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Evidence for an Anion-Carbene Pair

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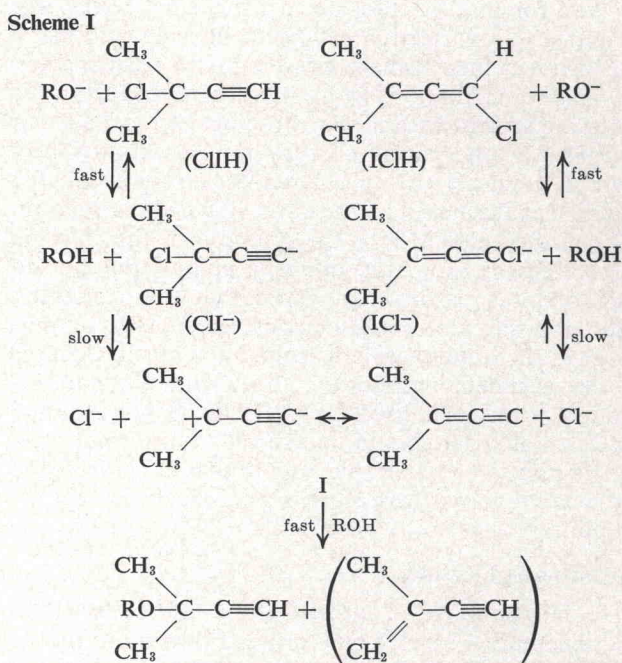
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Abstract: The activation volume of the base-promoted solvolysis of 1-chloro-3-methylbuta-1,2-diene in an ethanol-water mixture 80:20 vol/vol at 25° equals +5 cm³/mol. A combination of this value with that measured earlier for 3-chloro-3-methylbut-1-yne and with the densities of these two substrates shows that the two transition states have virtually identical volumes. This suggests that the two precursor anions are on their way to a common intermediate, an anion-carbene pair, preceding the carbene 3,3-dimethylpropenylidene. The acetylenic chloride isomerizes to a small extent (0.30%) to the allenic halide during solvolysis. The yield of the isomer depends on the concentration of added chloride in a way which is compared to those that theoretically characterize external and internal return; this analysis leads to the conclusion that 33% of the isomerization results from internal return and 67% from external return. Both the yield of the isomer and the fraction of internal return increase (to 0.86 and 82%, respectively) if large concentrations of bromide are also present, and the same is true if a solvent consisting of a 50/50 mixture of ethanol and *t*-butyl alcohol is used (3.21 and 84%, respectively).

Several authors have considered the mechanisms of the base-promoted solvolyses of 3-halo-3-methylbut-1-yne and of 1-halo-3-methylbuta-1,2-diene (it is convenient to symbolize these compounds by XIH and IXH, respectively). Hennion and Maloney² proposed in 1951 that the reactions of the chlorides, first order in base and in the organic substrate, take place *via* rate-limiting proton abstraction to give the anions CII⁻ and ICI⁻, respectively, followed by rapid loss of chloride to yield the common intermediate I (3,3-dimethylpropenylidene); I would subsequently react with the solvent to give ROIH. Since then Shiner^{3,4} has found that BrIH and IBrH in a basic deuterated solvent undergo exchange much faster than solvolysis; that result requires that the loss of bromide ion rather than the proton abstraction is rate determining. With that modification, the Hennion-Shiner mechanism still stands today (see Scheme I).

It is further known now that a small common ion effect operates, so that some capture of the intermediate I by halide ion must be occurring; that BrIH reacts approximately 50 times faster than IBrH, and that a small amount (about 1%) of the latter is formed during



basic solvolysis of the former.^{3,4} Hartzler^{5,6} has demonstrated that I can be generated and captured under non-solvolytic conditions in styrene to give the expected

(1) Paper XVIII in the series "Chemical Reactions under High Pressure."

(2) G. F. Hennion and D. E. Maloney, *J. Amer. Chem. Soc.*, **73**, 4735 (1951).

(3) V. J. Shiner and J. W. Wilson, *ibid.*, **84**, 2402 (1962).

(4) V. J. Shiner and J. S. Humphrey, *ibid.*, **89**, 622 (1967).

(5) H. D. Hartzler, *ibid.*, **83**, 4990 (1961).

(6) H. D. Hartzler, *ibid.*, **83**, 4997 (1961).

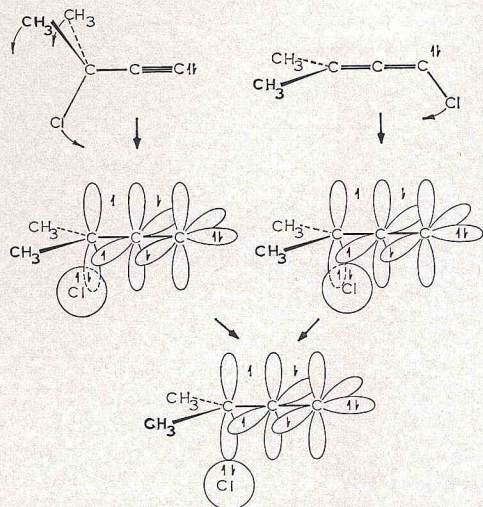


Figure 1. Formation of the first common intermediate (I, Cl⁻) from the precursor anions via very similar transition states.

propenyldenecyclopropanes; furthermore, both he⁷ and Shiner and Humphrey⁴ showed that identical product distributions are produced by the isomeric propargylic and allenic substrates if they are decomposed by base under identical circumstances.

We developed an interest in these reactions in the course of our work on the effects of high pressures on the rate of reactions occurring in solution.⁸ One of the reaction types that can be readily recognized is the decomposition of anions to form carbenes⁹ or nitrenes,¹⁰ as rather large, positive activation volumes are observed; these volume changes are interpreted in terms of a combination of bond fission and solvent reorganization. However, the volume of activation for the basic solvolysis of CIIH in an 80:20 ethanol-water mixture was found to be only +2 cm³/mol as compared to +16 cm³/mol for that of chloroform; this small value was attributed to polarization of I by the leaving chloride.¹¹ The incipient intermediate was judged to receive equal resonance contributions from the carbene and from the zwitterion structures, and the attraction of local solvent molecules by the partial charges (the well-known electrostriction effect) was considered to be responsible for the unusual absence of any pressure induced retardation.

When the anion ICl⁻ is the source of I, the chloride will be leaving from the opposite end of the carbon chain, and it is reasonable to expect that no polarization in the opposite sense need be considered (with a minus charge at the tertiary carbon atom and a positive charge on the acetylenic carbon). Thus, under conditions identical with those used for CIIH the base-promoted solvolysis of ICIH should be subject to a normal pressure retardation comparable, say, to that of chloroform. The work reported here started as a check on that assumption.

Discussion and Results

The measurement of an activation volume has been described earlier,⁸ so we may proceed directly to the results shown in Table I. ΔV_0^* , the activation volume at zero pressure, was calculated from these data by means

(7) H. D. Hartzler, *J. Org. Chem.*, **29**, 1311 (1964).

(8) W. J. le Noble, *Progr. Phys. Org. Chem.*, **5**, 207 (1967).

(9) W. J. le Noble and M. Duffy, *J. Amer. Chem. Soc.*, **86**, 4512 (1964).

(10) W. J. le Noble and D. Skulnik, *Tetrahedron Lett.*, 5217 (1967).

(11) W. J. le Noble, *J. Amer. Chem. Soc.*, **87**, 2434 (1965).

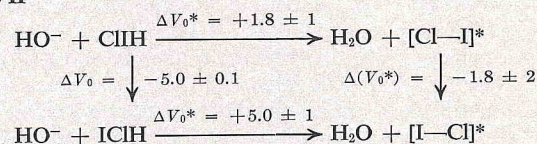
Table I. The Effect of Pressure on the Rate of Base-Promoted^a Solvolysis of ICIH at 25° in Ethanol-Water (80:20 vol/vol)

Pressure, kbar	10 ⁶ k ₂ , l./mol sec	No. of measurements
0.000	2.68 ^b	12
1.055	2.38	4
2.039	1.88	4
3.023	1.55	4
4.007	1.29	4
5.062	1.20	3
6.042	0.99	4

^a An excess of base was used; k_2 was evaluated from the rate of release of chloride during the first 5–10% of the reaction. The reproducibility was $\pm 1.5\%$. ^b Hennion's value² is 2.31.

of the expressions $\Delta V_0^* = -RT \partial \ln k / \partial p = -RT \cdot (ap^2 + bp + c)$; the result was found to be $+5 \pm 1$ cm³/mol—only marginally larger than that for the base-induced solvolysis of CIIH. Furthermore, since it is known that the parachor for two double bonds is 5 cm³ less than that of one triple bond,¹² it appeared that the volume difference between the two transition states $\Delta(V_0^*)$ might even be less than that. Measurements of the densities of CIIH and ICIH confirmed this suspicion: $\Delta(V_0^*)$ equals 1.8 ± 2 cm³/mol (Scheme II). This

Scheme II



deviation from the expected result is far too large to be ignored, and we believe it requires an additional detail in the Hennion-Shiner mechanism. The similarity in size of the two transition states makes sense if we consider the likely shapes of both the intermediates I and of the precursor anions. In CII⁻ there is little room for controversy: the chloride ion should be departing from an initially tetrahedral carbon atom in such a way as to leave a planar, trigonal carbon atom behind. In ICl⁻, the structure of the anion itself is unknown. Shiner and Humphrey⁴ felt on the basis of an "analogy with the structures of ketenimines (R₁R₂C=C=NR)" that the carbanion [*i.e.*, IBr⁻] would be linear."¹³ However, in the ketenimines in question R₁ and R₂ are phenylsulfonyl rather than methyl groups and the X-ray diffraction experiments resulted in typical triple bond values for the CN bond length; furthermore, though the C=C=NR skeleton is indeed linear when R is methyl, it is severely bent¹⁴ when R is ethyl. Shiner and Humphrey⁴ went on to argue on the basis of the non-common ion salt effect that in the transition state, the chain must become bent as the unshared pair seeks to move from a π to an sp hybrid orbital. We agree that increased bending must indeed occur during the reaction, but feel that this process begins at a stage that is bent already and leads to a transition state very similar to that derived from CII⁻. The polarization of the incipient carbene would in both cases be the same, and the principal distinction between the two transition states would be a small difference in the position of the halide ion. Figure 1, which is an attempt to illustrate

(12) O. R. Quayle, *Chem. Rev.*, **53**, 439 (1953).

(13) J. J. Daley, *J. Chem. Soc.*, 2801 (1961); P. J. Wheatley, *Acta Cryst.*, **7**, 68 (1954).

(14) R. K. Bullough and P. J. Wheatley, *ibid.*, **10**, 233 (1957).

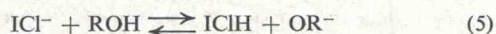
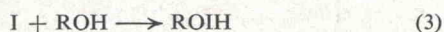
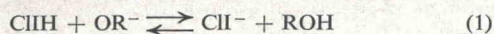
this similarity, suggests that the two anions are on their way to a common intermediate in which the chloride is still paired with the polarized carbene-zwitterion intermediate I; we refer to it as (I, Cl⁻), and in general terms as an anion-carbene or anion-zwitterion pair.¹⁵ The property most commonly associated with paired intermediates of this type is internal return,¹⁶ and the following experiments were designed to study the occurrence of such return in the present system.

The first question to be raised is whether there is any return of any kind. Shiner and Humphrey⁴ had observed that the reaction of BrIH produces about 1% of the allenic isomer. We were able to show by means of gas chromatography that ClIH during its hydrolysis produces 0.30% ICIH and that this product arises *via* the base-promoted path; at the concentration of chloride produced during the reaction and in the absence of base, both SN2' attack (which *can* be shown to occur to some degree at high chloride concentrations and under more drastic conditions) and unimolecular rearrangement are unobservable. These techniques permitted the measurement of small changes in the yield of ICIH with excellent accuracy.

Two approaches to the question of internal *vs.* external return were considered. In the first of these, the base-promoted solvolysis of ClIH would be carried out in the presence of chloride ion added in amounts comparable to that produced by the reaction itself. If the isomer were formed by internal return, its yield would be unaffected, and if it were formed by external return it yield should increase in a predictable way. In the second approach, the reaction would be carried out in the presence of a trap that would partially divert I from the normal products to others. If internal return were producing ICIH, the yield should be unaffected while the trap diminished the yield of ROIH; if return is exclusively external, then the yields of ROIH and ICIH should be depressed in the same ratio.

The decomposition of BrI⁻, the rate of which is lowered by the addition of bromide, is also slowed somewhat by chloride and perchlorate, and more so by the former than by the latter.³ This suggested that I is at any rate *able* to form ICIH *via* external return. We found in some initial experiments that the addition of high concentrations of chloride to the solvolysis mixture would indeed produce substantial yields of ICIH. It became, therefore, important to be able to predict precisely how the yield should be affected if return were *exclusively* external.

A complete analysis would be based on steps 1-5.



The effect of added chloride on the yield of ICIH is not easy to analyze in terms of this complete scheme;

(15) In this intermediate the chloride ion may not be "straight below" C-3, as Figure 1 implies. Repulsion between the chloride ion and the partial negative charge at C-1, the steric requirements of the methyl groups and of the propenylidene chain, and the presence of polar solvent molecules are factors that will determine the exact geometry.

(16) W. G. Young, S. Winstein, and H. L. Goering, *J. Amer. Chem. Soc.*, **73**, 1958 (1951).

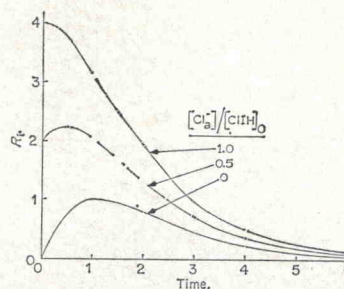


Figure 2. The rate R_i (in arbitrary units) as a function of time (in half-lives) at several concentrations of added chloride when the return is completely external. The area under each curve is the corresponding yield Y_i .

fortunately, three simplifying features apply that greatly facilitate such analysis. First, the base is in excess and its concentration may be considered constant, as may the ionic strength μ ; second, since the solvolysis rate is not depressed very much by low concentrations of chloride,³ we may neglect the competition that chloride offers the solvent in capturing the intermediate I; third, since the rate of solvolysis of ICIH is slow under our conditions we may regard it as a stable trace product. In other words, we may neglect the reverse reactions of steps 2, 4, and 5 and combine the forward steps of 4 and 5 to a single reaction (4'). The usual steady-state approximations yield

$$[\text{I}] = \frac{k_2}{k_3}[\text{ClI}^-]$$

$$[\text{ClI}^-] = \frac{k_1}{k_{-1} + k_2}[\text{ClIH}][\text{OR}^-]$$

$$[\text{I}] = \frac{k_1 k_2}{k_3(k_{-1} + k_2)}[\text{ClIH}][\text{OR}^-]$$

Therefore the rate of formation of the isomer ICIH may be written

$$\begin{aligned} R_i &= \frac{k_1 k_2 k_4}{k_3(k_{-1} + k_2)}[\text{ClIH}][\text{Cl}^-] \\ &= C[\text{ClIH}][\text{Cl}^-] \end{aligned}$$

Figure 2 shows how [ClIH] varies with time in the presence of various amounts of *added* chloride ($[\text{Cl}_a^-]$). We now define the yield of ICIH as

$$Y_i = \int_0^\infty R_i dt$$

Since

$$[\text{ClIH}] = [\text{ClIH}]_0 e^{-t \ln 2} \quad (t \text{ in half-lives of ClIH})$$

and

$$[\text{Cl}^-]/[\text{ClIH}]_0 = [\text{Cl}^-]_\infty/[\text{ClIH}]_0 - e^{-t \ln 2}$$

if these terms are substituted in the definition of Y_i , and if it is realized that

$$[\text{Cl}^-]_\infty = [\text{ClIH}]_0 + [\text{Cl}_a^-]$$

integration gives

$$Y_i = \frac{C[\text{ClIH}]_0^2}{2 \ln 2} \left\{ 1 + \frac{2[\text{Cl}_a^-]}{[\text{ClIH}]_0} \right\}$$

conveniently written as

$$Y_i = Y_i^0 (1 + 2[\text{Cl}_a^-]/[\text{ClIH}]_0)$$

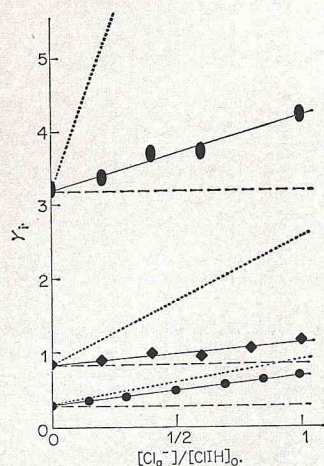


Figure 3. The dependence of the yield of ICIH (in per cent) on the concentration of added chloride in aqueous ethanol (circles, expt 1); in the presence of 30 equiv of bromide ion (squares, expt 2); in a mixture of ethanol and *t*-butyl alcohol (ellipses, expt 3). The solid lines represent the data; the dashed and dotted lines represent the yields expected if return is completely internal and external, respectively.

where Y_i^0 is the yield of the isomer in the absence of added chloride. Evidently, the presence of 1 equiv of added chloride should increase the yield of the allenic isomer by a factor of 3. If return is exclusively internal, then regardless of the value of $[Cl_a^-]$

$$Y_i = Y_i^0$$

Finally, if both types of return occur and f_{er} denotes the fraction of external return, we find that

$$f_{er} = \frac{Y_i - Y_i^0[ClIH]_0}{2Y_i^0[Cl_a^-]} \quad (6)$$

This analysis should be generally applicable when return leads to small amounts of a stable isomer.¹⁷

The solvolysis experiments were carried out at 48–50° for 30 min in ethanol–water mixtures in a 75:25 vol/vol ratio with a fourfold excess of lithium hydroxide. Vapor phase chromatography was employed as the analytical technique; *n*-butyl ether was used as an internal standard, and various experiments with known mixtures served to establish the reliability of the analysis to within a few per cent. All determinations were carried out at least in duplicate. A linear dependence of Y_i on $[Cl_a^-]$ was found as predicted by eq 6; internal return was found to occur to the extent of 33% (see experiment 1, Figure 3).

In the second experiment bromide ion was used to divert the intermediate I from the normal product; IBrH then becomes a major product. As explained earlier, equal decreases in the yields of ICIH and ROIH would indicate that all of the return is external; the absence of change in the former would show that all of the return is internal.¹⁸ It was observed, however,

(17) In the special case that the added chloride is labeled the final equation becomes

$$f_{er} = \frac{A}{2(A_0 - A)} [ClIH]_0 / [Cl_a^-]$$

where A denotes the specific activity of the ICIH and A_0 that of the added chloride.

(18) In all of these experiments small amounts of HOIH and 3-methyl-but-3-enyne are formed.^{3,4} The former of these products is not extracted by isopentane; the latter does show up in the chromatograms. Their presence is not essential to this discussion.

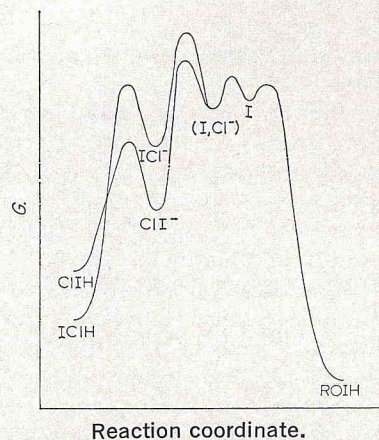


Figure 4. Free energy profiles for the base-promoted solvolyses of ICIH and ClIH.

Table II. Product Distribution^a in the Presence of Bromide Ion

No. of equivalents of bromide present	% EtOIH	% IBrH ^b	% ICIH ^c
0	99.7	0	0.30
10	86.2	13.4	0.40
20	77.8	21.6	0.69
30	58.5	40.6	0.86

^a Excluding the butynol; see Experimental Section. ^b At the highest concentrations of bromide, small amounts of BrIH could also be detected. ^c These small increases observed at high electrolyte concentrations clearly cannot account for the changes observed at chloride concentrations up to an equivalent (see text).

that the yield of ICIH rose as more and more bromide was added (see Table II). We are inclined to consider this the result of a decreasing activity of the solvent as the bromide ion concentration is increased; this would make it more difficult for the (I, Cl⁻) pair to dissociate. Such an explanation would suggest that at high bromide concentrations the return of chloride would be largely internal. A combination of the two approaches yielded the information that in the presence of 30 equiv of bromide ion more than 80% of the return of chloride is internal (see Figure 3, experiment 2).

Recently Hennion¹⁹ reported increased isomerization if the ethanol is replaced by *t*-butyl alcohol. It did indeed seem reasonable that the dissociation of the anion–carbene pair would be decreased by the use of a less polar solvent; it also seemed likely that return would be internal to a higher degree. We found that the use of 50:50 vol/vol ethanol–*t*-butyl alcohol led to a 3.21% yield of ICIH; experiments using added lithium chloride then revealed that 84% of the return is now internal (Figure 3, experiment 3).

A rough estimate of the energy profile is shown in Figure 4. The solvolysis product is the most stable molecule in the diagram under our conditions. Furthermore, the fact that ClIH can be isomerized nearly quantitatively to ICIH (see Experimental Section), the rapid D exchange of ICIH and the relatively high acidity of the acetylene can all be expressed in the diagram. The profile also reflects the facts that the (I, Cl⁻) pair undergoes only little return and that most of it dissociates to give I.

(19) G. F. Hennion and J. F. Motier, *J. Org. Chem.*, **34**, 1319 (1969).

It is conceivable that internal return may also have played a role in Shiner's difficulties³ in fitting his rate data for the solvolysis of BrIH to a rate law that included either a common ion effect or, alternatively, some noncommon ion isomerization; neither assumption fitted very well, but a 50:50 combination gave good agreement. Shiner and Humphrey⁴ later referred to this as "isomeric external return"; we suggest that partially internal return warrants consideration as a possible alternative explanation of their data. We were unable to verify this possibility, however; BrIH could not be obtained in a form completely free from traces of IBrH, and furthermore the former compound isomerized to the latter to a small degree during gas chromatographic analysis even under the most gentle conditions practicable. The iodo derivative IiH is apparently even more unstable; it explodes upon heating.²⁰

The intermediacy of the (I, Cl⁻) pair is in retrospect not so surprising. In neutral solvolysis ion pairs of more than one variety have been found,²¹ and in free-radical decompositions radical pairs are equally well known.²² A further example akin to that postulated here is the pyridine-triphenylmethylcarbonium ion pair suggested by Streitwieser²³ to account for data published by Ingold, *et al.*²⁴ The intermediacy of a pair consisting of an anion and a carbene—particularly the polarizable carbene I—is therefore an example of a phenomenon already encountered in other systems. If such pairs can be shown to be present in other solvolytic carbene reactions, this would provide a link between such reactions in polar media in which free carbenes are presumably present, and those in nonpolar media in which such freedom may not be attained.²⁵ It is of interest to speculate in this connection that the common intermediate conclusively shown by Hartzler⁷ to be present in the reactions of both ClIH or IClH with *t*-butoxide in styrene may have been the "carbenoid" (I, Cl⁻) rather than I. Further work on this question is in progress.

(20) T. L. Jacobs and W. L. Petty, *J. Org. Chem.*, **23**, 1360 (1963).

(21) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; p 148 ff, and p 167 ff.

(22) See, for example, W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **89**, 1741 (1967).

(23) Reference 19, p 82 and 83.

(24) E. Gelles, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2918 (1954).

(25) W. Kirmse, *Angew. Chem., Int. Ed. Engl.*, **4**, 1 (1965); G. Korbich, *ibid.*, **6**, 41 (1967). For recent contrary evidence on CCl₂, see P. S. Skell and M. S. Cholod, *J. Amer. Chem. Soc.*, **91**, 6035 (1969). See also R. A. Moss, *Chem. Eng. News*, **47**, 60 (June 16, 1969); **47**, 50 (June 30, 1960).

Experimental Section

Materials. 1-Chloro-3-methylbuta-1,2-diene was prepared essentially by the method of Hennon, Sheehan, and Maloney²⁶ from the isomeric 3-chloro-3-methylbut-1-yne, which in turn was prepared²⁷ from the commercially available alcohol. The isomerization, promoted by means of cuprous chloride, copper bronze, ammonium chloride, and hydrochloric acid, also produced some *trans*-1-chloro-3-methylbuta-1,3-diene (II); upon prolonged treatment, *cis*-II also appears. Collection was possible at 47° with an 8-ft column containing 20% squalane absorbed on 45–60 Chromosorb P; this yielded IClH in 95% purity. The contaminant was *trans*-II, which was shown not to produce any chloride under the conditions of the solvolysis; hence no attempt was made to purify the substrate further. The densities were measured by means of a thermometer which was calibrated, opened at the top, emptied, and then used as a densitometer; the weight of the mercury removed served to calculate its capacity. At 25°, the densities are 0.904 and 0.946 g/cm³ for ClIH and IClH, respectively.

Kinetics. A stock solution was prepared by diluting 1.5 g of IClH (precisely weighed) with ethanol containing 20% water by volume to 50 ml at 25°. Aliquots of 10 ml of this solution were in turn diluted at 25° to 25 ml by means of a solution 1.0 M in sodium hydroxide in the same ethanol-water mixture. After the desired time had elapsed, the solution was neutralized to methyl red with concentrated nitric acid and titrated electrometrically with 0.005 M silver nitrate. The high-pressure data were collected as described previously,²⁸ and fitted to the standard second-order rate law.

The Yield of IClH in the Solvolysis of ClIH. ClIH (7.5 mmol) was added to a mixture consisting of a solution prepared by the dissolution of 30 mmol of lithium hydroxide hydrate in 25 ml of water, and 75 ml of ethanol at 48°. After 45 min the reaction was quenched with ice and the resulting solution was neutralized and extracted four times with 100 ml of isopentane. The upper layers were combined and distilled to small volume by means of a Vigreux column and an oil bath held at 45–50°. An internal standard was added to the residue which was analyzed by means of an Aerograph A-90 operated at 60°; a 5 ft × 0.25 in. column was used, packed with 20% tricresyl phosphate supported on 35–80 Chromosorb P. The various materials encountered in this work had the following retention times in minutes: ClIH, 5.5; EtOIH, 6.4; BrIH, 12.9; IClH, 14.2; *n*-Bu₂O, 20.8; IBrH, 31.3. Similar experiments were done, (a) in which lithium bromide was also added to the aqueous solution (in three experiments: 75, 150, and 225 mmol); (b) in which small amounts of lithium chloride (up to 7.5 mmol) were added to this solution; (c) in which 225 mmol of lithium bromide and small amounts of lithium chloride (up to 7.5 mmol) were added; (d) in which the base was omitted. The experiments were done in duplicate and the results usually agreed to about 3%. The areas of the peaks were determined by weighing. In separate experiments it was shown that the extraction of all products by isopentane was complete except that of HOIH, which remains in the aqueous phase. Experiments with authentic mixtures were used to show the reliability of the VPC techniques.

Acknowledgment. This work was made possible by the generous support by the National Science Foundation.

(26) G. F. Hennon, J. J. Sheehan, and D. E. Maloney, *J. Amer. Chem. Soc.*, **72**, 3542 (1950).

(27) G. F. Hennon and K. W. Nelson, *ibid.*, **79**, 2142 (1957).

(28) W. J. le Noble, *ibid.*, **85**, 1470 (1963).