.)	0·00	0·67	1·35	2·05	2·60	3·58	5·05
Titre (ml.)	2·00	5·40	7·52	9·70	11·42	13·32	15·58
k_1 * (min.$^{-1}$)	—	0·253	0·216	0·213	0·218	0·205	0·193
Time (min.)	6·80	8·87	10·87	14·05	17·13	21·13	∞
Titre (ml.)	17·51	18·80	19·79	20·70	21·49	21·90	23·80
k_1 * (min.$^{-1}$)	0·183	0·166	0·156	0·137	0·131	0·116	—

* Values of k_1 are first-order rate-coefficients calculated by means of the usual formula $k_1 = 2{\cdot}303\,\{\log_{10}[a/(a - x)]\}/t$, where x is the amount of RCl which has reacted at time t. For a case such as this in which the rate-coefficients change with time, they represent a weighted average of the instantaneous rate-coefficients in the interval 0—t.

That the reaction is unimolecular was shown by examining the rate in the presence of added base. With 0·0371M-chloride, and 0·059M-potassium hydroxide, the extrapolated initial value of k_1 was 0·208 min.$^{-1}$, and this decreased to 0·12 min.$^{-1}$ at 90% reaction. The initial value of the rate coefficient and the decrease in rate as the reaction progresses are unaffected by the presence of alkali.

At 0·0°, similar experiments gave an initial value of k_1 = 0·0130 min.$^{-1}$; from this value and the extrapolated $k_{inst.}$ = 0·230 min.$^{-1}$ for reaction at 25°, the energy of activation for the reaction is calculated to be 18·5 kcal./mole.

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* The term y% ethanol refers to a solvent prepared by mixing y ml. of ethanol with (100 — y) ml. of water.

The following are results for the solvolysis of 3 : 3-dimethylallyl chloride at 25°. Samples (5·0 ml.) were pipetted into acetone and titrated with 0·0352N-sodium hydroxide, lacmoid being used as indicator.

Time (min.) ...	0·00	3·83	5·93	7·95	10·19	12·57	19·00	23·25	27·79	34·75	∞
Titre (ml.)	0·49	2·29	3·12	3·81	4·55	5·19	6·39	6·99	7·40	7·80	8·51
k_1 (min.$^{-1}$)	—	0·066	0·067	0·065	0·069	0·070	0·070	0·072	0·071	0·070	—

The reaction was followed over 91%, and the rate coefficients (mean, 0·069) do not fall. With added sodium hydroxide (0·0584N, 0·1050N), the mean rate coefficients were 0·071 and 0·066, respectively. At 0·0°, $k_1 = 0{\cdot}00338$ min.$^{-1}$, whence the activation energy is 19·4 kcal./mole.

Products of solvolysis in 75% ethanol. It is generally difficult to recover unchanged organic chloride from the product of the partial reaction of an allylic chloride with aqueous ethanol, since the products (ethers and alcohols) have boiling points near those of the chlorides, and azeotropes are often formed between the reactants. In the following experiment (*A*), 1 : 1-dimethylallyl chloride (26 g.; n_{D}^{25} 1·4175) was added to 700 ml. of a solution in 75% ethanol of 0·706N-lithium [^{36}Cl]chloride. After 4·8 min. at 25° the mixture was added to cold pentane, and was washed rapidly with ice-water several times. The pentane extract was dried (Na_2SO_4), and fractionated. After removal of the pentane the following fractions, which were analysed for chloride and for radioactivity, were collected:

B. p./120 mm.	40—42°	42—56°	56—61°	61—62°	62—65°
Wt.	0·9	2·3	2·2	1·4	1·1
n_{D}^{25}	1·4055	1·4082	1·4286	1·4400	1·4390
%-Purity (as C_5H_9Cl, by quantitative hydrolysis)	43·6	32·5	61·4	80·3	74·7
^{36}Cl (% in the organic chloride, based on the activity of inorg. Cl$^-$ at time of stopping the reaction)	37	40	61	63	64

The last fraction was analysed kinetically. A sample (1·026 g.) was added to 100 ml. of 75% ethanol at 25°. Samples (5·0 ml.) were removed at intervals and titrated with 0·0169N-sodium hydroxide in ethanol with lacmoid as indicator:

Time (min.)	0·00	2·00	4·00	8·20	10·66	16·50	20·35	∞
Titre (ml.)	1·69	4·12	6·31	10·20	12·02	15·20	16·80	21·72
k_1 (min.$^{-1}$)	—	0·065	0·066	0·067	0·068	0·068	0·069	—

The mean velocity coefficient agrees well with that for 3 : 3-dimethylallyl chloride.

To check the method of recovery the following experiment (*B*) was performed. 1 : 1-Dimethylallyl chloride (25 g.; n_{D}^{25} 1·4170) was added to 750 ml. of a 75% ethanolic solution of 0·675N-lithium [^{36}Cl]chloride. The reaction was stopped within 1 min. and the material was worked up as before giving the following fractions:

B. p./124 mm.	34—36°	36—58°	58—60°	residues *
Wt. (g.)	4·7	0·7	1·1	0·3
n_{D}^{25}	1·4158	1·4260	1·4411	—
%-Purity (as C_5H_9Cl, by quantitative hydrolysis)	86	76	81	—
^{36}Cl (% in the organic chloride, based on the activity of the original Cl$^-$)	3	13	20	—

* From column and still-pot, by titration of the chloride produced on hydrolysis; this figure is recorded to show that almost all of the chloride had been distilled.

Very much less rearranged chloride, containing a very much smaller proportion of ^{36}Cl, was produced in experiment *B* than in *A*.

The following are the results of an experiment (*C*), in which 3 : 3-dimethylallyl chloride (37 g.) was allowed to react for 5 min. at 25° with 900 ml. of a 75% ethanolic solution of 0·584N-lithium [^{36}Cl]chloride. From the product there was obtained an initial fraction (0·75 g.), b. p. 40—44°/124 mm., containing 34% of C_5H_9Cl (by quantitative hydrolysis), and 40% of ^{36}Cl in the organic chloride (based on the activity of the Cl$^-$ in the solution when the reaction was stopped). A final fraction of unchanged 3 : 3-dimethylallyl chloride, b. p. 63°/124 mm., n_{D}^{25} 1·4472, had a corresponding ^{36}Cl activity of 20%. The initial fraction was analysed kinetically by adding a sample (0·706 g.) to 50 ml. of 75% ethanol at 25°. Samples (5·0 ml.) were titrated with 0·0169N-alkali in chilled ethanol, with lacmoid as indicator:

Time (min.)	0·00	0·80	1·62	2·73	4·12	6·25	∞
Titre (ml.)	1·29	2·95	4·50	6·14	7·60	9·05	13·40
x (% reaction)	10	22	34	46	57	68	100
k_1 (min.$^{-1}$)	—	0·184	0·190	0·187	0·179	0·164	—

The accordance between this result and that recorded above for 1 : 1-dimethylallyl chloride shows that there has been isolated a small quantity of this product of rearrangement, probably contaminated with 1 : 1- and 3 : 3-dimethylallyl ethyl ether.

Kinetics of solvolysis in ethanol. The reaction of 1 : 1-dimethylallyl chloride in ethanol at 44·6° has k_1 = 0·0110 min.$^{-1}$. With addition of 0·097N-sodium ethoxide, k_1 is 0·0124 min.$^{-1}$. The following are the results for the reaction with addition of 0·053N-sodium ethoxide. Portions (5·53 ml.) were added to 100 ml. of chilled ethanol containing 5·00 ml. of 0·0871N-acid, and were back-titrated with 0·0110N-sodium hydroxide.

Time (min.)	0·00	12·00	18·00	31·50	46·00	68·00	95·00	153·5	162·0	∞
Titre (ml.) ...	13·32	14·82	15·55	16·78	18·19	19·44	20·79	22·40	22·70	24·35
k_1 (min.$^{-1}$) ...	—	0·0121	0·0125	0·0119	0·0126	0·0119	0·0119	0·0113	0·0118	—

These details show that k_1 in this solvent is sensibly constant over the whole course of the reaction. With added M-lithium chloride, k_1(0·0143 min.$^{-1}$) is constant over at least 50% reaction. 3 : 3-Dimethylallyl chloride reacts more slowly; at 60·4° k_1 = 0·0192, and at 35°, k_1 = 0·00132 min.$^{-1}$, whence E = 22·2 kcal./mole. In contrast with that of its allylic isomer, the reaction of this compound is accelerated by sodium ethoxide, showing the incursion of a bimolecular substitution, which becomes the dominant reaction (k_2 = 0·064 l. mole^{-1} min.$^{-1}$ at 35·0°) when the concentration of ethoxide ion becomes sufficiently large (*e.g.*, >0·1M).

Products of solvolysis in ethanol. 3 : 3-Dimethylallyl chloride was solvolysed in ethanol at 60—70°, the solution being stirred and kept neutral during the reaction by titration with alcoholic sodium ethoxide with lacmoid as indicator.* The product was extracted with *n*-pentane, and the extracts were washed with water and fractionated, a 3′ helix-packed, jacketed column being used. The following fractions were collected :

Wt. (g.) ...	3·31	1·31	1·90	1·87	3·08	1·86	2·00	1·26	3·44	0·47
B. p.	40—90°	90—94°	94—96°	96—98°	98—105°	105—120°	120—126°	126°	126°	residues
n_D^{25}	1·3762	1·3938	1·3972	1·3989	1·3993	1·4045	1·4142	1·4160	1·4162	1·4278

It being assumed that the fractions are binary mixtures of *n*-pentane (n_D^{25} 1·3550) and 1 : 1-dimethylallyl ethyl ether (n_D^{25} 1·3991), or of the latter and 3 : 3-dimethylallyl ethyl ether (n_D^{25} 1·4162), it can be estimated that the product (75% yield, the residues being neglected) contained 60% of 1 : 1-dimethylallyl ethyl ether and 40% of 3 : 3-dimethylallyl ethyl ether. A similar experiment, with 1 : 1-dimethylallyl chloride, gave a mixture containing 70% of 1 : 1-dimethylallyl ethyl ether and 30% of 3 : 3-dimethylallyl ethyl ether. We consider the difference between these proportions to be greater than the experimental error which we consider to be ±3%.

Although the corresponding methyl ethers have been described by Ultée (*Rec. Trav. chim.*, 1949, **68**, 352), and 3 : 3-dimethylallyl ethyl ether has been characterised by Claisen, Kremers, Roth, and Tietze (*J. pr. Chem.*, 1922, **105**, 80), 1 : *1-dimethylallyl ethyl ether* has not been reported previously. Refractionation of bulked fractions from the above two solvolyses gave a product of constant b. p. 98—99° and n_D^{25} 1·3991, having a camphoraceous odour (Found : C, 73·8; H, 12·4. $C_7H_{14}O$ requires C, 73·7; H, 12·3%).

Kinetics of solvolysis in 50% ethanol. In 50% ethanol at 0°, 3 : 3-dimethylallyl chloride solvolyses rapidly (k_1, 0·093 min.$^{-1}$). The corresponding reaction of 1 : 1-dimethylallyl chloride is extremely rapid, and its small solubility makes it difficult to obtain a point at an early stage in the reaction. The rate coefficient is initially probably rather greater than 0·5 min.$^{-1}$, and drops to 0·17 min.$^{-1}$ at 90% reaction, showing that rearrangement accompanies the solvolysis in this solvent.

Search for products of elimination. The most likely product of elimination from either of these chlorides is isoprene, which has an intense absorption maximum in the neighbourhood of 2200 Å (ε = 19,800); 1 : 1-dimethylallyl chloride has no appreciable absorption in this region, but 3 : 3-dimethylallyl chloride has some absorption (in ethanol : ε = 3000 at 2150 Å, ε = 2300 at 2200 Å). This absorption, which was measured with a Unicam ultra-violet spectrophotometer, Model SP 500, disappears when the compound solvolyses in ethanol, and hence the ethers produced by solvolysis have little or no absorption in this region. Reaction

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* It is estimated that the solution never contained more than M/8000-OEt$^-$, whence it is estimated that a bimolecular reaction with ethoxide contributed no more than 1% to the total reaction. A bimolecular reaction with ethanol molecules would have contributed less than 2%, if a ratio of 10^5 is assumed for the bimolecular rate coefficients for OEt$^-$ and EtOH.

mixtures were analysed for isoprene by measuring the absorption at 2200 Å, with the following results:

Compound	Solvent	[Alkali]	Temp.	Isoprene
3 : 3-Dimethylallyl chloride	75% Ethanol	—	25·1°	$\ngtr$2·0%
1 : 1-Dimethylallyl chloride	75% Ethanol	—	25·1	$\ngtr$3·7
1 : 1-Dimethylallyl chloride	Ethanol	0·06M	44·6	$\ngtr$1·7

The conclusion is that significant amounts of products of elimination are not formed in the S_N1 reactions of these compounds.

DISCUSSION

Both 1 : 1- and 3 : 3-dimethylallyl chloride undergo unimolecular solvolysis in aqueous ethanol, the reactions not being accelerated by added base. In ethanol the solvolyses themselves are still unimolecular, but the reaction of 3 : 3-dimethylallyl chloride becomes bimolecular on addition of sodium ethoxide, though it requires about 0·1M-ethoxide ions to make the latter mode of reaction dominant. The following Table summarises the effect of solvent on the rate coefficients.

Rates (k_1, *min.*$^{-1}$) *of Unimolecular Solvolyses.*

Compound	Temp.	k_1 in ethanol	k_1 in 75% ethanol	k_1 in 50% ethanol
1 : 1-Dimethylallyl chloride	0·0°	—	0·013	*ca.* 0·5
	25·1	0·0011	0·23	—
3 : 3-Dimethylallyl chloride	0·0	—	0·0034	0·098
	25·1	0·00039 *	0·069	—

* Extrapolated from measurements at 60° and 35°.

As expected for a reaction whose rate is determined by an ionisation, the velocity is very much greater in aqueous ethanol than in pure ethanol. As is generally characteristic of anionotropically related halides, the more stable thermodynamically of the two isomers is the less reactive.

In ethanol the reaction is not significantly complicated by rearrangement, and for both isomers the solvolysis is substantially unimolecular. Both isomers give a mixture of ethers, in which the tertiary isomer predominates, and the proportions of tertiary and primary compound are to a first approximation the same, as would be expected if a mesomeric carbonium ion were formed from each isomer and became completely free from the departing anion before reacting with the solvent. Several cases of approximations to this behaviour have been recorded (cf. Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603; Roberts, Young, and Winstein, *J. Amer. Chem. Soc.*, 1942, **64**, 2157; Catchpole, Hughes, and Ingold, *J.*, 1948, 8). Generally, as in the present example, there is a small difference in the observed proportions in the direction expected if the reaction of the 3-substituted halide had a small bimolecular component. If our estimates of the bimolecular reaction between ethanol and 3 : 3-dimethylallyl chloride are correct, then in the present example the discrepancy is real, requiring another interpretation; but in view of the uncertainty in this calculation, the matter remains open. The present experiments supplement those of Ultée, who showed (*locc. cit.*) that both chlorides in aqueous sodium carbonate give similar mixtures of alcohols, and that methanolysis of the tertiary chloride gives a mixture of tertiary and primary methyl ethers.

The Chloride-catalysed Rearrangement.—Our main concern has been to examine the rearrangement of 1 : 1-dimethylallyl chloride in 75% ethanol, and to discover the rôle, if any, played by added chloride ions in this solvent. The kinetic results illustrated in the Figure show that in the course of solvolysis of 1 : 1-dimethylallyl chloride the value of the instantaneous rate coefficient falls to that corresponding to the rearranged isomer. This decrease is more rapid in the presence of M-lithium chloride solution, indicating that the more slowly reacting 3 : 3-isomer is produced more rapidly in the presence of chloride ions. Young, Winstein, and Goering (*loc. cit.*) found no such increased rate of decrease for the same reaction in acetic acid, but their test involved the addition of a very much smaller concentration of chloride ions.

The latter workers showed that the rate of the rearrangement, k_i, is given by the formula $k_i = 2{\cdot}303\{\log_{10}[a/(a - x)F]\}/t - k_T$, where F is the value of the fraction

$(k_{\text{inst.}} - k_P)/(k_T - k_P)$, $k_{\text{inst.}}$ having reference to a time t, and k_P and k_T being the initial first-order rate coefficients for the solvolyses of the 3 : 3- and 1 : 1-isomers, respectively. This formula is valid for an intramolecular rearrangement, or for a rearrangement dependent on halide ions provided that the concentration of these does not change much during the reaction. On these assumptions, and k_P and k_T being taken as 0·071 min.$^{-1}$ and 0·234 min.$^{-1}$ respectively (these values being consistent with the results illustrated in the Figure), $k_i = 0{\cdot}081$ min.$^{-1}$ in the absence of lithium chloride, and 0·162 in the presence of 0·98N-lithium chloride; the assumption of these values gives the measured course of the reaction to a good approximation which is certainly within the experimental error.

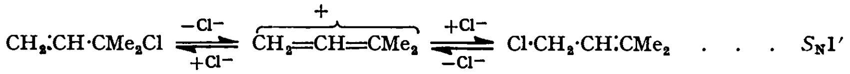
Consistently with these kinetic results, it has been shown that 3 : 3-dimethylallyl chloride can be isolated from the product of solvolysis of 1 : 1-dimethylallyl chloride in 75% ethanol. Thus in Experiment *A*, the last two fractions of recovered halide consisted largely of 3 : 3-dimethylallyl chloride, as shown by the boiling points, refractive indices, and kinetic analysis. The ratio ^{36}Cl : Cl$^-$ was shown to be relatively low in the early fractions recovered which would have been expected to contain much inactive starting material in this experiment. The last three fractions, however, gave a higher, nearly constant value, which was about 63% of the corresponding value for the free chloride ion in the solution. This indicates that only a part of the 3 : 3-dimethylallyl chloride was obtained by intervention of external chloride ions; the remainder must have come from the starting material by intramolecular rearrangement.

In considering possible ways in which the rearranged material containing ^{36}Cl could have been formed, the possibility must be excluded that isomerisation occurred during the isolation of the product. In Experiment *B*, a replica of Experiment *A* except that the reaction was stopped much earlier, very much less 3 : 3-dimethylallyl chloride was isolated, and the material that was obtained contained a much smaller proportion of ^{36}Cl. This indicates that the rearranged product was not an artifact.

Another possible route to the rearranged product is by bimolecular attack of chloride ions on 1 : 1-dimethylallyl chloride, accompanied by synchronous rearrangement (the S_N2' reaction), but this can also be excluded, in our opinion, on the grounds that the bimolecular S_N2' reaction of this compound with chloride ions could not possibly be as fast as the observed reaction in such an ionising solvent. Thus, chloride ions do not normally compete successfully with ethoxide ions as nucleophilic reagents; and we know from the ineffectiveness of ethoxide ions in accelerating the solvolysis (cf. Part IV, *loc. cit.*) that even these ions cannot compete in a bimolecular process with the S_N1 reaction of this compound; to observe the S_N2' reaction a much more powerfully nucleophilic reagent, such as the thiophenoxide ion, must be used. These arguments apply to ethanol as solvent and more especially to the more ionising conditions of our experiments, since bimolecular reactions of ions with neutral molecules are in general little facilitated by increase in the ionising power of the solvent. Our results show that the chloride-catalysed rearrangement is very powerfully accelerated by the addition of water to the solvent. This is in agreement with, and supports, the view that this reaction is dependent on a S_N1' rate-determining ionisation.

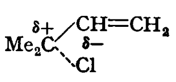
The product of solvolysis of 3 : 3-dimethylallyl chloride in the presence of ^{36}Cl in 75% ethanol has also been examined (Experiment *C*). Since in this case the product of the rearrangement is solvolysed more rapidly than the starting material, its isolation is much more difficult. There was, however, obtained from the reaction a low-boiling sample, containing, from its behaviour on kinetic analysis, 1 : 1-dimethylallyl chloride as essentially the only organic chloride. This material contained about twice as much ^{36}Cl, per unit of organic chloride present, as the later fractions which, as expected, were nearly pure 3 : 3-dimethylallyl chloride. Less than half of the rearranged material can therefore have been derived from the starting material, which at the beginning of the reaction was inactive and at the end of the reaction was only slightly active. The rearranged material must have been formed mainly by a S_N1' halide-catalysed rearrangement.

Our observations show that two mechanisms are concerned in the interconversion of 1 : 1- and 3 : 3-dimethylallyl chloride in aqueous ethanol. One is intramolecular and involves no exchange with radioactive chloride ions present in the solution, and the other, which increases in importance as the chloride-ion concentration is increased, involves exchange with radioactive chloride ions, and leads to the introduction of ^{36}Cl into both rearranged and unrearranged products. It is considered that this exchange occurs after the rate-determining stage of the reaction. The process is formulated as follows (cf. Catchpole, Hughes, and Ingold, *J.*, 1948, 8):

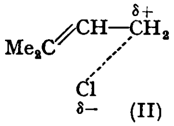


$$\mathrm{CH_2{:}CH{\cdot}CMe_2Cl} \underset{+\mathrm{Cl}^-}{\overset{-\mathrm{Cl}^-}{\rightleftharpoons}} \overset{+}{\overbrace{\mathrm{CH_2{=}CH{=}CMe_2}}} \underset{-\mathrm{Cl}^-}{\overset{+\mathrm{Cl}^-}{\rightleftharpoons}} \mathrm{Cl{\cdot}CH_2{\cdot}CH{:}CMe_2} \quad . \quad . \quad . \quad S_N1'$$

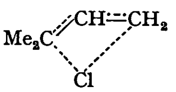
The intramolecular rearrangement can be formulated as an S_Ni' reaction, involving a transition state of the type indicated in the canonical structures I, II, III:



(I)



(II)



III)

To accommodate the powerful influence of increased ionising power of the solvent on the rate of reaction, solvation of the incipient carbonium centre must not be greatly diminished by distribution of the charge over the anionotropic system: in this example this assumption does not seem unreasonable, seeing that there is considerable congestion at the 1-carbon atom where solvation forces must in any case be considerably reduced both by steric effects and by the charge-distributing effect of C–H hyperconjugation. Young, Winstein, and Goering (*loc. cit.*) have preferred to consider that the reaction involves an ion-pair which is formed in the rate-determining reaction, and subsequently either collapses to give rearranged chloride (internal return) or dissociates to give free ions.

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