Solvolysis Mechanisms. β-Deuterium Isotope Effects for *t*-Butyl Chloride Solvolysis at Constant Ionizing Power and Effect of Structure of Reactant on SN1 Transition-State Geometry[1-3]

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Abstract: The isotope effects (k_H/k_D) for the solvolysis at 25° of *t*-butyl chloride and *t*-butyl-d_9 chloride in six solvent mixtures with the same "ionizing power," *i.e.*, the same rate constant for undeuterated *t*-butyl chloride, are as follows: pyridine–water (51:49), 2.46 ± 0.03; 2-propanol–water (48:52), 2.42 ± 0.07; acetic acid–water (63:37), 2.41 ± 0.07; acetone–water (49:51), 2.40 ± 0.08; ethanol–water (54:46), 2.35 ± 0.03; acetic acid–formic acid (29:71), 2.30 ± 0.05. The numbers in parentheses are per cent by volume before mixing. The near-constancy of these isotope effects, despite considerable differences in electrophilic or nucleophilic properties of the various solvents, suggests that the structures of the solvolysis transition states (*e.g.*, the extent of bond breaking) depend almost entirely on the *amount* of solvent assistance and *not* on the detailed *nature* of the assistance. This idea is reasonable if, as recent evidence strongly indicates, the transition state is ion pair like. A theoretical explanation of the transition-state geometry of SN1 and SN1–SN2 borderline reactions, which accounts for the puzzling features of these reactions, is suggested.

In view of the extensive similarities between SN2 and SN1 reactions, and especially the fact that reactions of certain substrates seem to be "borderline," *i.e.*, to involve some characteristics of both types, it seems very possible that the major distinguishing characteristic is the selectivity of the substrate toward nucleophilic attack. In the case of high selectivity, a powerful nucleophile could successfully compete with the high concentration of solvent molecules (SN2); in the case of low selectivity, such a powerful nucleophile could not compete with solvent (SN1). Obviously, cases of intermediate selectivity would be possible, but then some substrate molecules would react with solvent (SN1) and some with added nucleophile (SN2).

Since selectivity is a continuous variable, this interpretation requires that there be no basic distinction between SN1 and SN2 mechanisms—merely a difference in selectivity. Although the two main problems in this SN mechanism, the *extent* of nucleophilic participation and the question whether an intermediate carbonium ion forms, are in principle separate, it is expected that strong nucleophilic participation will lead to direct displacement, while weak nucleophilic participation will permit carbonium ion formation if energetically feasible.[4]

We next describe experiments designed to detect differences in nucleophilic interaction in the transition states for solvolysis of *t*-butyl chloride in solvents of different relative nucleophilic and electrophilic properties. Then we suggest a theoretical explanation of the mechanisms of SN reactions for different types of substrates based on a recent theory[5] of substituent effects on transition-state geometry.

Results

It appeared likely that subtle differences in transition-state structure for solvolysis of *t*-butyl chloride in different solvents might be measured by the β-deuterium isotope effects [$(CH_3)_3$–Cl *vs.* $(CD_3)_3C$–Cl]. We have found that these isotope effects (Table I) are closely similar, in spite of the fact that the nucleophilic component of the solvent varies from pyridine to acetic acid, though a trend toward lower isotope effect appears. Originally, we hoped that by measuring these isotope effects at constant ionizing power, *i.e.*, constant Y value,[6] we could isolate effects associated with changing solvent nucleophilic participation. We believe the slight trend observed is best explained in the latter way, but the effects are, unfortunately, rather small. There is a report of a significantly different value of k_H/k_D for the reaction in pure methanol,[7] 2.274 at 55.87° *vs.* 2.086 calculated for 50% aqueous ethanol (v/v) at this temperature. This rather large difference between methanol and aqueous ethanol must result from some combination of changes in ionizing power on the one hand and nucleophilic assistance on the other, but we cannot separate these effects. Other values of k_H/k_D for this reaction, already in the literature, include 2.45 in water at 20°,[7] 2.387 and 2.542 in 50% aqueous ethanol at 25 and 5.686°, respectively,[7] and 2.3271 in 60% aqueous ethanol (v/v) at 25°.[8]

Since our reaction rates were followed by a precise vapor phase chromatographic method, it was possible to determine relative amounts of the products formed. The yields are not so precise as the rates, difficulty in

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(1) Preliminary communication: G. J. Frisone and E. R. Thornton, *J. Amer. Chem. Soc.*, **86**, 1900 (1964); *cf.* also T. C. Jones and E. R. Thornton, *ibid.*, **89**, 4863 (1967).

(2) Supported in part by the Air Force Office of Scientific Research through Grant AF-AFOSR-431-63.

(3) For further details, *cf.* G. J. Frisone, Ph.D. Dissertation in Chemistry, University of Pennsylvania, 1965; *Dissertation Abstr.*, **26**, 3038 (1965); University Microfilms No. 65-13, 329 (1965).

(4) For a summary of evidence relating to these problems, see (a) E. R. Thornton, "Solvolysis Mechanisms," The Ronald Press Co., New York, N. Y., 1964, Chapter 4; (b) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; (c) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., Amsterdam, 1963.

(5) E. R. Thornton, *J. Amer. Chem. Soc.*, **89**, 2915 (1967).

(6) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951); E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

(7) L. Hakka, A. Queen, and R. E. Robertson, *ibid.*, **87**, 161 (1965). A similar effect has been noted in solvolysis of α-phenylethyl-β-d_3 chloride in ethanol containing 4–10% water: A. Guinot and G. Lamaty, *Chem. Commun.*, 960 (1967).

(8) V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, *J. Amer. Chem. Soc.*, **85**, 2413 (1963).

Table I. Rates and Isotope Effects for Solvolysis of *t*-Butyl Chloride in Solvents of Constant Y at 25°

Solvent[a]	(k_H,[b] sec^{-1}) × 10^5 [$(CH_3)_3C$–Cl]	(k_D,[b,c] sec^{-1}) × 10^5 [$(CD_3)_3C$–Cl]	k_H/k_D
Ethanol–water (54:46)	22.4 ± 0.3	9.52 ± 0.06	2.35 ± 0.03
Acetone–water (49:51)	22.5 ± 0.3	9.40 ± 0.26	2.40 ± 0.08
Acetic acid–water (63:37)	22.7 ± 0.3	9.32 ± 0.25	2.41 ± 0.07
Pyridine–water (51:49)	22.3 ± 0.2	9.08 ± 0.06	2.46 ± 0.03
2-Propanol–water (48:52)	22.4 ± 0.6	9.28 ± 0.12	2.42 ± 0.07
Acetic acid–formic acid (29:71)[d]	23.3 ± 0.3	10.15 ± 0.16	2.30 ± 0.05

[a] Numbers in parentheses are per cent by volume before mixing. [b] Average rate constant (in most cases for three or four runs), followed by standard deviation from mean. [c] >99% deuterated. [d] Acetic acid used contained 0.02 *M* acetic anhydride; 0.2 *M* anhydrous lithium formate added.

Table II. Product Analyses for *t*-Butyl Chloride Solvolyses at 25°

Solvent[a]	Product[b]	Average results[c] (normalized) $(CH_3)_3C$-Cl	$(CD_3)_3C$-Cl
Ethanol–water (54:46)	Isobutylene	0.083	0.044
	t-BuOEt	0.224	0.247
	t-BuOH	0.693	0.710
2-Propanol–water (48:52)	Isobutylene	0.081	0.038
	t-BuOPr^i	0.081	0.091
	t-BuOH	0.839	0.871
Pyridine–water (51:59)	Isobutylene	0.128	0.068
	t-BuOH	0.872	0.932
Acetic acid–water (63:37)	Isobutylene	0.131	0.083
	t-BuOAc	0.222	0.266
	t-BuOH	0.647	0.652
Acetic acid–formic acid (29:71)	Isobutylene	0.118	0.069
	t-BuOAc	0.115	0.108
	t-BuOCHO	0.736	0.784

[a] Numbers in parentheses are per cent by volume before mixing. [b] *t*-Bu = *t*-butyl; Et = ethyl; Pr^i = isopropyl; Ac = acetyl. [c] Analyses taken at *ca.* one to two half-lives; compositions were somewhat time dependent for acetic acid–water and acetic acid–formic acid.[3]

avoiding loss of isobutylene being the major factor (Table II).[3] Certain relative isotope effects can be calculated, the largest being the primary isotope effect for isobutylene formation of *ca.* 2, which is quite reasonable for attack of base (solvent or chloride ion within ion pair[9]) on a relatively labile carbonium ion. The relative constancy of isobutylene yield with change in solvent basicity may be taken as evidence that no appreciable bimolecular elimination reaction of *t*-butyl chloride with solvent occurs; such elimination has generally been thought to be negligible.[6] The relatively lower yield of ether in the case of 2-propanol–water as compared with ethanol–water is probably largely a result of steric hindrance disfavoring nucleophilic attack of 2-propanol more than ethanol, both relative to water.

Discussion

The lack of much solvent dependence of these β-deuterium isotope effects seems to require a transition state with very little interaction between the solvent and the *t*-butyl group. This small interaction appears to be conclusively demonstrated by the calculation of the isotope effect for the *equilibrium* between *t*-butyl chloride and *t*-butyl cation from infrared and Raman spectra,[10] giving k_H/k_D = 2.358 at 25° and 2.511 at 5.686°, essentially the same as the *kinetic* isotope effects.

It seems probable that the characteristics of the transition states for *t*-butyl chloride solvolyses are typical of tertiary esters and, indeed, of many systems which are capable of forming relatively stable carbonium ions. These characteristics are, primarily, extensive C---Cl bond breaking and very little nucleophile-to-carbon bond making. Relative to the "tight" transition states characteristic of SN2 reactions,[4] both entering and leaving group are less tightly bound to the central carbon atom.

The difference between SN2 and SN1 reaction mechanisms is therefore a difference in degree of bond making and bond breaking, both becoming larger or smaller together. This conclusion immediately suggests an explanation for SN1 mechanism data, namely that many SN1 transition states have the structure and properties predicted[5] for a very loose SN2 transition state. In contrast to this suggestion, the commonly held idea that all SN1 transition states are almost unimolecular can be shown to disagree with certain (admittedly ambiguous) evidence concerning substituent effects on transition-state geometry.[5] Not only does the above suggestion explain substituent effect data, it also explains the effect of changing the alkyl group of the substrate from primary to secondary to tertiary and rationalizes a great deal of information on SN reactions, much of which was previously difficult to understand.

The new feature of this proposed mechanism is that, if the SN1 transition state (eq 1) has nearly equally strong SR and RX bonds, even though both bonds are

$$\begin{gathered} \mathrm{S} + \mathrm{RX}\text{—}[\mathrm{S}\text{----}\mathrm{R}\text{----}\mathrm{X}]^{\ddagger} \longrightarrow \\ (\mathrm{S} = \text{solvent}) \end{gathered} \tag{1}$$

very weak, the effect of changing substituents in R will not affect motion along the reaction coordinate (parallel motion),[5] *i.e.*, reactant-like:product-like character, but will change the SR and RX bond lengths in the same direction (perpendicular motion),[5] just as in a tight SN2 transition state[5] (see eq 2). The effect of changing

$$\begin{array}{rl} \text{parallel motion:} & \mathrm{S}\!\rightarrow\ \leftarrow\!\mathrm{R}\ \mathrm{X}\!\rightarrow \\ \text{perpendicular motion:} & \leftarrow\!\mathrm{S}\qquad \mathrm{R}\ \mathrm{X}\!\rightarrow \end{array} \tag{2}$$

R on the parallel normal coordinate motion will be very small, because any change which makes the RX bond easier to break will make the SR bond more difficult to form[5] and if S and X are equally tightly bound to R, the net effect will be nearly zero. In contrast, the

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[9] M. Cocivera and S. Winstein, *J. Amer. Chem. Soc.*, **85**, 1702 (1963).

[10] J. C. Evans and G. Y.-S. Lo, *ibid.*, **88**, 2118 (1966); G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *ibid.*, **86**, 1360 (1964).

effect of changing R on the perpendicular motion should be important, because any change which makes the RX bond easier to stretch will also make the SR bond easier to stretch. It is, therefore, predicted[5] that a change in R which makes the RX bond easier to stretch (which will also make the SR bond easier to stretch, since both S and X are nucleophiles) will produce a transition state with a lengthened perpendicular normal coordinate, *i.e.*, with longer SR and RX bonds.

This hypothesis is very similar to the "push-pull" mechanism suggested by Swain;[11] variable tightness and near-equality of SR and RX bond strengths are its two distinguishing features.

Changing R from primary to secondary to tertiary alkyl, or introduction of phenyl groups or other conjugating groups, is predicted to give a transition state with longer SR and RX bonds, on the basis of both steric and electronic effects. As a result, such changes in R will give transition states in which R is more carbonium ion like. This prediction very simply explains the two major differences between SN2 and SN1 mechanisms. (1) Based on other types of selectivity relationships, such as the Brønsted catalysis laws, it is predicted that the tight transition state (*e.g.*, with a primary alkyl group) will have a large selectivity between nucleophiles; thus, an added powerful nucleophile might successfully compete with solvent in forming a SN transition state from RX. For a loose transition state (*e.g.*, with a tertiary alkyl group), the selectivity between nucleophiles would be much less, so that powerful nucleophiles could not, under most conditions, compete with solvent. (2) It is expected that a tight transition state would have sufficient interaction between nucleophile and R that no carbonium ion (or ion pair) formation would be likely, while a loose transition state might lead to a carbonium ion if carbonium ion formation were energetically favorable.

Our hypothesis that the transition state normally involves a nucleophilic solvent molecule leads naturally to the $[S\text{---}R\text{---}X]^+$ ion pair structure for the first-formed intermediate (if any), as proposed in the famous paper of Doering and Zeiss.[12]

Under proper conditions (possibly extremely low solvent nucleophilicity) it is conceivable that a truly unimolecular (SN1) mechanism may operate. It is only when the solvent molecule has similar nucleophilicity to the leaving group that nearly equally strong SR and RX (eq 1) bonds can be expected.[5] The substituent effect at R for the unimolecular mechanism is predicted[5] to be opposite from that for the bimolecular (whether tight or loose) mechanism.

The greater selectivity of triphenylmethyl than of benzhydryl cation for ionic nucleophiles *vs.* water[13] is not predicted for S---R---X transition states, and it therefore seems possible that triphenylmethyl halides solvolyze by a classical SN1 mechanism,[5] or by rate-determining nucleophilic attack on an ion pair. Selectivity relative to water is a special case, however, since it is the solvent and would be present in a solvated ion pair $S\text{---}R^+\text{---}X^-$ as well as a solvated carbonium ion $S\text{---}R^+\text{---}S$. Benzhydryl cations seem to show virtually no selectivity between chloride and azide ions.[13] However, for the S---R---X transition state it is predicted that the R---X bond would be longer with electron-supplying substituents, *i.e.*, for a more stable intermediate R^+, implying less selectivity among nucleophiles, in contrast to commonly accepted reasoning based on a R---X transition state. Selectivity among nucleophiles may be difficult to interpret, because inversions of the normal ordering of nucleophilicity occur;[13] isotope effects are likely to provide less ambiguous information but are not presently available.

Changing X would have the effects predicted for SN2 reactions,[5] as would changing the nucleophile. Changing S, in a solvolysis reaction, would, unfortunately, have effects which are not easily predicted, since solvation of the whole transition state would be changed along with the change in solvent. The present theory does, however, suggest experiments which may lead to a detailed understanding of changing the solvent. At present, the only pertinent data seem to be that presented in this paper. It may be argued that, by studying isotope effects at constant ionizing power (Y), the solvation effects have been kept constant. If so, then the higher k_H/k_D observed for a solvent containing a strong nucleophile (pyridine) than for the weakly nucleophilic acetic acid–formic acid is explained by the parallel effect for changing the nucleophile.[5] The more basic nucleophile is expected to have a longer bond to R in the transition state, and, if the effect on this bond is slightly greater than the effect on the RX bond (which would be shortened by the parallel effect, but which is farther removed from the site of change in nucleophile), the R group would be somewhat more loosely bound in the strong-nucleophile transition state (more carbonium ion character), thus giving a greater k_H/k_D.

Though it must be emphasized that most experimental evidence on SN1 mechanisms is ambiguous in determining transition-state geometry, the present theory does explain the SN2 extreme,[5] where unambiguous evidence is available, and is capable of rationalizing all of the many "indications" of changes in transition-state geometry for SN1 reactions.[4,5]

Space does not permit a review of the SN1 experimental evidence, but there are a few points that are now relatively clear and should be mentioned. The greater solvent sensitivity, implying more carbonium ion character, for solvolysis of cumyl chlorides substituted with electron-donating groups[14] is explained as the perpendicular effect of an electron-donating group in R, which should make SR and RX stretching easier and therefore make these bonds longer in the transition state. The salt-like character[15] of the transition state for solvolysis of *t*-butyl chloride is accounted for. The fact that the rate of attack of the conjugate base of the solvent, relative to solvolysis, decreases in the series $CH_3X > CH_3CH_2X > (CH_3)_2CHX > (CH_3)_3CX$[16] is reasonably explained by the decreased selectivity expected on going from primary to tertiary SN transition

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[11] C. G. Swain, *J. Amer. Chem. Soc.*, 70, 1119 (1948); C. G. Swain and R. W. Eddy, *ibid.*, 70, 2989 (1948).

[12] W. von E. Doering and H. H. Zeiss, *ibid.*, 75, 4733 (1953).

[13] C. G. Swain, C. B. Scott, and K. H. Lohmann, *ibid.*, 75, 136 (1953); L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

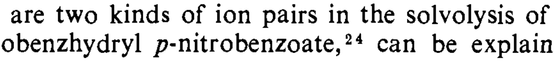
[14] Y. Okamoto, T. Inukai, and H. C. Brown, *J. Amer. Chem. Soc.*, **80**, 4972 (1958).

[15] E. M. Arnett, W. G. Bentrude, and P. M. Duggleby, *ibid.*, **87**, 2048 (1965).

[16] R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953); *cf.* also M. J. Bird, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 634 (1954).

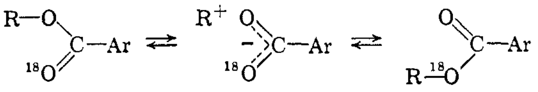
states. The ratio of rates of solvolysis of ROTs (OTs = p-toluenesulfonate) to RBr increases greatly in the series $CH_3CH_2 < (CH_3)_2CH < (CH_3)_3C$, indicating increasing charge separation between alkyl group and leaving group in the transition state.[17] The entropy of activation, $\Delta S^{\ddagger}$, for hydrolysis of chlorides, bromides, and toluenesulfonates becomes less negative along the series CH_3, CH_3CH_2, $(CH_3)_2CH$,[18] which suggests decreasing nucleophilic assistance along the series. The fact that the ratio of solvolysis rates at constant Y value, $(k_{EtOH-H_2O}/k_{AcOH})_Y$, in aqueous ethanol *vs.* acetic acid is smaller for 1-bromobicyclo[2.2.2]octane than for *t*-butyl chloride[19] supports the idea that there is some (but very little) solvent nucleophilic assistance in the transition state for the latter, which is sterically prohibited for the former. The possibility of nucleophilic assistance, even in displacement at a tertiary carbon atom, is supported by the observation of anchimeric assistance by an amino group in the reaction of a tertiary chloride.[20] Carbon isotope effects in SN reactions, which tend to be large for SN2 reactions[21] and small for reactions leading to carbonium ions,[22] must presumably be interpreted as resulting from conjugation in the incipient carbonium ion[22] ("hyperconjugation" in the case of *t*-butyl), which is supported by the detailed experimental and theoretical study of formation of triphenylmethyl cation from triphenylmethyl chloride,[23] giving an *inverse* carbon isotope effect for the central carbon atom.

It has been found that the oxygen-18 scrambling reaction observed for many reactions of p-nitrobenzoate esters does not occur with *t*-butyl p-nitrobenzoate (eq 3).[24] We believe this observation and others, such as



$$R{-}O{-}\underset{\underset{O^{18}}{\|}}{C}{-}C_6H_4NO_2\text{-}p \rightleftharpoons R{-}O^{18}{-}\underset{\underset{O}{\|}}{C}{-}C_6H_4NO_2\text{-}p \qquad (3)$$

the trapping experiment with azide ion which indicates there are two kinds of ion pairs in the solvolysis of p-chlorobenzhydryl p-nitrobenzoate,[24] can be explained by assuming that there are different ion-pair conformations in such reactions. In simplest terms, it could be that ionization according to eq 4 gives possible oxygen-18 scrambling by internal return, but ionization according to eq 5 gives no scrambling (Ar = p-nitrophenyl).



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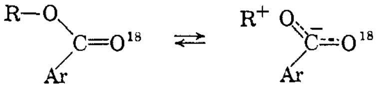

(5)

The *t*-butyl result could be explained by supposing the conformation of eq 4 could not be attained at a reasonable rate because of the bulky *t*-butyl group, so that most ion pairs would form in a skew conformation with the *t*-butyl group's central carbon atom not coplanar with the atoms of the CO_2 group. Thus we see no unambiguous evidence for intimate and solvent-separated ion pairs as discrete intermediates, though results such as the trapping experiments[24] argue strongly for two "kinds" of ion pairs.

Finally, we should mention the chlorine isotope effect for *t*-butyl chloride ethanolysis,[25] $k_{35}/k_{37} = 1.008$. This effect is not a maximal effect for chlorine, but we believe that account must be taken of solvation of chloride ion; even if the transition state is ion pair like, the chloride ion is strongly bound by solvent molecules, which should produce vibrations of the chloride ion, maintaining some zero-point energy and giving a lower isotope effect. In addition, the perpendicular vibration of the transition state involves motion of chlorine and, therefore, preserves some of the zero-point energy of the carbon–chlorine bond of the reactant.

Experimental Section

Materials. *t*-Butyl-d_9 chloride was purchased from Merck Sharpe and Dohme of Canada Limited (Lot No. 63CD099). Isotope content was found to be 99.3% by the finding of 6% of *t*-butyl-d_8 chloride using the mass spectrometric peak of m/e 65.

t-Butyl chloride was purchased from Eastman Organic Chemicals (Lot No. 2065). This sample showed the presence of approximately 0.5% *t*-butyl alcohol and a smaller concentration of isobutylene. A sample was purified by preparative gas chromatography on a Wilkens Autoprep A-700 using a 20-ft, $^3/_8$-in. column of 20% N,N-bis(2-cyanoethyl)formamide[26] on 60–80 mesh Chromosorb Z operating at 60°. Rechromatographing the collected sample did not show any isobutylene or *t*-butyl alcohol when examined on an analytical column using a 10-μl sample at maximum sensitivity of a thermal conductivity cell.

Solvolyzing Solutions. Each of the solvolyzing solutions was prepared according to the method of Winstein and Fainberg,[27] *i.e.*, equilibrated at 25 ± 0.01° before mixing and prepared as per cent by volume before mixing. These solvents were examined gas chromatographically and did not show any contaminants greater than 0.5%. The final solvolyzing solutions were arrived at by experimentation. The acetic acid–formic acid solvent was composed of acetic acid which had been refluxed with acetic anhydride, formic acid, and lithium formate. The lithium formate was prepared from lithium carbonate and formic acid plus a 10% excess of formic acid. The precipitate of lithium formate was filtered and then dehydrated in a vacuum oven at 105° for 12 hr.

Apparatus. The kinetic runs were performed by gas chromatographic analysis on an Aerograph A-350-B chromatograph using a 12-ft stainless-steel thin-walled column packed with 20% N,N-bis-(2-cyanoethyl)formamide on 60–80 mesh Chromosorb Z. The conditions for the instrument were: injector temperature, 110°; detector temperature, 160°; column temperature, 60°; collector temperature, 130°; carrier gas, helium at 40 cc/min; filament current, 250 ma; sensitivity, X1. A back-flushing system was installed such that the inlet of the back-flush was between the column and the detector cell. This device was needed to remove the solvolyzing solution from the previous run before a new sample could be injected; putting the back-flush inlet between the column and the cell avoided disturbing the thermal equilibrium of the detector. The column could be back-flushed and would return to equilibrium in 5–10 min as compared to 20–25 min for a conventional back-flushing system where the back-flushing gas is passed directly through the cell.

The constant-temperature bath was of conventional design. Temperature was maintained at 25.00 ± 0.01° using a Jumo temperature-control thermometer which was connected to a Fisher unitized bath control. A Beckmann thermometer calibrated

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[17] H. M. R. Hoffmann, *J. Chem. Soc.*, 6762 (1965).

[18] R. L. Heppolette and R. E. Robertson, *Can. J. Chem.*, **44**, 677 (1966).

[19] W. von E. Doering and M. Finkelstein, quoted in ref 4b.

[20] A. M. Braun, C. E. Ebner, C. A. Grob, and F. A. Jenny, *Tetrahedron Letters*, 4733 (1965).

[21] M. L. Bender and G. J. Buist, *J. Amer. Chem. Soc.*, **80**, 4304 (1958); K. R. Lynn and P. E. Yankwich, *ibid.*, **83**, 3220 (1961).

[22] J. B. Stothers and A. N. Bourns, *Can. J. Chem.*, **40**, 2007 (1962).

[23] A. J. Kresge, N. N. Lichtin, K. N. Rao, and R. E. Weston, Jr., *J. Amer. Chem. Soc.*, **87**, 437 (1965); see also **87**, 5809 (1965).

[24] H. L. Goering and J. F. Levy, *ibid.*, **84**, 3853 (1962); H. L. Goering, R. G. Briody, and J. F. Levy, *ibid.*, **85**, 3059 (1963); H. L. Goering and J. F. Levy, *ibid.*, **86**, 120 (1964).

[25] R. M. Bartholomew, F. Brown, and M. Lounsbury, *Can. J. Chem.*, **32**, 979 (1954).

[26] G. J. Frisone, *Nature*, **193**, 370 (1962).

[27] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956).

against a National Bureau of Standards platinum resistance thermometer was used to set the thermoregulator.

To facilitate the gas chromatographic analysis of the solvolysis a special reaction chamber was designed to allow for sampling during a kinetic run while maintaining a pressure-tight system. It consisted of a small glass vial (2 drams) fitted with a plastic screw cap. The liner of this cap was removed and a $^1/_{16}$-in. hole was drilled slightly off center into the cap. The liner was replaced with a circle of neoprene rubber ($^1/_2 \times {}^1/_8$ in.) and a circle of Teflon ($^9/_{16} \times {}^1/_{16}$ in.). These were placed into the cap with the rubber against the cap and the Teflon on top of the rubber. At the start of a kinetic run this special cap was screwed tight and the outside of the cap was wrapped with plastic tape covering the space between the cap and the glass. The Teflon disk was necessary to prevent the internal standard (CCl_4) from being absorbed by the neoprene rubber septum. When a sample was withdrawn the only portion of the rubber in contact with the solvolysis solution was the small hole made by the syringe needle.

During a kinetic run this vial was clamped to the shaft of an air stirrer and immersed into the constant-temperature bath where it was allowed to come to equilibrium.

Kinetic Procedure. To a glass vial, dried in a 105° oven, was added 2.5 ml of solvent, together with 5 μl of carbon tetrachloride. The cap was screwed on, tape wrapped around the cap, and the bottle mounted on the stirrer shaft and immersed into the constant-temperature bath. After thermal equilibrium had been reached, the stirrer was stopped, the vial lifted from the constant-temperature bath, the cap dried off, and 5 μl of *t*-butyl chloride injected through the cap. The vial was again immersed into the constant-temperature bath and the stirrer restarted. After 3 min the above procedure was repeated with the exception that 15 μl of solution was withdrawn. The syringe was adjusted to deliver 10 μl of sample and 5 μl of air, and this was injected into the gas chromatograph. The recorder was continuously running and was used to measure the elapsed time between samples. The order of elution on the chromatogram was air, *t*-butyl chloride, and carbon tetrachloride. After the carbon tetrachloride peak was eluted, the gas chromatograph was back-flushed for approximately 10–15 min. After this time the chromatograph was restored to conventional flow and the system was allowed to reach equilibrium (approximately 5 min). At this point, the chromatograph was ready for another sample to be injected. The syringe used was a constant-delivery syringe (Hamilton Co. No. CR-700), total capacity 20 μl.

To avoid the difficulty of not being able to inject precisely the same size sample into the chromatograph an internal standard was used. The internal standard chosen was carbon tetrachloride since it would be nonreactive and has an elution time close to the peak to be measured. Commonly accepted standardizing procedures were used and the results showed a linear response with an average deviation of $\pm 1\%$.

The time scale (chart drive) was calibrated against an electric timer and was found to be better than 99.9% correct.

A steel rule divided into 0.01-in. units was used to measure the peak heights and the time scale. A comparison of the results of a kinetic run using area measurements and peak height measurements only revealed no significant difference. As a consequence the reported data are from peak height measurements only.

The rate constant for the solvolysis was calculated from the integrated equation for first-order kinetics. The concentration of *t*-butyl chloride remaining was determined by measuring the heights of both the *t*-butyl chloride and the carbon tetrachloride peak and normalizing the *t*-butyl chloride peak to the carbon tetrachloride peak. The time was measured by inches of chart paper and converted to seconds. The time for the individual points was measured from air peak to air peak.

Product Analysis. The identification and measurement of the products of solvolysis were performed on samples prepared in the exact manner as for the kinetic run with the exception that 40 μl of sample was injected into the gas chromatograph instead of 10 μl. Area measurements were used to obtain a realistic comparison of relative concentrations. Identification of the peaks was obtained by matching retention times with known samples. The following were identified: isobutylene, ethyl *t*-butyl ether, isopropyl *t*-butyl ether, *t*-butyl acetate, *t*-butyl formate, and *t*-butyl alcohol.