

Rates and Mechanism for the Solvolysis of *N*-*tert*-Alkylpyridinium Cations in a Variety of Solvents¹

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Abstract: Solvolysis rates are measured for 1-(1-adamantyl)-, 1-*tert*-butyl-, and 1-(1-methyl-1-phenylethyl)pyridinium cations. Rates are almost independent of solvent and show less variation with the substrate structure than do analogues with leaving groups departing as anions. No evidence is found for any nucleophilic assistance by solvent in the solvolysis of these *tert*-alkylpyridinium cations. Previously measured solvolysis rates for *N*-*sec*-alkylpyridinium cations plot as straight lines with small negative slopes against E_T : positive deviations for AcOH and *n*-pentyl alcohol support nucleophilic assistance in these solvents. This criterion provides no support for nucleophilic assistance in the case of *tert*-butyldimethylsulfonium cation solvolyses.

We have recently made extensive studies of the mechanism of nucleophilic replacement at sp^3 -hybridized carbon atoms in which pyridines were used as leaving groups.² This enables the variation of the charge carried by the leaving group—both neutral and anionic pyridines (with SO_3^- or CO_2^- substituents) were utilized:³ in particular the use of neutral leaving groups considerably assists the mechanistic interpretation because S_N1 -type reactions become much less disfavored in non-nucleophilic solvents, allowing distinction between the effects of solvent polarity and nucleophilicity.

Our results have been interpreted in terms of the five alternative mechanisms shown in Scheme I.⁴ Detailed studies of primary alkyl substrates⁵ have indicated that for less nucleophilic solvents reaction occurs via ion-pair intermediates formed without synchronous rate-enhancing H^+ or R^+ migration. Close examination⁶ of secondary alkyl substrates has shown that such reactions occur by three different mechanisms: classical S_N2 reaction, rate-determining ion-pair formation, or rate-determining ion-pair dissociation depending on the conditions.

In particular, no evidence was found in these systems for any "merging" of the S_N1 - S_N2 reaction type or for the " S_N2 intermediate" mechanism which has been advocated by Bentley and Schleyer.⁷

We have more recently turned our attention to tertiary alkyl substrates and report our findings in the present paper. *tert*-Alkyl nucleophilic displacements have generally been assumed to occur exclusively by a unimolecular S_N1 -type mechanism, with⁸ or without⁹ the intermediacy of ion-pairs: for a recent review see March.¹⁰ However, recently Bentley and his co-workers have advocated nucleophilic solvent assistance in the solvolysis reaction of *tert*-alkyl substrates.¹¹ This suggestion has already attracted criticism¹² and we found no evidence to support it in our system.

(1) This paper is considered as Part 24 in the following series: Kinetics and Mechanism of Nucleophilic Displacements with Heterocycles as Leaving Groups. For Part 23, see: *Can. J. Chem.* **1986**, *64*, 1161.

(2) For a comprehensive review, see: Katritzky, A. R.; Musumarra, G.; Sakizadeh, K. *Heterocycles* **1985**, *23*, 1765.

(3) See: (a) Katritzky, A. R.; Gonzalez, A. *J. Chem. Soc., Perkin Trans.* **2** **1985**, 1613. (b) Katritzky, A. R.; Yousaf, T. I. *J. Chem. Soc., Perkin Trans.* **2** **1985**, 1619.

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(7) (a) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7658. (b) Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1.

(8) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd edition; Cornell University Press: New York, 1969; p 460.

(9) Harris, J. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 89.

(10) March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985; pp 225-446.

(11) (a) Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. *J. Am. Chem. Soc.* **1979**, *101*, 2486. (b) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5741.

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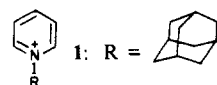
Table I. Solvolysis Rate Constants for 1-(1-Methyl-1-phenylethyl)pyridinium Perchlorate (3) in Water^a

| entry no. | pH | temp (°C) | $10^5 k_{\text{obsd}}$ (s ⁻¹) | corr coeff | rxn ^f (%) |
|-----------|-------------------------|-----------|---|------------|----------------------|
| 1 | 1.0 ^b | 78.2 | 2.77 ± 0.05 | 0.9996 | 77.9 |
| 2 | 7.0 ^c | 78.2 | 2.76 ± 0.07 | 0.9992 | 77.7 |
| 3 | 13.0 ^d | 78.2 | 2.79 ± 0.05 | 0.9996 | 77.5 |
| 4 | 10.4 ^e | 60.0 | 0.19 ± 0.01 | 0.9988 | 22.0 |
| 5 | 10.4 ^e | 70.0 | 0.89 ± 0.01 | 0.9996 | 59.8 |
| 6 | 10.4 ^e | 78.2 | 2.80 ± 0.15 | 0.9979 | 65.4 |
| 7 | 10.4 ^e | 80.0 | 3.15 ± 0.07 | 0.9987 | 67.4 |
| 8 | 10.4 ^e | 93.0 | 18.33 ± 0.80 | 0.9988 | 62.8 |
| 9 | 10.4 ^e | 100.0 | 34.18 ± 2.62 | 0.9971 | 86.8 |
| 10 | (2% NEt ₃) | 78.2 | 3.08 ± 0.06 | 0.9995 | 68.0 |
| 11 | (2% piperidine) | 78.2 | 2.61 ± 0.13 | 0.9965 | 67.6 |
| 12 | (10% NaN ₃) | 78.2 | 2.72 ± 0.04 | 0.9994 | 75.0 |

^a Concentration of pyridinium 1.2×10^{-4} mol L⁻¹. ^b 0.1 N HCl. ^c Buffer NaH₂PO₄-NaOH (0.1 M). ^d 0.1 N NaOH. ^e Buffer Na₃B-O₃-Na₂CO₃ (0.1 M). ^f Percent to which reaction was followed.

We now report investigations of the solvolyses of 1-(1-adamantyl)- (1), 1-*tert*-butyl- (2), 1-(1-methyl-1-phenylethyl)- (3), 1-(1,1-diphenylethyl)- (4), and 1-(triphenylmethyl)pyridinium (5) cations. We found that the 4 and 5 reacted too rapidly for measurement by the normal techniques at 20 °C in H₂O or alcohols: kinetic results were obtained for 1, 2, and 3.

Block 1



- 1: R =
- 2: R = *t*-Bu
- 3: R = PhCMe₂
- 4: R = Ph₂CMe
- 5: R = Ph₃C

Solvolysis of 1-(1-Methyl-1-phenylethyl)pyridinium Perchlorate (3). This was found to occur at convenient rates at 60–100 °C and was followed spectrophotometrically. In unbuffered water (and also in methanol and *n*-butanol), an initial decrease in absorption followed by an increase is due to acid-base equilibria: these were suppressed either (a) by carrying out the reaction in the presence of triethylamine or (b) by diluting the kinetic solutions with ethanol containing NEt₃ prior to measurement of the absorbance. With this precaution, all reactions showed good pseudo-first-order behavior.

The data observed in water (Table I) show that the rate is not affected by pH change, nor by the presence of NEt₃, piperidine, nor NaN₃. Activation parameters were determined: heat of activation 31.6 ± 1.2 kcal/mol and entropy of activation $+10.1 \pm 3.5$ cal/(mol-deg); the latter positive value is characteristic of an S_N1 -type reaction.¹³

(13) Hartshorn, S. R. *Aliphatic Nucleophilic Substitution*; Cambridge University Press: London, 1973; p 81.

Scheme I. Nucleophilic Substitutions with Pyridine Leaving Groups

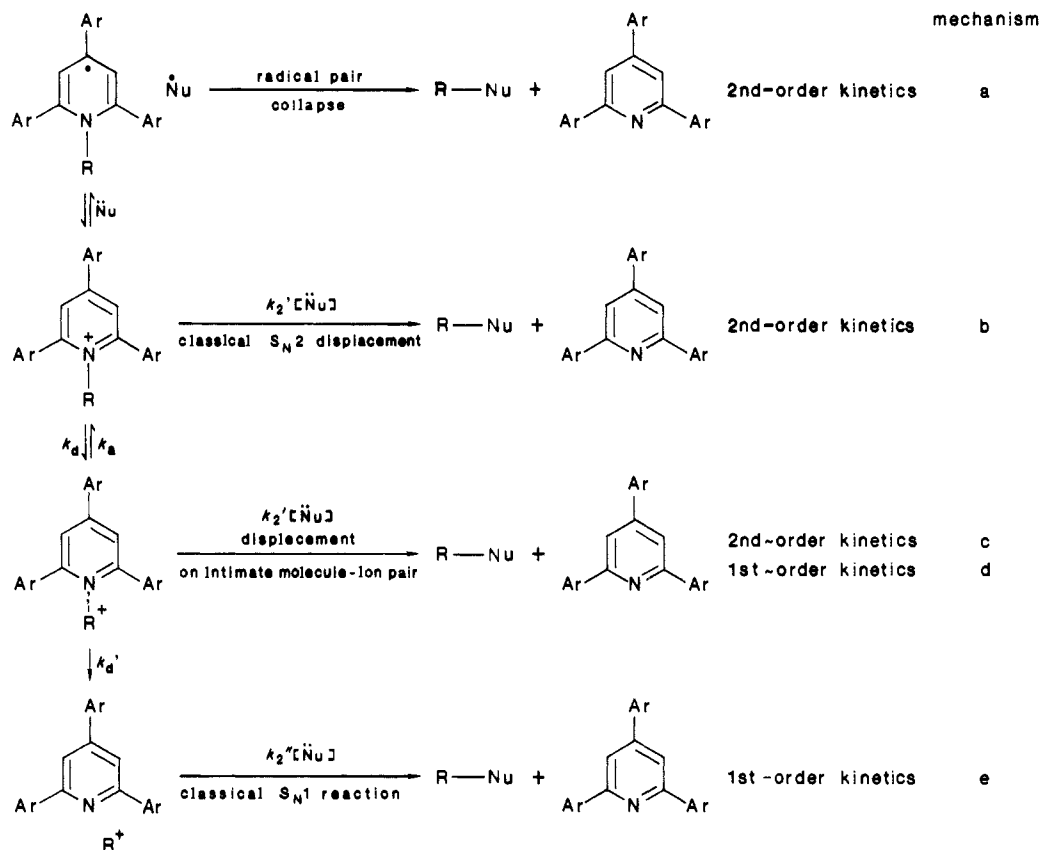


Table II. Solvolysis Rate Constants for 1-(1-Methyl-1-phenylethyl)pyridinium Perchlorate (**3**) in Solvents Other than Water^a

| entry no. | solvent | temp (°C) | $10^5 k_{\text{obsd}}$ (s ⁻¹) | corr coeff | rxn ^b (%) |
|-----------|---|-----------|---|------------|----------------------|
| 1 | methanol ^b | 80.0 | 3.94 ± 0.06 | 0.9998 | 67.4 |
| 2 | ethanol ^b | 78.2 | 3.46 ± 0.08 | 0.9995 | 63.0 |
| 3 | <i>n</i> -butanol ^c | 80.0 | 3.60 ± 0.05 | 0.9996 | 70.8 |
| 4 | <i>n</i> -butanol ^d | 80.0 | 3.60 ± 0.05 | 0.9996 | 70.9 |
| 5 | trifluoroethanol | 78.2 | 9.69 ± 0.11 | 0.9999 | 93.8 |
| 6 | acetic acid | 80.0 | 2.06 ± 0.08 | 0.9965 | 49.9 |
| 7 | trifluoroacetic acid | 80.0 | 1.32 ± 0.05 | 0.9985 | 29.5 |
| 8 | 1,4-dihydroxybutane ^b | 78.2 | 2.07 ± 0.03 | 0.9997 | 66.5 |
| 9 | acetonitrile ^b | 78.2 | 2.61 ± 0.11 | 0.9947 | 54.0 |
| 10 | dioxane ^e | 78.2 | 3.35 ± 0.13 | 0.9988 | 58.1 |
| 11 | 50% trifluoroethanol-water ^f | 78.2 | 5.51 ± 0.24 | 0.9982 | 69.5 |
| 12 | 50% trifluoroethanol-ethanol ^f | 78.2 | 6.22 ± 0.29 | 0.9971 | 73.0 |

^a Concentration of pyridinium 1.2×10^{-4} mol L⁻¹ (except for entry no. 10). ^b Solvent contained triethylamine, 1×10^{-3} mol L⁻¹. ^c Solvent contained triethylamine, 1.44×10^{-4} . ^d Solvent contained triethylamine, 1.8×10^{-3} mol L⁻¹. ^e Kinetic solutions of the pyridinium (1.2×10^{-3} mol L⁻¹) were diluted to UV concentration using a 4% (v/v) solution of triethylamine in ethanol before UV measurement. ^f On a mole-mole basis. ^g Percent to which reaction was followed (λ_{max} 257–260 nm, log ϵ 3.30–3.56).

The data obtained in other solvents (Table II) disclose relatively little influence of the nature of the solvent on the solvolysis rate: this variation is contrasted in Figure 1a with that for the solvolysis (at 25 °C) of the analogous chloride PhCMe₂Cl (Figure 1b). In Figure 1, the solvent polarity parameter of Dimroth, E_T ,¹⁴ is used as a comprehensive measure of the overall solvation ability of the solvent. Correlations of log k_{obsd} vs. Grunwald-Winstein's Y , Smith-Fainberg-Winstein's log k_{ion} or Brownstein's S as measures of solvent ionizing power were similar to that found with E_T . It is noticeable that the solvolysis rates of **3** in the nonprotic solvents

(14) The values of E_T were taken from the following: Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 98. E_T for trifluoroacetic acid was estimated as 60.2 kcal/mol: ref 6b.

Table III. Solvolysis Rate Constants for 1-*tert*-Butylpyridinium Perchlorate (**2**)

| entry no. | solvent | temp (°C) | $10^5 k_{\text{obsd}}$ (s ⁻¹) | corr coeff | rxn ^b (%) |
|-----------|----------------------------------|-----------|---|------------|----------------------|
| 1 | water ^a | 130 | 0.38 ± 0.01 | 0.9989 | 68.3 |
| 2 | water ^a | 140 | 1.39 ± 0.07 | 0.9919 | 72.4 |
| 3 | water ^a | 150 | 3.91 ± 0.13 | 0.9991 | 59.0 |
| 4 | water ^a | 160 | 10.08 ± 0.30 | 0.9993 | 73.1 |
| 5 | water ^a | 170 | 27.89 ± 1.35 | 0.9982 | 75.9 |
| 6 | water ^a | 180 | 68.92 ± 3.00 | 0.9988 | 83.7 |
| 7 | acetic acid | 180 | 75.90 ± 7.9 | 0.9959 | 88.9 |
| 8 | 1,4-dihydroxybutane ^a | 180 | 43.80 ± 2.27 | 0.9987 | 73.0 |
| 9 | trifluoroethanol | 180 | 154.00 ± 21.00 | 0.9949 | 71.2 |

^a Kinetic solutions of the pyridinium (1.2×10^{-3} mol L⁻¹) were diluted to UV concentration (1.2×10^{-4} mol L⁻¹) using 4% (v/v) of triethylamine in ethanol before UV measurement. ^b Percent to which reaction was followed (λ_{max} 258–260 nm, log ϵ 3.51–3.60).

Table IV. Solvolysis Rate Constants for 1-(1-Adamantyl)pyridinium Perchlorate (**1**)

| entry no. | solvent | temp (°C) | $10^5 k_{\text{obsd}}$ | corr coeff | rxn ^b (%) |
|-----------|--------------------|-----------|------------------------|------------|----------------------|
| 1 | water ^a | 190 | 7.67 ± 0.81 | 0.9932 | 86.0 |
| 2 | acetic acid | 190 | 5.43 ± 0.14 | 0.9939 | 45.0 |
| 3 | trifluoroethanol | 190 | 12.04 ± 1.23 | 0.9968 | 68.2 |

^a Kinetic solutions of the pyridinium (1.2×10^{-3} mol L⁻¹) were diluted to UV concentration (1.2×10^{-4} mol L⁻¹) using 4% (v/v) of triethylamine in ethanol before UV measurement. ^b Percent to which reaction was followed (λ_{max} 258–261 nm, log ϵ 3.54–3.58).

MeCN and dioxan are very similar to those found in protic solvents. A factor of <8 is found between the fastest rate (in TFE) and the slowest (in TFA) for **3** (see Table II): the origin of this rather small variation is not understood.

Thus whereas halide solvolysis rates show a large sensitivity to solvent polarity, the pyridinium species show by contrast a small sensitivity. We interpret this to the fact that charge is created in the transition state of the former class of compounds, but not in the latter.

Table V. Solvolysis Rate Constants and Relative Rates for *tert*-Butyl Chloride, Cumyl Chloride, and 1-Adamantyl Chloride at 25 °C

| solvent | <i>t</i> -butyl chloride | cumyl chloride | | 1-adamantyl chloride | |
|-------------|---|---|---|---|---|
| | $k_{\text{obsd}} \text{ (s}^{-1}\text{)}$ | $k_{\text{obsd}} \text{ (s}^{-1}\text{)}$ | $k_{\text{obsd}}/k_{\text{obsd}}(\textit{t}\text{-BuCl)}$ | $k_{\text{obsd}} \text{ (s}^{-1}\text{)}$ | $k_{\text{obsd}}/k_{\text{obsd}}(\textit{t}\text{-BuCl)}$ |
| water | 3.30×10^{-2a} | | | 3.0×10^{-4d} | 9.09×10^{-3} |
| methanol | 8.20×10^{-7a} | 5.11×10^{-3b} | 6.23×10^3 | | |
| ethanol | 9.70×10^{-8a} | 3.94×10^{-4b} | 4.06×10^3 | | |
| 80% ethanol | 9.24×10^{-6a} | | | 7.59×10^{-9c} | 8.21×10^{-4} |
| acetic acid | 2.13×10^{-7e} | | | 2.00×10^{-10d} | 9.39×10^{-4} |
| formic acid | 1.10×10^{-3a} | | | 1.28×10^{-5d} | 1.16×10^{-2} |

^aGrunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846. ^bOkamoto, Y.; Inukai, T.; Brown, H. C. *J. Am. Chem. Soc.* **1958**, *80*, 4972. ^cSchleyer, P. v. R.; Nicholas, R. *J. Am. Chem. Soc.* **1961**, *83*, 2700. ^dSee ref 12. ^eFainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2770.

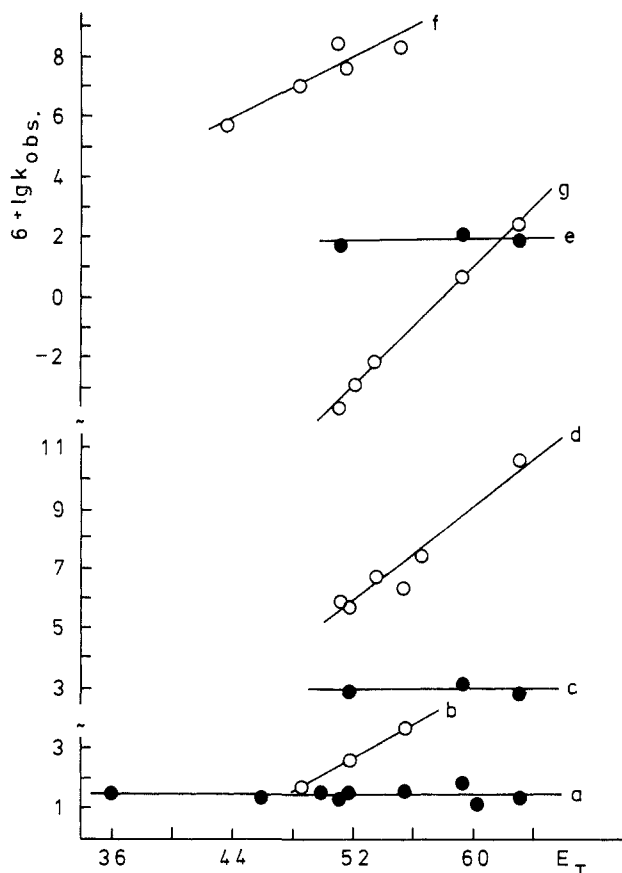


Figure 1. Plots of logarithms of observed rate constants for the solvolysis in various solvents of (a) 1-(1-methyl-1-phenylethyl)pyridinium perchlorate (**3**) at 80 °C, (b) cumyl chloride at 25 °C, (c) 1-*tert*-butylpyridinium perchlorate (**2**) at 180 °C, (d) *tert*-butyl chloride at 180 °C, (e) 1-(1-adamantyl)pyridinium perchlorate (**1**) at 190 °C, (f) 1-adamantyl tosylate at 190 °C, and (g) 1-adamantyl chloride at 50 °C, all plotted against E_T values taken from ref 14.

Solvolytic of 1-*tert*-Butylpyridinium Perchlorate (2**).** Solvolysis occurred at a convenient rate at 180 °C. Observed rates (Table III) again show little effect of solvent character, and once again this is in strong contrast with the variation for *tert*-butyl chloride in a variety of solvents at 180 °C (Figure 1c,d). The study of the temperature variation of the rate in water gave the heat of activation 36.8 ± 1.1 kcal/mol and the entropy of activation $+7.6 \pm 2.5$ cal/(mol-deg).

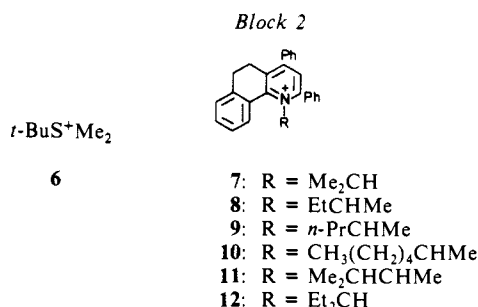
Solvolytic of 1-(1-Adamantyl)pyridinium Perchlorate (1**).** Solvolysis rates for three solvents at 190 °C are given in Table IV: again the small variation is contrasted with that for the corresponding tosylate and chloride (Figure 1e,f,g). With use of the measured heats of activation, rates were calculated for substrates **2** and **3** in water at 190 °C as $18.10 \times 10^{-4} \text{ s}^{-1}$ for 1-*tert*-butylpyridinium and as 1.9 s^{-1} for 1-(1-methyl-1-phenylethyl)pyridinium. This corresponds to a relative rate ratio of 1:23.5:24500 for substrates **1**, **2**, and **3**, respectively. Unfortunately, it is not possible to make direct comparisons with the corresponding chlorides in water. However, cumyl chloride

solvolyzes at ca. 40 000 times the rate of *t*-BuCl in MeOH and at 60 000 times the rate in EtOH (Table V). In water a somewhat smaller ratio would be expected but still significantly greater than the factor of ca. 1000 that we find for the neutral pyridine leaving group.

Rate ratios for solvolysis rates of *t*-BuCl:1-adamantyl chloride vary from 1000 in 80% ethanol–water to 3 in 97% hexafluoroisopropyl alcohol–water, and this has been interpreted by Bentley and Carter^{11b} as evidence for nucleophilic assistance in *tert*-butyl chloride solvolysis. However, our results suggest a different explanation. In the solvolysis of a *tert*-butyl substrate, as the leaving group moves away, angle strain in the developing carbonium center can be relieved much more effectively than in the corresponding case for the solvolysis of a 1-adamantyl substrate. This means that the TS for *tert*-butyl solvolysis would be earlier along the reaction coordinate, and therefore that less charge would develop in the TS for the solvolysis of a neutral *tert*-butyl than a neutral 1-adamantyl substrate.¹⁵ An alternative explanation is that there is steric hindrance to the solvation of the leaving chloride ion in the solvolysis of *tert*-butyl chloride in hexafluoroisopropyl alcohol, which slows the rate. Either of these postulates would explain the greater sensitivity of 1-adamantyl chloride to solvent polarity than that of *tert*-butyl chloride.

Significantly, we now find that neither the corresponding adamantyl- (Figure 1e) nor the *tert*-butyl-pyridinium salt (Figure 1c) is much affected as regards solvolysis rate by the change of solvent polarity;¹⁶ this appears to rule out any difference in solvent participation in the TS for *tert*-butyl and adamantyl. A similar explanation has been given by other authors for analogous effects.¹²

The rate difference between *t*-BuSMe₂⁺ and 1-adamantyl-SMe₂⁺ solvolyses can be estimated as ca. 6 in H₂O at 50 °C (rate for former is $6.09 \times 10^{-6} \text{ s}^{-1}$, rate for the latter at 70 °C is $4.1 \times 10^{-6} \text{ s}^{-1}$).¹⁷ The somewhat smaller difference could indicate that there is less strain relief in the *tert*-butyl TS when the bulky SMe₂ is the leaving group.



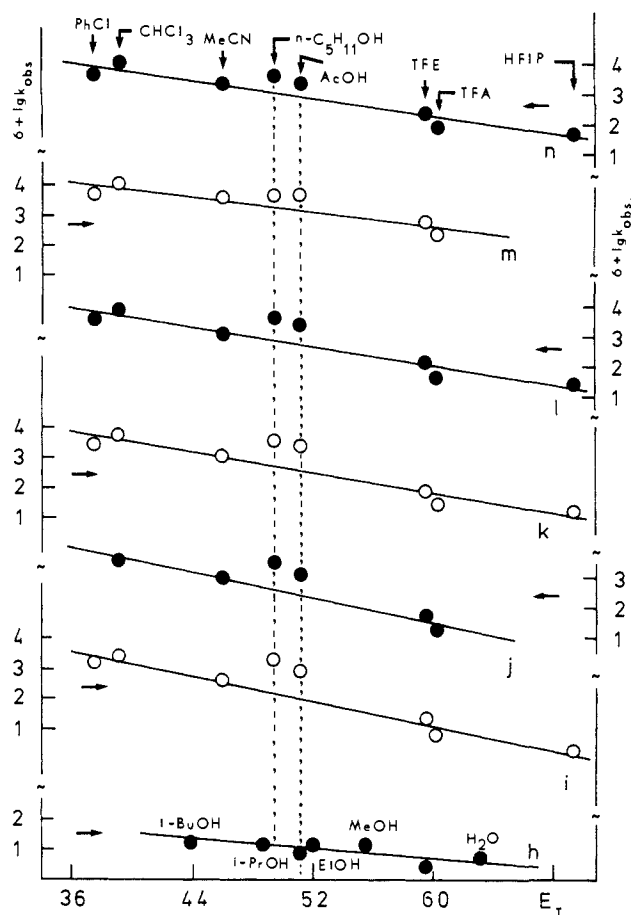
(15) As pointed out by a referee, explanations in terms of early or late TS are fraught with difficulty; reaction energetics are dominated by solvation dynamics into which our insight is primitive (see: Ritchie, C. D. In *Solute-Solvent Interactions*; Coetzee J. F., Ritchie, C. D., Eds.; Marcel Dekker: New York, 1976, Vol. 2, p 265). Detailed studies of the Menschutkin reaction show that energy correlations with TS are simple only for cases which closely fit Hammond's original criteria (Arnett, E. M.; Reich, R. *J. Am. Chem. Soc.* **1980**, *102*, 5892).

(16) The point for 1,4-dihydroxybutane is not included in Figure 1c because no E_T value is available; however, if the E_T for 1,3-dihydroxybutane (52.8¹⁴) is used, the point falls close to the line drawn.

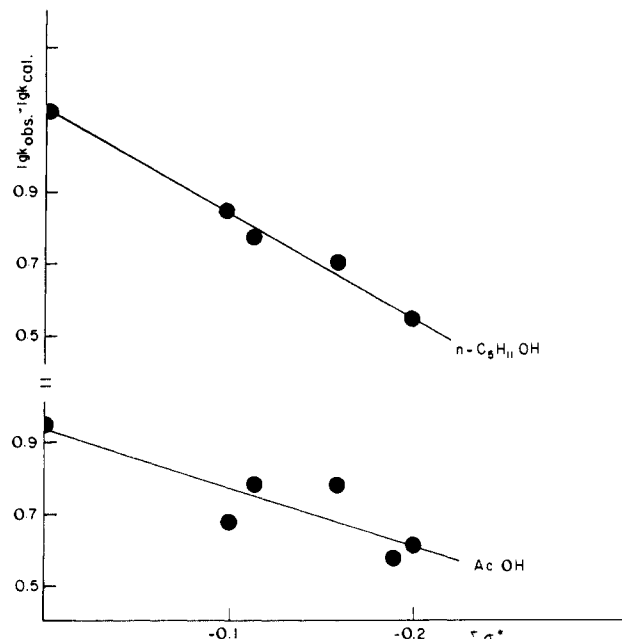
(17) Kevill, D. N.; Kamil, W. A.; Anderson, S. W. *Tetrahedron Lett.* **1982**, 23, 4635.

Table VI. Correlation of Solvolysis Rates ($\log k_1$) for 1-(*sec*-Alkyl)-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium Tetrafluoroborates at 100 °C with E_T

| substituent | slope ^a | error (%) | $6 + \log k_1$ | | | | | |
|-------------------|--------------------|-----------|----------------|------|--------------|---|------|--------------|
| | | | AcOH | | | <i>n</i> -C ₅ H ₁₁ OH | | |
| | | | calcd | obsd | obsd - calcd | calcd | obsd | obsd - calcd |
| isopropyl | -0.097 | 15.6 | 2.00 | 2.95 | 0.95 | 2.22 | 3.35 | 1.13 |
| <i>sec</i> -butyl | -0.102 | 16.2 | 2.45 | 3.11 | 0.66 | 2.67 | 3.50 | 0.83 |
| 2-pentyl | -0.082 | 20.4 | 1.57 | 3.35 | 0.78 | 2.75 | 3.51 | 0.76 |
| 2-heptyl | -0.079 | 20.9 | 2.68 | 3.44 | 0.76 | 2.85 | 3.53 | 0.68 |
| 3-methyl-2-butyl | -0.058 | 51.8 | 3.16 | 3.71 | 0.55 | 3.29 | 3.62 | 0.33 |
| 3-pentyl | -0.076 | 42.3 | 2.90 | 3.49 | 0.59 | 3.07 | 3.58 | 0.51 |

^aSlope calculated by least-squares treatment omitting points for AcOH and *n*-C₅H₁₁OH.**Figure 2.** Plots of logarithms of observed rate constants for the solvolysis in various solvents of (h) *t*-BuS⁺Me₂ (CF₃SO₃⁻ as gegenion in *t*-BuOH, *i*-PrOH, AcOH, TFE, and H₂O at 50.0 °C and Cl⁻ as gegenion in MeOH and EtOH at 50.4 °C) and (i-n) of respectively (i) 1-isopropyl-, (j) 1-*sec*-butyl-, (k) 1-(2-pentyl)-, (l) 1-(2-heptyl)-, (m) 1-(3-methyl-2-butyl)-, (n) 1-(3-pentyl)-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborates (12) at 100 °C, all plotted against E_T values (for reference see Figure 1).

Influence of Solvent on Solvolysis Mechanism of Secondary Substrates. Figure 2 shows plots against E_T of solvolysis rates for the *tert*-butyldimethylsulfonium cation (6, Figure 2h) taken from the work of Kevill¹⁷ and Swain¹⁸ and for our own previously published^{6b} rates of 1-isopropyl- (7, Figure 2i), 1-*sec*-butyl- (8, Figure 2j), 1-(2-pentyl)- (9, Figure 2k), 1-(2-heptyl)- (10, Figure 2l), 1-(3-methyl-2-butyl)- (11, Figure 2m), and 1-(3-pentyl)-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborates (12, Figure 2n). For all the secondary substrates, the points for the solvents other than *n*-pentanol and acetic acid lie on straight lines which possess negative slopes in the range 0.058–0.102 (Table VII): rather large uncertainties in these slopes hinder the eval-

**Figure 3.** Hammett-Taft plot of $\log k(\text{obsd}) - \log k(\text{calcd})$ for solvolysis of 1-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborates in acetic acid and *n*-pentanol at 100 °C, plotted against $\Sigma\sigma^*$.

uation of their variation. As discussed previously,^{6b} we believe that the rates for compounds 7–12 in *n*-pentanol and acetic acid disclose S_N2 components in which nucleophilic assistance by the solvent molecules is increasing the rate, and this interpretation is supported by the positive deviations of these points in plots of 7–11 for these solvents.

The negative slopes found for the secondary substrates 7–12 contrast to the slopes of essentially zero found for compounds 1, 2, and 3 (Figure 1a,c,e). A possible reason is that the TS is earlier for the secondary alkyl substrates, and thus the charge is still spread to a considerable extent over the heterocyclic ring. In the later TS for *tert*-alkyl substrates, the charge is becoming concentrated at the tertiary carbon atom in the TS.

Interestingly, the amount of the nucleophilic solvent assistance provided by *n*-pentanol and by acetic acid to 7–12 varies systematically with the nature of the N substituent. Figure 3 shows a plot against σ^* ¹⁹ of the positive deviations (Table VI) of the rates found in acetic acid and in *n*-pentanol from the lines defined for 7–12 by the other solvents in Figure 2. Figure 3 clearly shows that the amount of solvent assistance decreases as the steric situation becomes more hindered, and for *n*-pentanol a good correlation with σ^* is found.²⁰

No evidence is shown for nucleophilic assistance by the solvent for the *tert*-butyldimethylsulfonium cation 6: when compared with the other plots in Figure 2, plot 2h shows no deviations from the

(19) The reasons for using σ^* are discussed in ref 6a.

(20) Figure 3 excludes the point for 3-methyl-2-butyl where, for reasons explained in detail in ref 6a, a correlation is neither found nor expected.

(18) Swain, C. G.; Kaiser, L. E.; Kneec, T. E. C. *J. Am. Chem. Soc.* **1958**, *80*, 4092.

Table VII. Solvolysis Products

| substrate R of PyR ⁺ | solvent R' of R'OH | GC (°C) | R'OH | | Olefin | |
|------------------------------------|---------------------------------|------------------|------------|-----------|-------------------|-----------|
| | | | mol (%) | RT (s) | mol (%) | RT (s) |
| PhCMe ₂ | H | 100 ^a | 98.3 | 311 | 1.2 | 230 |
| PhCMe ₂ | CH ₃ | 50 ^a | 96.8 | 731 | 3.2 | 601 |
| PhCMe ₂ | CF ₃ CH ₂ | 100 ^a | 25.8 | 304 | 16.9 ^c | 202 |
| PhCMe ₂ | CH ₃ CO | 50 ^a | | | 100 | 604 |
| Me ₃ C | CF ₃ CH ₂ | 30 ^b | 100 | 148 | | |
| Ada | H | 50 ^a | 100 | 964 | | |
| Ada | CH ₃ CO | 100 ^a | 100 | 716 | | |
| Ada | CF ₃ CH ₂ | 100 ^a | 100 | 493 | | |

^a 3% SP 2100 column. ^b 10% Carbowax-20M column. ^c Three further peaks believed to be due to olefin dimers also found: 48.0% (854), 7.3% (901), 2.0% (928 sec).

line for AcOH and *i*-PrOH solvents in contrast to the other substrates.

Identification of Solvolysis Products. Solvolysis products were analysed by GC/MS (Table VII). The adamantyl solvolysis in AcOH, H₂O, and CF₃CO₂H gave cleanly only the corresponding adamantyl acetate, alcohol, and trifluoroacetate, respectively: no olefin was formed, unsurprising in view of the strain that would thereby develop. However, for the 1-*tert*-butylpyridinium solvolysis in CF₃CH₂OH, we also found only the ether which supports our assumption that these solvolyses result in solvent capture of the carbenium ion and not in elimination.

Solvolysis of the 1-methyl-1-phenylethyl compound yields mainly alcohol in water, ether in methanol, mostly olefin in trifluoroethanol, and only olefin in acetic acid. This may be due to decomposition of the acetate on the column, because we showed that PhCMe₂OAc was unstable under the GC conditions.

Conclusions

We believe that the present work again illustrates the advantages of the use of positively charged substrates for the elucidation of nucleophilic substitution mechanisms in that the non-creation of charge in the formation of the transition state from ground state much reduces the influence of solvent polarity on rate. For the tertiary cationic substrates investigated, plots of solvolysis rates vs. E_T show almost zero slopes. The secondary cationic substrates show small negative slopes, with clear positive deviations caused by the incursion of reaction by an alternative S_N2 reaction mode. The tertiary neutral substrates show the expected large positive slopes.

Experimental Section

UV spectra of reactants and products were measured on a Pye Unicam PU 8800 spectrophotometer. ¹H NMR and ¹³C NMR spectra were measured with Varian Model EM 3604 and Joel FX 100 spectrometers, respectively (Me₄Si as an internal standard). IR spectra were recorded with Perkin Elmer Model 283B spectrophotometer. Melting points (mp) were determined with a hot stage microscope.

Gas chromatography/mass spectral analysis utilized an AEI MS-30 mass spectrometer (using a Kratos DS-55 data system) interfaces to a Pye 104 gas chromatograph. The column packings employed were 3%

SP-2100 on 100/120 Supelcoport or 10% Carbowax 20M or 100/120 Supelcoport (5 or 6 ft × 4mm) in glass columns, 30 mL/min of helium as the carrier gas at flow rates and temperatures as specified (Table VI).

Preparation of Compounds. The following were prepared by the literature methods quoted: 1-(1-adamantyl)pyridinium perchlorate (1), mp 254–256 °C [lit.²¹ mp 256–258 °C], 1-*tert*-butylpyridinium perchlorate (2), mp 215–216 °C [lit.²¹ mp 215–217 °C], 1-(triphenylmethyl)pyridinium tetrafluoroborate (5), mp 173–178 °C dec [lit.²² mp 177–186 °C dec]. Samples of 1-(triphenylmethyl)pyridinium tetrafluoroborate used in this work were free from hydrolysis products as shown by the absence of IR absorption at 3460 and 3240 cm⁻¹.

1-(1-Methyl-1-phenylethyl)pyridinium Perchlorate (3). To dry pyridine (0.06 mol) and 1-methyl-1-phenylethyl chloride (0.02 mol) in dry nitromethane (5 mL) was added silver perchlorate (0.02 mol) in dry nitromethane (100 mL) with stirring over 45 min at 0 °C. The mixture was stirred at 0 °C for 1 h. Silver chloride was centrifuged off. The solution was diluted with ether: the crude salt (92%) was recrystallized from ethanol to give the perchlorate (81%), mp 122–124 °C [lit.²¹ mp 124 °C]. At 130–135 °C, the salt undergoes thermolysis to give pyridinium perchlorate (mp 283 °C) by elimination of α -methylstyrene.

1-(1,1-Diphenylethyl)pyridinium tetrafluoroborate (4) was prepared according to above method with silver tetrafluoroborate instead of silver perchlorate: mp 140–141 °C. (Found: C, 64.91; H, 5.50; N, 3.86; C₁₉H₁₈NBF₄ requires C, 65.72; H, 5.23; N, 4.04.) Recrystallization of the crude salt from acetone-ethyl alcohol (10:1) converts this compound to pyridinium tetrafluoroborate (mp 194 °C).

Kinetic Measurements. Reaction vessels (sealed glass tubes of 28 cm × 14 mm diameter) were controlled to ± 1 °C in hot blocks (Statim Model 252). Kinetics were followed by UV spectrophotometry monitoring the decrease or the increase of absorbance of the pyridinium salts at fixed wavelengths using the procedure already described.²³ Except trifluoroacetic acid, acetic acid, and trifluoroethanol, other solvents contained small amounts of triethylamine (1×10^{-3} mol L⁻¹) or the kinetic solutions of the pyridinium compound (1.2×10^{-3} mol L⁻¹) were diluted to UV concentration (1.2×10^{-4} mol L⁻¹) using a 4% (v/v) solution of triethylamine in ethanol before UV measurement (this converted acid-base equilibria into free base) (see footnotes to tables).

Pseudo-first-order rate constants were calculated from the slope of conventional plots of $\ln[(\epsilon_1 - \epsilon_2)/(\epsilon - \epsilon_2)]$ vs. time.²⁴ Such plots were linear to at least 70% completion, and k_{obsd} values were reproducible to ca. 5%.

Solvolysis Procedure for GC/MS Study. The pyridinium salt (1 mg) in 0.5 mL of solvent was heated in a sealed glass tube at 80, 180, or 190 °C for 24 h. The tube was opened immediately before use for the GC/MS study.

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Registry No. 1, 93588-29-5; 2, 93588-25-1; 3, 93588-27-3; 4, 104550-49-4; pyridine, 110-86-1; 1-methyl-1-phenylethyl chloride, 934-53-2; 1,1-diphenylethyl chloride, 947-40-0.

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