The Kinetics and Mechanisms of Nucleophilic Displacements in Allylic Systems. Part VII.* Solvent Effects in the Reactions of the Dichloropropenes and Related Compounds.

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Since *trans*-1 : 3-dichloropropene releases 50% of its chlorine on solvolysis in aqueous ethanol, it may be deduced that this reaction is a first-order bimolecular solvolysis. The extent by which the rate of the reaction is increased by alkali may be used as a guide in the examination of other compounds, in which the molecularity of the solvolysis is difficult to determine. Misconceptions concerning the mechanisms and products of the reactions of 3 : 3- and 1 : 3-dichloropropene are corrected. Solvent effects on the S_N2 reactions of these compounds with nucleophilic reagents, and on the S_N2' reactions of 3 : 3-dichloroprop-1-ene and of 3 : 3 : 3-trichloro-2-methyl-prop-1-ene with thiophenoxide ions, are discussed.

To decide whether the first-order solvolysis of an organic chloride is uni- or bi-molecular is frequently difficult. This problem becomes particularly acute in dealing with allyl and substituted allyl halides, since the allyl structure favours both S_N1 and S_N2 mechanisms. Kirrmann, Schmitz, and Saito (*Bull. Soc. chim.*, 1952, **19**, 515) recently discussed the solvolyses of allyl halides in ethanol, ethanol–water mixtures, and dioxan–water mixtures, and concluded that the first-order reactions observed in the absence of alkali are probably unimolecular.

In earlier papers (Parts I, II, and IV, de la Mare and Vernon, *J.*, 1952, 3325, 3331; 1953, 3555), the bimolecular reactions of 3 : 3-dichloroprop-1-ene in ethanol were discussed, and it was shown that the S_N2' reaction is of considerable importance; on the other hand, allylic rearrangement was by no means complete, but represented in general less than 50% of the total reaction. Theoretical considerations would suggest that allylic shift should also be incomplete in most systems under conditions of unimolecular solvolysis; for, as is well exemplified by examples from the literature (cf. Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., London, 1953, pp. 586—590), the unimolecular solvolysis of an allylic halide gives a mesomeric cation, which may react at either of the potential carbonium ionic centres to give a mixture of isomeric products. Kirrmann, Schmitz, and Saito (*loc. cit.*) claim, however, that this compound is solvolysed unimolecularly with total allylic shift, which, they consider, is scarcely compatible with a bimolecular reaction of this compound. This claim deserves further attention, therefore, more especially since earlier work (cf. Kirrmann, Pacaud, and Dosque, *Bull. Soc. chim.*, 1934, **1**, 860) suggests that the products of allylic rearrangement are in a wide range of examples formed in poor yield.

The 1 : 3-dichloropropenes are also of particular interest; for with these compounds, the S_N2 reaction releases initially only one chlorine atom, whereas the S_N1 reaction will in general lead to the release of more than one equivalent of chlorine, with the corresponding formation of derivatives of acraldehyde. With these compounds, in contrast with the behaviour of 3 : 3-dichloroprop-1-ene, the S_N2 reaction is sufficiently rapid to obscure completely any S_N2' reaction. Hence release of one equivalent of chloride from the

compound may be taken as diagnostic of the S_N2 reaction, even in solvolyses, in which the ordinary kinetic tests are unavailable.

Investigation and clarification of these points, as discussed in more detail below, have led us also to document more fully the effect of changes of solvent on the rates of S_N2 and S_N2' reactions of allylic halides.

EXPERIMENTAL

(a) *Material and Methods.*—Most of these have been described in previous papers (de la Mare and Vernon, *locc. cit.*; Part III, *J.*, 1952, 3628; Part VI, *loc. cit.*; Part V, Vernon, *J.*, 1954, 423). Solutions of sodium formate in formic acid were prepared by dissolving sodium metal in the anhydrous acid. 1-Chloro-3-hydroxyprop-1-ene, prepared from 1 : 3-dichloropropene and sodium carbonate, had b.p. 85°/57 mm., n_D^{25} 1·4657.

(b) *Reactions of 3 : 3-Dichloroprop-1-ene in Ethanol–Water Mixtures.*—The following are details of the rate of production of acid by the solvolysis of 3 : 3-dichloroprop-1-ene in 50% ethanol * at 64·0°. Samples (5·17 ml.) were removed at intervals for titration with 0·0165N-sodium hydroxide :

Time (min.)	0·0	20·0	93·0	142	199	281	1445	1589	∞
Titre (ml.)	0·70	1·32	2·81	4·02	4·92	6·69	17·93	18·64	22·04
$10^3 k_1$ (min.$^{-1}$)	—	1·02	1·12	1·19	1·11	1·17	1·14	1·15	—

Values of k_1 are calculated from the formula $k_1 = 2·303 \{\log_{10} H_\infty^+/(H_\infty^+ - H_t^+)\}/t$. Separate experiments showed that the stable infinity-value for the development of acid (in agreement with the value obtained by titration of liberated chloride) represented the release of 59·3% of the chlorine in the organic chloride, and hence represented the formation of 82% of rearranged products. The mean rate coefficient ($k_1 = 0·00113$ min.$^{-1}$) was unaffected by the addition initially of 0·080N-hydrochloric acid, and was increased only slightly (to $k_1 = 0·00141$ min.$^{-1}$) by the presence initially of 0·15N-potassium hydroxide; under the latter conditions, the release of chloride was increased slightly, to about 63%, presumably by incursion of a bimolecular reaction. Values at other temperatures ($k_1 = 0·0092$ min.$^{-1}$ at 84·6°; 0·000133 min.$^{-1}$ at 44·6°) lead to a value of $E = 23·5$ kcal./mole.

Despite the report, made by Kirrmann, Schmitz, and Saito (*loc. cit.*; cf. Pourrat and Schmitz, *Bull. Soc. chim.*, 1952, **19**, 525; Schmitz, *ibid.*, p. 509), to the contrary, the product of normal substitution can be obtained from this reaction. 3 : 3-Dichloroprop-1-ene (2 ml.) was refluxed for 4 hr. with 200 ml. of 50% ethanol in the presence of 10 g. of barium carbonate, added to keep the solution neutral. The alcohol and the acraldehyde were then distilled off into excess of a 0·1% solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid. Filtration gave the 2 : 4-dinitrophenylhydrazone of acraldehyde (0·45 g., yield *ca.* 50%, assuming 18% of unrearranged product); this, after recrystallisation from aqueous ethanol, had m. p. 157°, unchanged on admixture with an authentic specimen. Treated in the same way, neither *cis*-nor *trans*-1 : 3-dichloropropene gave more than a trace (<0·05 g.) of 2 : 4-dinitrophenylhydrazone.

The reaction of 3 : 3-dichloroprop-1-ene in 75% ethanol with sodium thiophenoxide (0·309N) at 45·7° was followed as described in Part II (*loc. cit.*). The infinity-value, stable over the range 10—30 half-lives for the reaction, represented the liberation of 86·4% of the chlorine in the compound. This value being assumed, the total second-order rate coefficient, substantially constant over 80% reaction, was found to be $k_2 = 0·190$ l. mole^{-1} min.$^{-1}$.

(c) *Reactions of trans-1 : 3-Dichloropropene in Ethanol–Water Mixtures.*—Determination of the percentage release of chloride from this compound gave the following results. In 50% ethanol, at 64·9°, 49·4%; + 0·025N-KOH, 48·9%. In 75% ethanol, at 64°, 49·7%; + 0·025N-KOH, 49·8%. Rate coefficients for these reactions are included in later Tables in the discussion. The following data show the very small extent to which the solvolysis results in the production of derivatives of acraldehyde. 1 : 3-Dichloropropene was allowed to solvolyse in 50% ethanol at 100°, and at intervals, samples were removed for the determination (a) of chloride and (b) of acraldehyde and its derivatives, by comparison with standard acraldehyde solutions, the method adapted from that of Circle, Stace, and Boruff (*Ind. Eng. Chem. Anal.*, 1945, **17**, 259), described in Part I (*loc. cit.*), being used.

* A solvent " x% ethanol " is a mixture of x parts by vol. of ethanol with $(100-x)$ parts by vol. of water.

The fact that the ratio of acraldehyde derivatives to chloride rises towards the end of the reaction suggests that the small amount produced, or at least a substantial part of it, comes

Time (min.)	0·00	6·0	9·0	12·0	15·0	18·0
Cl⁻ (ml. 0·01N-AgNO₃)	0·72	1·72	2·12	2·45	3·03	3·45
$10k_1$ (min.$^{-1}$)	—	1·52	1·45	1·37	1·50	1·51
[Deriv. of acraldehyde]/[Cl⁻]	—	0·00	0·00	0·00	0·00	0·006

Time (min.)	23·0	28·0	35·0	78·0	106·0	∞
Cl⁻ (ml. 0·01N-AgNO₃)	4·02	4·62	5·38	8·55	9·65	12·18
$10k_1$ (min.$^{-1}$)	1·48	1·48	1·49	1·47	1·47	—
[Deriv. of acraldehyde]/[Cl⁻]	0·007	0·007	0·007	0·008	0·009	—

by rearrangement of the alcohol produced in the reaction, autocatalysed by the developing acid. Certainly the amount formed towards the beginning of the reaction is negligibly small, and represents less than 1% of the total reaction.

(d) *Reactions of 3 : 3-Dichloroprop-1-ene and* trans-1 : 3-*Dichloropropene in Anhydrous Formic Acid.*—The ratio [acraldehyde derivatives]/[chloride] was followed in anhydrous formic acid at 100° in a similar manner. Any interference by the formic acid with the measurements of acraldehyde was allowed for by estimating standard samples of acraldehyde in the presence of formic acid at the same time. With *trans*-1 : 3-dichloropropene, the production of acraldehyde was autocatalytic in the absence of formate ions, but followed the development of chloride closely when formate ion was added. It is presumed that the function of added formate was to inhibit the acid-catalysed rearrangement of the formate produced in the solvolysis; it was shown in a separate experiment that 1-chloro-3-hydroxyprop-1-ene rearranges rapidly in the absence of formate ions in formic acid at 100°, but that liberation of chloride is almost completely inhibited by the addition of 0·016M-sodium formate. The following data illustrate the constancy of the [derivatives of acraldehyde]/[chloride] ratio, in the reaction of *trans*-1 : 3-dichloropropene in anhydrous formic acid with added 0·0233M-sodium formate at 100°, determined as in (c) above.

Time (min.)	0	7	14	21·5	28	35	42	49	56	∞
Chloride (ml. 0·01N-AgNO₃)	3·50	4·75	5·98	7·20	8·30	9·48	10·67	11·60	12·60	167·8
Derivs. of acraldehyde (arbitrary Spekker reading)	0·045	0·092	0·138	0·185	0·231	0·279	0·323	0·364	0·415	—
[Derivs. of acraldehyde]/[chloride]	—	0·085	0·085	0·085	0·088	0·088	0·087	0·089	0·091	—

With either 0·0429N- or 0·0621N-sodium formate the corresponding ratio was 0·085.

Under similar conditions, 3 : 3-dichloroprop-1-ene consistently gave higher ratios of [acraldehyde derivatives]/[chloride] (*ca.* 0·20; cf., in 50% ethanol, 0·18; cf. also de la Mare and Vernon, *Research*, 1953, 6, 56S).
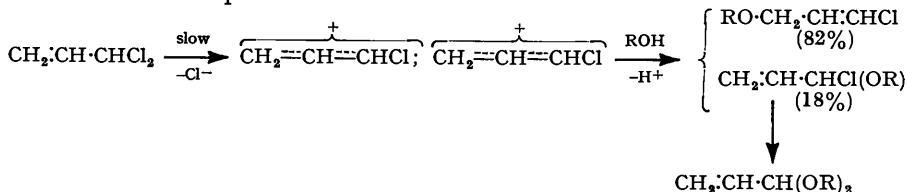
(e) *Reaction of* trans-1 : 3-*Dichloropropene with Aqueous Cuprous Chloride in Acid Solution.*—Cuprous chloride (0·5 g.) was heated with 0·1N-hydrochloric acid (200 ml.) in a current of nitrogen. The solution was filtered, and an aliquot part (100 ml.) was sealed with 6·145 g. of *trans*-1 : 3-dichloropropene and kept for 2 weeks at 45°, with occasional shaking. An aliquot part (20 ml.) of the solution, in which most of the chloride had solvolysed, was added to excess of 2 : 4-dinitrophenylhydrazine (0·1% in 2N-HCl). The precipitate was collected by filtration and weighed 0·082 g. This recovery represents an [acraldehyde]/[chloride] ratio for the total solvolysis of 0·04. After a further 2 weeks at 45°, another aliquot part, treated similarly, gave 0·081 g. of acraldehyde 2 : 4-dinitrophenylhydrazone.

(f) *Reactions of 1 : 1 : 1-Trichloro-2-methylprop-1-ene with Thiophenoxide Ions in Ethanol–Water Mixtures.*—To confirm that the S_N2' reaction is somewhat increased in rate by an increase in the ionising power of the solvent, the reactions of 1 : 1 : 1-trichloro-2-methylprop-1-ene with sodium thiophenoxide was studied at 25° in 90% and in 75% ethanol. The results, given in the discussion, are second-order rate coefficients, calculated from the weight of chloride taken, on the basis that one chlorine atom is released in the reaction. These values were constant within experimental error over the 75% of the reaction studied.

DISCUSSION

(a) *Unimolecular Solvolysis of 3 : 3-Dichloroprop-1-ene.*—In 50% ethanol, the solvolysis of 3 : 3-dichloroprop-1-ene is clearly unimolecular, since the rate of reaction is but little accelerated by the addition of alkali to the solvent. Under these conditions, release of chloride shows that 82% of rearranged products (CHCl:CH·CH₂·OR; R = OH, OEt) are produced. Derivatives of acraldehyde can be obtained from the products, and, since

these do not themselves rearrange under the conditions of the measurements, the reaction is considered to follow the path :

$$CH_2\!:\!CH\cdot CHCl_2 \xrightarrow[-Cl^-]{slow} \overset{+}{[CH_2\!=\!CH\!=\!CHCl]}\,;\; \overset{+}{[CH_2\!=\!CH\!=\!CHCl]} \xrightarrow[-H^+]{ROH} \begin{cases} RO\cdot CH_2\cdot CH\!:\!CHCl \\ (82\%) \\[4pt] CH_2\!:\!CH\cdot CHCl(OR) \\ (18\%) \end{cases}$$

$$\downarrow$$

$$CH_2\!:\!CH\cdot CH(OR)_2$$

Kirrmann, Schmitz, and Saito's conclusion (*loc. cit.*) that this particular solvolysis is unimolecular, is therefore correct, but it was reached by the incorrect reasoning that the reaction involves complete allylic shift; in fact, both unrearranged and rearranged products are obtained, as is the common experience in anionotropic systems. It should be noted that the proportion of rearrangement (82%) differs considerably from that observed under bimolecular conditions, either in ethanol (with OEt⁻, *ca.* 40%; cf. Part I; with SPh⁻, 38%; cf. Part II); or in aqueous ethanol (with SPh⁻, 28%; cf. this paper).

(b) *Unimolecular Solvolysis of* trans-1 : 3-*Dichloropropene.*—To obtain a substantially unimolecular solvolysis of this compound, it has been necessary to work in anhydrous formic acid. Here the reaction cannot be followed to completion seeing that it is reversible, and also because the solvent slowly decomposes (cf. Part V, *loc. cit.*). When rearrangement of the products of solvolysis is minimised by the addition of sodium formate (which does not affect the rate of production of chloride ion), the ratio [acraldehyde derivatives]/[chloride] is substantially constant, and corresponds with the liberation of 54% of the chlorine from the organic chloride (*i.e.*, *ca.* 8% rearrangement).* It is to be noted that this result disagrees with Hatch, Morgan, and Tweedie's opinion (*J. Amer. Chem. Soc.*, 1952, **74**, 1826). They examined the solvolysis, in water, catalysed by cuprous chloride, of the 1 : 3-dichloropropenes, and showed by tracer methods, using [36]Cl, that the vinylic chlorine of the dichloride is partly removed in the reaction, and that the CHCl:CH·CH₂·OH formed as product becomes partly labelled with [36]Cl. They proposed a scheme (their Fig. 2, *loc. cit.*, p. 1827) of the S_N1' type, involving a mesomeric cation, $CHCl\!:\!CH\cdot\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}HCl\cdot CH\!:\!CH_2$. This they regard as reacting reversibly with [36]Cl to form [36]Cl·CHCl·CH:CH₂, thus partly labelling the organic chloro-alcohol.† Any significant reaction by the proposed route would, however, result in the liberation of more than 50% of the organic chlorine as chloride ions, with the consequent formation of derivatives of acraldehyde. They regard the latter possibility as excluded by their experimental finding that only 50% of chlorine is released as chloride; we, on the other hand, regard this observation as inconsistent with their tracer experiments and with their explanation of the course of the reaction, since both 3 : 3-dichloroprop-1-ene and 1 : 3-dichloropropene in our experience form derivatives of acraldehyde when solvolysed by S_N1 reactions.

Although we have not examined in detail the hydrolysis catalysed by cuprous chloride, since this reaction may be mechanistically complicated and not adequately represented by the S_N1 mechanism, the solvolysis of *trans*-1 : 3-dichloropropene in the presence of cuprous chloride has been repeated. Our experience is that, when the solvolysis has been allowed to proceed nearly to completion at 45° in a sealed tube, the solution contains acraldehyde, identifiable as its 2 : 4-dinitrophenylhydrazone, in amount consistent with the occurrence of the S_N2 and S_N1' reactions, each contributing equally, assuming that, as in formic acid, reaction of this compound by the latter mechanism gives a ratio of [acraldehyde]/[chloride] of *ca.* 0·08. The products on further standing under the conditions of the reaction released no additional acraldehyde, and hence it is concluded that acraldehyde is a genuine product of the solvolysis, and not a product of rearrangement of the chloro-alcohol produced as the other main organic product.

(c) *Bimolecular Solvolysis of* trans-1 : 3-*Dichloropropene.*—Kirrmann, Schmitz, and

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* The fact that this ratio is different from that found with 3 : 3-dichloroprop-1-ene has been discussed elsewhere (de la Mare and Vernon, *loc. cit.*; cf. de la Mare, *Ann. Reports*, 1953, **50**, 139) and will be the subject of a future communication.

† They do not, however, exclude that the labelling might be introduced in a bimolecular process.

Saito (*loc. cit.*) concluded that the solvolysis of this compound, in aqueous alcohol or in aqueous dioxan, was probably unimolecular. In our view, this conclusion is incorrect. The reaction in aqueous ethanol releases, within experimental error, 50% of the chlorine from the compounds as chloride ion, and results in the formation of less than 1% of derivatives of acraldehyde. If the reaction proceeded through a mesomeric cation, it would be expected that there would be produced, as there is in anhydrous formic acid, some 8% of derivatives of acraldehyde by rearrangement.

The following Table shows the effect of added alkali on the rate of liberation of acid from the 1 : 3-dichloropropenes in ethanol and in mixtures of ethanol and water.

The bimolecular solvolyses (first half of Table) are strongly accelerated by increase in the ionising power of the solvent, in agreement with Hughes and Ingold's theory (*J.*, 1935, 252) for a reaction, such as this, in which two neutral molecules react, producing a transition state in which charges develop. The change in rate, on going from ethanol to 50% ethanol, involves a rate-factor of about 40. This may be contrasted, first, with the much greater increase observed for similar solvent changes in unimolecular processes (a factor of about

Solvent effect on the bimolecular reactions of the 1 : 3-*dichloropropenes at* 44·6°.

1 : 3-Dichloropropene	$10^5 k_1$ (min.$^{-1}$) for solvolysis in :			$10^5 k_2$ (l. mole^{-1} min.$^{-1}$) with added OR^- = 0·16M in :		
	EtOH	75% EtOH	50% EtOH	EtOH	75% EtOH	50% EtOH
trans-	0·23	3·3	9·9	3100	2620	2560
cis-	0·22	3·1	9·9	2690	2930	3520

4000; cf. Part VI, *loc. cit.*, for a typical example). Such a difference would be expected, seeing that, in the latter reaction charge-development in the transition state is likely to be greater, and will be spread over a smaller volume. Secondly, comparison may be made with a bimolecular displacement of an anion on a neutral molecule (cf. second half of Table). In this case, a large change in solvent results in only a small change in rate; in the present example, one of the compounds shows a small decrease, and the other a small increase, when the ionising power of the solvent is increased. These results are in substantial agreement with those of Andrews and Kepner (*J. Amer. Chem. Soc.*, 1948, **70**, 3456).

The consequence of the difference in behaviour when the solvent is changed, between the bimolecular solvolysis and the bimolecular reaction with alkali, is that the acceleration in rate of a bimolecular solvolysis when a given amount of alkali is added, is reduced when water is added to the alcoholic solvent, by a factor of about 40 on going from ethanol to 50% ethanol. The present results establish the situation for a case in which the solvolytic reaction can be proved to be substantially bimolecular, and hence can be used as a guide in other cases, as will be discussed by one of us in a later paper.

(d) *Solvent Effects in the* S_N2' *Reaction.*—In a previous paper (Part VI, *loc. cit.*), it was argued on general grounds that the effect of change of solvent on the rate of an S_N2' reaction would not be likely to be large, since other bimolecular processes involving ions and neutral molecules are usually not much affected by such changes. It is desirable, however, to have definite information on this point, and so we have examined the reaction of 3 : 3 : 3-trichloro-2-methylprop-1-ene with sodium thiophenoxide in ethanol–water mixtures, with the following results : 3 : 3 : 3-trichloro-2-methylprop-1-ene + SPh$^-$ at 25·0°; k_2 (l. mole^{-1} min.$^{-1}$), 6·5 × 10^{-3} in ethanol (Part III, *loc. cit.*); 8·2 × 10^{-3} in 90% ethanol; 13·0 × 10^{-3} in 75% ethanol. Similarly, 3 : 3-dichloroprop-1-ene reacts in 75% ethanol with SPh$^-$ at 45·7° to release 86% of its chlorine as chloride, and with rate coefficient, based on this release of chloride, k_2 = 0·190 l. mole^{-1} min.$^{-1}$. Comparison with the results given in Part II for reactions in ethanol (total k_2, 0·064 l. mole^{-1} min.$^{-1}$ at 45·2°; 81% chlorine released at infinity) shows that both S_N2 and S_N2' processes have been accelerated by increase in the ionising power of the solvent, and the former process is accelerated rather more than the latter.

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