reacted with titanous chloride in the presence of acrylonitrile to yield a white solid which began to appear after 20 min of reaction. After 8 hr at 80° titanous chloride was completely consumed, and 47% of the iodonium salt had reacted. A control reaction under identical conditions, but without iodonium salt, showed no change after 8 hr. The solid was collected, washed and triturated in turn with water, methanol and ether, yielding 5.0 g (63% based on starting acrylonitrile) of polyacrylonitrile. The polymer was dissolved in a minimum of dimethylformamide at 80–90°, and the solution was filtered hot through Celite. Water was slowly added to the cooled solution until no more precipitation occurred. The collected solid was dried to yield 3.0 g of polyacrylonitrile, mp 250° dec (lit.[13] 250–310° dec).

Identification was made from solubility characteristics and infrared and nmr spectra. The polymer was found to be insoluble in water, alcohols, acetone, ethylacetate, ether, methylene chloride and pentane but was soluble in dimethylformamide.[13] An infrared spectrum (potassium bromide pellet) exhibited strong peaks at 2230 (–CN), 1450 (CH, $CH_2$) and 1050 $cm^{-1}$ (C–C skeletal).[13] An nmr spectrum (on a Varian A-60 spectrometer) of a solution in deuterated dimethyl sulfoxide exhibited broad signals at $\tau$ 7.9 and 6.8 and a very weak signal at 2.7.

**Registry No.**—Diphenyliodonium chloride, 1483-72-3; titanous chloride, 7705-07-9; chromous chloride, 10049-05-5.

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# Deuterium Isotope Effect upon a Bimolecular Dehydrochlorination of *t*-Butyl Chloride in Acetonitrile

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We have extended our recent study of the secondary deuterium isotope effect upon the unimolecular dehydrochlorination of *t*-butyl chloride in acetonitrile[1] to a study of the deuterium isotope effect under conditions for bimolecular reaction in this solvent. It is known that bimolecular reactions of tertiary halides in dipolar aprotic solvents frequently show a small amount of substitution reaction accompanying dehydrohalogenation[2,3] and complications of this type have been avoided by use of chloride ion as the reagent to promote the bimolecular dehydrochlorination. Chloride ion in acetonitrile is quite efficient in this capacity[4] and, with this reagent, any substitution reaction will be symmetrical. The dehydrochlorination of *t*-butyl chloride is subject to marked reversal and, in the absence of reagents which remove hydrogen chloride, the reaction in aprotic solvents comes to an early equilibrium.[5] In the unimolecular dehydrochlorination,[1] added pyridine reacted with the hydrogen chloride to form pyridinium chloride[6] and prevent complications due to movement toward an equilibrium. In the presence of chloride ion, hydrogen chloride is effectively coordinated to give the hydrogen dichloride anion[7] and pyridine can be omitted.

A serious complication to the kinetic pattern is that the unimolecular reaction will be subject to a positive salt effect upon addition of tetraethylammonium chloride and the dehydrochlorination rate increase will consist of two components—one due to the superimposed bimolecular reaction and one due to a positive salt effect upon the underlying unimolecular reaction. In order to analyze the kinetics of the bimolecular reaction, we have attempted to arrive at the magnitude of salt effects upon the unimolecular reaction by assessing the rate increase upon addition of identical concentrations of tetraethylammonium perchlorate—a salt containing an anion which, relative to chloride ion, is ineffective in promoting bimolecular dehydrohalogenation in acetonitrile.[8] Perchlorate ion does not coordinate with hydrogen chloride and our studies of the effect of added tetraethylammonium perchlorate were carried out in the presence of pyridine (Table I).

Our kinetic results can be analyzed provided that we make the assumption that the salt effects upon the unimolecular reaction are identical (or, at least, very nearly so) for additions of either tetraethylammonium chloride or tetraethylammonium perchlorate (Table II).

The deuterium isotope effect ($k_2^H/k_2^D$) is 3.81 ± 0.21. The magnitude of this effect has important implications with respect to the mechanism of bimolecular, merged substitution and elimination which was given a detailed description several years ago,[4] and which recently appears to have gained wider,[9,10] but not universal,[11,12] acceptance. In assessing the extent of carbon–hydrogen bond breaking, and interpreting in terms of a mechanism in which carbon–chlorine heterolysis is running ahead of carbon–hydrogen heterolysis, we are on a scale of roughly 2.6:6 and not, as in most previous investigations, of roughly 1:6. With this in mind, the value of 3.8 is comparable with the values of between 2 and 3 observed for halide ion promoted elimination from tertiary $\alpha$-halogenated ketones in acetonitrile.[13]

Under the same conditions of temperature and solvent, the deuterium isotope effect is significantly higher than the value of 2.62 ± 0.02 observed for E1 reaction.[1] This is consistent with a loose intermediate or transition state (approaching an ion triplet) and incorporating a moderate weakening of a carbon–hydrogen bond in the transition state of the rate-determining step.[13] If a transition state was involved which featured only SN2 character superimposed upon a E1-type process, then one might expect, related to the extent that the positive charge on the $\alpha$ carbon was reduced, an isotope effect for the bimolecular reaction diminished below that observed for the E1 reaction.

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(2) D. N. Kevill, G. A. Coppens, and N. H. Cromwell, *J. Org. Chem.*, **28**, 567 (1963).

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(4) D. N. Kevill and N. H. Cromwell, *Proc. Chem. Soc.*, 252 (1961); *J. Amer. Chem. Soc.*, **83**, 3812, 3815 (1961).

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TABLE I

EFFECT OF TETRAETHYLAMMONIUM PERCHLORATE UPON THE FIRST-ORDER RATE COEFFICIENTS, $k_1^1$ (sec$^{-1}$), FOR PYRIDINIUM ION PRODUCTION FROM ~0.2 $M$ $t$-BUTYL CHLORIDE OR ~0.2 $M$ $t$-BUTYL CHLORIDE-$d_9$ IN ACETONITRILE AT 45.0°, IN THE PRESENCE OF 0.04 $M$ PYRIDINE

(i) $t$-Butyl Chloride

| $[NEt_4ClO_4]$ | 0.000 | 0.100 | 0.200 | 0.300 | 0.400 | 0.500 |
|---|---|---|---|---|---|---|
| $10^8k_1^1$ | 2.66 | 3.52 | 4.30 | 5.09 | 5.73 | 6.39 |

(ii) $t$-Butyl Chloride-$d_9$

| $[NEt_4ClO_4]$ | 0.000 | 0.100 | 0.125 | 0.200 | 0.251 | 0.300 | 0.375 | 0.400 | 0.500 |
|---|---|---|---|---|---|---|---|---|---|
| $10^8k_1^1$ | 1.01 | 1.58 | 1.64 | 1.77 | 1.96 | 2.18 | 2.26 | 2.41 | 2.48 |

TABLE II

EFFECT OF $NEt_4Cl$ UPON THE INITIAL SPECIFIC RATES, $k_1^{11}$ (sec$^{-1}$), FOR ACID PRODUCTION FROM ~0.2 $M$ $t$-BUTYL CHLORIDE OR ~0.24 $M$ $t$-BUTYL CHLORIDE-$d_9$ IN ACETONITRILE AT 45.0°, AND APPLICATION OF CORRECTION FOR INITIAL SPECIFIC RATES, $k_1^1$ (sec$^{-1}$), ON REPLACEMENT OF $NEt_4Cl$ WITH AN IDENTICAL CONCENTRATION OF $NEt_4ClO_4$

(i) $t$-Butyl Chloride

| $[NEt_4Cl]$ | 0.0100 | 0.0200 | 0.0400 | 0.0800 | 0.100 | 0.150 | 0.200[c] |
|---|---|---|---|---|---|---|---|
| $10^8k_1^{11}$ | 3.16 | 3.78 | 4.94 | 7.67 | 9.23 | 12.60 | 15.33 |
| $10^8k_1^1$ [a] | 2.75 | 2.83 | 3.00 | 3.35 | 3.52 | 3.89 | 4.30 |
| $10^8\Delta k_1$ [b] | 0.41 | 0.95 | 1.94 | 4.32 | 5.71 | 8.71 | 11.03 |

| $[NEt_4Cl]$ | 0.200[d] | 0.200[e] | 0.200 | 0.300 | 0.400 | 0.400 |
|---|---|---|---|---|---|---|
| $10^8k_1^{11}$ | 15.36 | 15.48 | 15.05 | 22.19 | 29.58 | 28.04 |
| $10^8k_1^1$ [a] | 4.30 | 4.30 | 4.30 | 5.09 | 5.73 | 5.73 |
| $10^8\Delta k_1$ [b] | 11.06 | 11.18 | 10.75 | 17.10 | 23.85 | 22.31 |

$$10^8\Delta k_1^{H} = 10^8k_2^{H}[NEt_4Cl] = (56.2 \pm 1.1)[NEt_4Cl]$$

(ii) $t$-Butyl Chloride-$d_9$

| $[NEt_4Cl]$ | 0.0964 | 0.1925 | 0.289 | 0.385 | 0.385[f] |
|---|---|---|---|---|---|
| $10^8k_1^{11}$ | 3.00 | 4.60 | 6.35 | 8.17 | 7.85 |
| $10^8k_1^1$ [a] | 1.54 | 1.86 | 2.10 | 2.30 | 2.30 |
| $10^8\Delta k_1$ [b] | 1.46 | 2.74 | 4.25 | 5.87 | 5.55 |

$$10^8\Delta k_1^{D} = 10^8k_2^{D}[NEt_4Cl] = (14.7 \pm 0.6)[NEt_4Cl]$$

[a] Obtained by graphical interpolation within the data of Table I. [b] $\Delta k_1 = k_1^{11} - k_1^1$. [c] [$t$-BuCl]; 0.100 $M$. [d] [$t$-BuCl]; 0.300 $M$. [e] [$t$-BuCl]; 0.400 $M$. [f] [$t$-BuCl-$d_9$]; 0.120 $M$.

TABLE III

(A) [$t$-$C_4D_9Cl$], 0.2405 $M$; [$C_5H_5N$], 0.200 $M$; 2.00-ml aliquots; titers in milliliters of 0.00579 $N$ methanolic NaOMe

| Time, hr | 0.00 | 136.87 | 183.47 | 256.20 | 329.62 | 401.17 | 526.38 | 598.98 | 618.57 |
|---|---|---|---|---|---|---|---|---|---|
| Titer | 0.00 | 0.46 | 0.57 | 0.76 | 0.96 | 1.15 | 1.61 | 1.84 | 1.89 |
| $10^8k_1$, sec$^{-1}$ |  | 1.127 | 1.042 | 0.996 | 0.979 | 0.965 | 1.033 | 1.039 | 1.033 |

Mean value for $k_1$ is $(1.027 \pm 0.016) \times 10^{-8}$ sec$^{-1}$

(B) [$t$-$C_4D_9Cl$], 0.1548 $M$; [$C_5H_5N$], 0.0400 $M$; [$NEt_4ClO_4$], 0.300 $M$; 2.00-ml aliquots; titers in milliliters of 0.00579 $N$ methanolic NaOMe

| Time, hr | 0.00 | 66.30 | 114.30 | 168.73 | 219.66 | 264.54 | 309.01 | 359.56 |
|---|---|---|---|---|---|---|---|---|
| Titer | 0.15 | 0.42 | 0.62 | 0.84 | 1.05 | 1.25 | 1.45 | 1.71 |
| $10^8k_1$, sec$^{-1}$ |  | 2.13 | 2.15 | 2.14 | 2.15 | 2.19 | 2.22 | 2.29 |

Mean value for $k_1$ is $(2.18 \pm 0.021) \times 10^{-8}$ sec$^{-1}$

(C) [$t$-$C_4H_9Cl$], 0.200 $M$; [$NEt_4Cl$], 0.100 $M$; 5.00-ml aliquots; titers in milliliters of 0.01158 $N$ methanolic NaOMe

| Time, hr | 0.00 | 13.53 | 23.35 | 36.18 | 49.53 | 61.33 | 70.57 | 159.63 |
|---|---|---|---|---|---|---|---|---|
| Titer | 0.02 | 0.41 | 0.69 | 1.05 | 1.41 | 1.74 | 2.06 | 4.55 |
| $10^8k_1$, sec$^{-1}$ |  | 9.25 | 9.26 | 9.21 | 9.10 | 9.09 | 9.27 | 9.35 |

Mean value for $k_1$ is $(9.23 \pm 0.11) \times 10^{-8}$ sec$^{-1}$

## Experimental Section

**Materials.**—Tetraethylammonium chloride and tetraethylammonium perchlorate (Eastman) were recrystallized from acetone and dried under vacuum, at 70°, for 12 hr. Acetonitrile (Mallinckrodt "Nanograde") was purified[14] by placing 800 ml in a round-bottomed flask, together with 10 g of anhydrous $Na_2CO_3$ and 15 g of $KMnO_4$. The acetonitrile was distilled at 5–10 ml/min. The distillate was made slightly acidic with concentrated $H_2SO_4$ and decanted from precipitated ammonium sulfate. The acetonitrile was then distilled through a fractionating column at 10 ml/hr with a reflux ratio of 20:1. A small forecut was discarded. Pyridine was purified by the method of Burgess and Kraus,[15] dried with $CaH_2$, and fractionated. The $t$-butyl chloride (Eastman) was fractionally distilled and the $t$-butyl chloride-$d_9$ (Merck Sharp and Dohme of Canada product of 99% minimum isotopic purity on atom % D basis) was used as received.

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[14] J. F. O'Donnell, J. T. Ayres, and C. K. Mann, *Anal. Chem.*, **37**, 1161 (1965).

[15] D. S. Burgess and C. A. Kraus, *J. Amer. Chem. Soc.*, **70**, 706 (1948).

**Kinetic Methods.**—All runs were carried out in stoppered volumetric flasks. Stock solutions of reactants were maintained at 45.0° and used to prepare reaction mixtures for kinetic runs. For runs with *t*-butyl chloride, 5.00-ml aliquots were removed from 50 ml of reaction mixture. For runs with *t*-butyl chloride-$d_9$, 2.00-ml aliquots were removed from 25 ml of the reaction mixture. The extent of dehydrochlorination was determined by addition of the aliquots to 20 ml of acetone, previously rendered neutral to resorcinol blue (Lacmoid) indicator, followed by titration against a standard solution of sodium methylate in methanol. In the three illustrative runs in Table III, the first-order rate coefficients are the integrated first-order rate coefficients with respect to the *t*-butyl chloride or *t*-butyl chloride-$d_9$. The errors quoted along with the mean values are standard errors of the mean.

**Registry No.**—*t*-Butyl chloride, 507-20-0; *t*-butyl chloride-$d_9$, 918-20-7; $NEt_4Cl$, 56-34-8; $NEt_4ClO_4$, 2567-83-1; acetonitrile, 75-05-8.

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# Acid-Catalyzed Reactions of α- and β-Styryl Azides[1]

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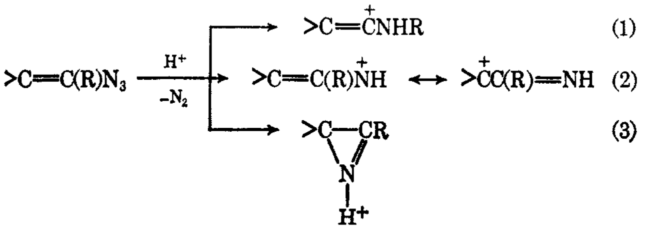
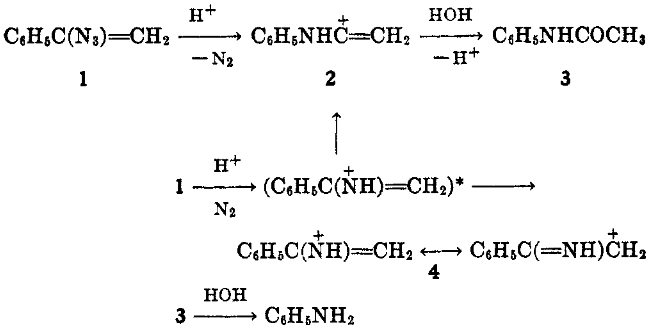
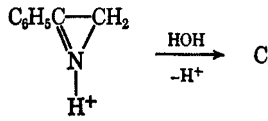
Rearrangement during acid degradation of certain alkyl azides is concerted with the evolution of nitrogen.[2] Both rearrangement[3] by path 1 and azirine ring closure by path 3 may be concerted with nitrogen evolution from a vinyl azide and an unrearranged hybrid cation may be available by path 2. If formed, it should afford certain products derived from an unrearranged carbonium ion and others from a nitrenium ion[4a] as well as rearrange to a new carbonium ion or cyclize to an azirinium ion.



Acid degradation of two vinyl azides, α- (1) and β-styryl azide (5), has been investigated. In ethanolic sulfuric acid, 1 is nearly quantitatively (94%) transformed into a mixture of acetanilide, 3, and aniline, presumably formed by hydrolysis of 3 during work-up (Scheme I).[4b] This appears to be a reaction according to path 1 and/or path 2 if in the latter event a "hot" nitrenium ion is produced and rearranged before it loses energy and becomes a resonance hybrid cation. An unrearranged hybrid cation, 4, was not detected insofar as products of rearrangement from carbon to carbon were not formed[5] and other carbonium ion reactions, *e.g.*, solvation, were not detected. Hydrolysis of the 2-phenylazirinium cation to phenacylamine,[6] without the formation of acetanilide, eliminated path 3 in the acid degradation of 1.

Scheme I





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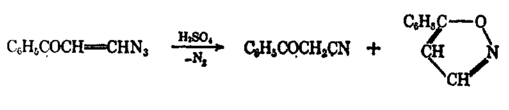
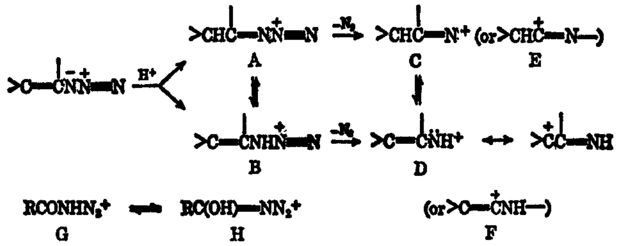
[1] Financial assistance from NASA Grant No. NGR 14-012-004.

[2] P. A. S. Smith in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, pp 468–471.

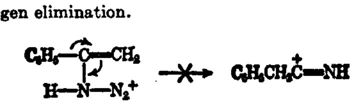
[3] A. N. Nesmeyanov and M. I. Rybinskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 816 (1962); p 761 reports



[4] (a) From the assignment of a higher energy to $RNH^+$ (from $RNHN_2^+$) relative to $RCH_2^+$ (from $RCH_2N_2^+$) by R. F. Tietz and W. E. McEwen, *J. Amer. Chem. Soc.*, **77**, 4007 (1955), the hybrid cation, 4 would be expected to react as a carbonium ion excited state. (b) A referee suggested that product formation may require the intermediacy of protonation at carbon rather than at nitrogen. From the recognition that organic azides in general are protonated at nitrogen (P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, Inc., New York, N.Y., 1966, pp 225–226) we assumed that protonation at carbon in a vinyl azide would be relatively unimportant to account for the observed products. In failing to recognize the two pairs of tautomers, A ⇌ B and C ⇌ D (or the rearranged cations, E ⇌ F), the referee apparently overlooked this intimate relationship of intermediates available from the two conceivable initial steps. This reaction of a vinyl azide is reminiscent of the acid-catalyzed Curtius and the Schmidt reactions where tautomers G and H must each be recognized as a possible intermediate (P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, Inc., New York, N. Y., 1966, p 227; P. A. S. Smith in P. de Mayo, "Molecular Rearrangements," Vol. 1, John Wiley & Sons, Inc., New York, N. Y., 1963, p 529; J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp 319–321).



[5] This evidence also eliminates a migration from carbon to carbon concerted with nitrogen elimination.



[6] G. Smolinsky [*J. Org. Chem.*, **27**, 3557 (1962)] reports nmr (solvent unspecified) δ 5.32 (s) and 4.32 (s).