J. Am. Chem. Soc. 1984, 106, 1361–1372

Formation and Stability of Ring-Substituted 1-Phenylethyl Carbocations[1]

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Revised Manuscript Received November 3, 1983

Abstract: The solvolysis of 1-phenylethyl derivatives with electron-donating 4-substituents in 50:50 trifluoroethanol:water (v:v) occurs at a rate that is independent of azide concentration but gives yields of the corresponding azide adducts of up to 98% by trapping a carbocation intermediate. Rate constants for reactions of the cations with solvent range from $2 \times 10^3\ \mathrm{s}^{-1}$ (4-$\mathrm{Me_2N}$) to $4 \times 10^9\ \mathrm{s}^{-1}$ (4-Me), assuming a diffusion-controlled rate constant of $5 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ for their reactions with azide and thiol anions. Correlation of the rate constants following the Yukawa–Tsuno treatment gives $\rho^n = 2.5$, $\rho^r = 5.2$, and $r^+ = 2.1$ for the reaction with trifluoroethanol, and $\rho^n = 2.7$, $\rho^r = 4.9$, and $r^+ = 1.8$ for the reaction with water. The reverse reaction, acid-catalyzed cleavage of substituted 1-phenylethyl alcohols to give the corresponding carbocation, follows $\rho^n = -4.9$, $\rho^r = -4.4$, and $r^+ = 0.9$. This gives values of $\rho^n = -7.6$, $\rho^r = -9.3$, and $r^+ = 1.2$ for formation of the cations at equilibrium. There is an imbalance in the development of resonance delocalization, analogous to the "nitroalkane anomaly", that is consistent with a dependence of the fraction of maximal resonance delocalization on the fraction of rehybridization or C–X bond cleavage. Solvent effects on carbocation stability in aqueous–organic mixtures are relatively small. They depend mainly on the nucleophilicity of the solvent components and a specific solvent effect of trifluoroethanol on the reactivity of hydroxylic nucleophiles, including trifluoroethanol itself. The "ionizing power" of the solvent has only a small effect on cation stability, and there is little effect of the concentration or nature of added salts.

In his classic work, Ingold clearly defined a series of reaction mechanisms for nucleophilic substitution at carbon and provided qualitative explanations for why one mechanism is preferred over another.[2] Refinements and extensions of the Ingold nomenclature, to describe the large and complex "borderline" region, include the classification of $\mathrm{S_N1}$ mechanisms according to the type of carbocation intermediate—free carbocations and intimate or solvent separated ion pairs[3]—and proposals that there is nucleophilic assistance to leaving group expulsion in reactions that proceed through an "ion sandwich" intermediate or an "$\mathrm{S_N2}$ intermediate" mechanism.[4]

By comparison, relatively little attention has been directed at the questions of how and why reaction mechanisms change with changing substrate structure and reaction conditions, and what is the relationship of the reaction mechanism to the lifetime of carbocation intermediates. In particular, it is not known if all concerted $\mathrm{S_N2}$ mechanisms are *enforced* because the carbocation does not exist and cannot be an intermediate in the presence of a particular nucleophile, or whether the concerted mechanism can provide an alternative, low-energy reaction path when the intermediate of a stepwise mechanism has a significant lifetime.[5] A number of reactions that involve general acid–base catalysis have been shown to follow mechanisms that are enforced by the lifetimes of intermediate species, but some concerted reactions in this series occur concurrently with stepwise reactions that proceed through an intermediate.[6,7]

A semiquantitative approach to this problem is possible by using diffusion-controlled trapping of carbocations by nucleophiles as a "clock" to estimate their lifetimes. Trapping of oxocarbonium ions with sulfite led to the prediction that the lifetime of the $\mathrm{CH_3OCH_2^+}$ ion in water would be too short to permit its existence as a free intermediate,[8] and several methoxymethyl derivatives were found to undergo second-order displacement reactions with nucleophiles in aqueous solution. In at least some of these reactions the mechanism appears to be a concerted $\mathrm{S_N2}$ substitution that is enforced by the nonexistence of the carbocation in the presence of nucleophilic reagents, although the transition state closely resembles a carbocation.[9,10]

The experiments described in this series of papers were undertaken to examine the relationship between reaction mechanisms and the lifetimes of intermediates formed from 1-phenylethyl derivatives. These compounds represent a classic series of solvolysis substrates that span a range of some 10^{13} in reaction rate,[11,12] which should permit examination of changes in mechanism that are brought about by changes in substrate structure and reaction conditions in a single reaction series. It was predicted and observed that changes in the lifetimes of intermediate 1-phenylethyl carbocations would give rise to a U- or V-shaped reactivity–selectivity profile and the reactions of these compounds with azide ion in 50:50 trifluoroethanol:water were found to proceed through well-defined $\mathrm{S_N1}$ and $\mathrm{S_N2}$ mechanisms with only a narrow borderline region, as has been reported in preliminary communications.[7,13,14]

In this paper we describe the use of azide and thiol anions as diffusion-controlled trapping reagents to estimate the rate constants for the reactions of 1-phenylethyl carbocations with solvent and solvent components as a function of carbocation structure, solvent composition, and salt concentration. The structure–reactivity behavior is described satisfactorily by eq 1, which weighs separately

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[1] Supported by grants from the National Institutes of Health (GM-20888) and National Science Foundation (PCM 77-08369). Dr. Richard was supported by a grant from the National Institutes of Health (AM 07251).

[2] Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, NY, 1969; pp 418–610.

[3] Winstein, S.; Robinson, G. C. *J. Am. Chem. Soc.* **1958**, *80*, 169–181. Harris, J. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 89–173.

[4] Bordwell, F. G.; Wiley, P. F.; Mecca, T. G. *J. Am. Chem. Soc.* **1975**, *97*, 132–136. Bentley, T. W.; Schleyer, P. v. R. *Ibid.* **1976**, *98*, 7658–7666. Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *Ibid.* **1976**, *98*, 7667–7674. Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1–67. Bentley, T. W.; Bowen, C. T. *J. Chem. Soc., Perkin Trans. 2* **1978**, 557–562. Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466–5475.

[5] Jencks, W. P. *Chem. Soc. Rev.* **1981**, *10*, 345–375.

[6] Jencks, W. P. *Acc. Chem. Res.* **1976**, *9*, 425–432. Palmer, J. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6466–6472.

[7] Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161–169.

[8] Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238–8248.

[9] Craze, G.-A.; Kirby, A. J.; Osborne, R. *J. Chem. Soc., Perkin Trans. 2* **1978**, 357–368.

[10] Knier, B. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6789–6798.

[11] Calculated from a two-parameter Yukawa-Tsuno equation using values of −5.0 and 1.15 respectively for ρ and r^+ obtained for the solvolysis of 1-phenylethyl chlorides in 80:20 acetone:water at 45 °C.[12]

[12] Tsuno, Y.; Kusuyama, Y.; Sawada, M.; Fujii, T.; Yukawa, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3337–3346.

[13] Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 4689–4691.

[14] Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 4691–4692.

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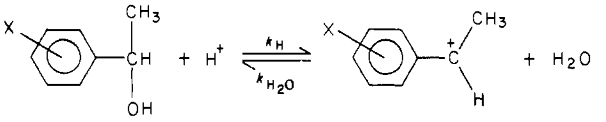
$$\log (k/k_0) = \rho^n\sigma^n + \rho^r\sigma^r \qquad (1)$$

the polar and the large resonance interactions between ring substituents and the 1-carbon atom.[8,12,15] Combination of the rate constants for reaction of the carbocations with water and for acid-catalyzed cleavage of 1-phenylethyl alcohols provides estimates of the equilibrium constants for carbocation formation (eq 2) and a picture of the development and distribution of positive charge as the transition state is approached from both directions.



(2)

Experimental Section

Materials. Reagent grade inorganic salts were used without further purification. Commercially obtained acetophenones were purified by distillation or recrystallization. Trifluoroethanol, Gold Label grade from Aldrich, was used without further purification and water was glass distilled. Unless otherwise stated, commercially available organic chemicals used as reagents for synthesis were reagent grade and were not further purified.

Synthesis. The procedures for the synthesis of substrates used in this and the following three papers are given here. Compounds were synthesized by using standard methods. All compounds showed their predicted NMR spectra and, unless otherwise stated, stable compounds used as substrates for solvolysis were shown by HPLC analysis to be >98% pure. 1-(4-Methylphenyl)ethyl chloride and substituted 1-phenylethyl bromides more unstable than 1-(3-methoxyphenyl)ethyl bromide showed substantial reaction with the methanol:water elution solvent used for HPLC analysis. The purity of these compounds was demonstrated by showing that the solvolysis products for reaction in a number of mixed methanol:water and trifluoroethanol:water solvents were >98% pure.

4-(Methylthio)acetophenone and 4-phenoxyacetophenone were prepared by Friedel–Crafts acetylation of the appropriate substituted benzene[16] and 3-nitro-4-methoxyacetophenone was prepared by nitration of 4-methoxyacetophenone.[17]

4-Methoxyacetophenone (0.17 mol in 1.5 L of 50% methanol in water) was converted to 3-bromo-4-methoxyacetophenone by the addition of 1 equiv of bromine in 0.5 L of methanol followed by heating to 40 °C for 5 h, at which point HPLC analysis showed that ~80% of the starting ketone had reacted. Excess bromine was removed with allyl alcohol, methanol was removed by rotary evaporation, and the product was extracted into diethyl ether[18] and crystallized from ethanol:water. Repeated recrystallizations from petroleum ether gave the ketone in >99% purity.

Substituted 1-phenylethyl alcohols were synthesized by $LiAlH_4$ reduction of the appropriate ketone[19] except for the 4-cyano-, 4-nitro-, 3-nitro-4-methoxy-, and 3-bromo-4-methoxy-substituted 1-phenylethyl alcohols, which were synthesized by $NaBH_4$ reduction of the precursor acetophenone.[20] Most substituted 1-phenylethyl alcohols were purified by vacuum distillation. 1-(3,4-Dimethoxyphenyl)ethyl alcohol was found to be unstable at 3.5 mmHg and 145 °C and was used without further purification. No attempt was made to purify 1-(3-bromo-4-methoxyphenyl)ethyl alcohol by distillation; the final purity of this compound by HPLC was similar to that of the precursor acetophenone, >99%. 1-(4-(Methylthio)phenyl)ethyl alcohol, mp 44–45 °C [lit.[12] 47–48 °C], and 1-(3-nitro-4-methoxyphenyl)ethyl alcohol, mp 50–51 °C, were recrystallized from petroleum ether. 1-(4-(Dimethylamino)phenyl)ethyl alcohol was prepared by reaction of 4-(dimethylamino)benzaldehyde with methyl magnesium bromide[21] and was recrystallized from petroleum ether, mp 56–57 °C [lit.[22] 59–60 °C].

The 4-methyl-, 4-fluoro-, 3-methyl-, and 3-nitro-4-methoxy-substituted 1-phenylethyl chlorides were synthesized by bubbling hydrochloric acid through an ethereal solution of the corresponding 1-phenylethyl alcohol.[12] 1-(3-Bromophenyl)ethyl chloride was synthesized by a similar procedure with $ZnCl_2$ as a catalyst.[19] 1-Phenylethyl chloride and 1-(3-methoxyphenyl)ethyl chloride were prepared from the corresponding alcohols and thionyl chloride.[12] 1-(4-Cyanophenyl)ethyl chloride and 1-(4-nitrophenyl)ethyl chloride were synthesized from the phenylethyl alcohols and PCl_5 in benzene.[23] Purification of all 1-phenylethyl chlorides was by distillation in vacuo, except for the 3-nitro-4-methoxy-substituted compound which was used as an oil without purification. Reaction of the unpurified compound in methanol containing 1 equiv of triethylamine at 50 °C gave 1-(3-nitro-4-methoxyphenyl)ethyl methyl ether in >98% purity. 1-(4-Nitrophenyl)ethyl chloride was collected over a boiling point range of 79–86 °C (0.1 mmHg) [lit.[23] 119–120 °C (1.6 mmHg)]. The product was pure by HPLC and NMR and underwent solvolysis with clean first-order kinetics. HPLC analysis of crude samples of 1-phenylethyl chlorides showed traces of the corresponding styrenes, which were magnified by the UV detection method due to the large extinction coefficients of the substituted styrenes. Since distillation was ineffective at removing styrene, styrene was removed prior to distillation by treatment of an ethereal solution of the 1-phenylethyl chloride with sufficient Br_2 to give an orange color, followed by addition of allyl alcohol to remove excess Br_2. HPLC analysis of products at the λ_{max} of the 1-phenylethyl alcohol gave an apparent purity of >98%, with styrene being the only detectable impurity.

1-Phenylethyl bromides were synthesized by bubbling hydrogen bromide through an ethereal solution of the 1-phenylethyl alcohol.[19] The catalyst $ZnBr_2$ was used for the synthesis of 1-(3-bromophenyl)ethyl bromide. In all cases purification was by distillation after treatment of the product with bromine to remove styrene, as described above.

The 4-nitrobenzoate and 3,5-dinitrobenzoate esters of substituted 1-phenylethyl alcohols were prepared by reaction of the alcohol in pyridine with the acyl chloride at 100 °C.[24] The pentafluorobenzoate esters were prepared similarly at an initial temperature of 0 °C followed by reaction at room temperature for 10–15 min. The esters were purified by recrystallization from ethanol:water. The following melting points were obtained: 1-(4-methylphenyl)ethyl pentafluorobenzoate, 63–64 °C; 1-(3,4-dimethylphenyl)ethyl pentafluorobenzoate, 73–74 °C; 1-(4-phenoxyphenyl)ethyl 3,5-dinitrobenzoate, 82–83 °C; 1-(4-methylthio)-phenyl)ethyl) 3,5-dinitrobenzoate, 129–130 °C; 1-(4-methoxyphenyl)ethyl 4-nitrobenzoate, 63–64 °C (lit.[25] 64–65 °C); 1-(4-methoxyphenyl)ethyl 3,5-dinitrobenzoate, 66–68 °C; 1-(3,4-dimethoxyphenyl)ethyl 3,5-dinitrobenzoate, 107–108 °C; 1-(3-bromo-4-methoxyphenyl)ethyl pentafluorobenzoate, 99–100 °C.

The chloroacetate ester of 1-(4-methoxyphenyl)ethyl alcohol was synthesized by adding a 10% molar excess of chloroacetic anhydride to a solution of the 1-phenylethyl alcohol in pyridine at 0 to −10 °C. After 15 min the reaction was quenched with 10% aqueous $NaHCO_3$ and the product was extracted into ether. The ethereal solution was washed with 10% $NaHCO_3$, 1.0 M HCl, water, and finally saturated $NaHCO_3$. The ether was evaporated and the chloroacetate ester was used without further purification (>99% pure by HPLC); vacuum distillation gave substantial amounts of an impurity, probably 4-methoxystyrene.

1-(4-Methoxyphenyl)ethyl phenyl ether was synthesized by reacting 1-(4-methoxyphenyl)ethyl 4-nitrobenzoate (4.6 g) with sodium phenoxide (1.8 g) in 100 mL of 50:50 phenol:benzene (v:v) at room temperature for 16 h.[26] The reaction mixture was extracted with copious amounts of 2 M NaOH to remove phenol and the product was distilled in vacuo by using a short-path distillation apparatus, bp 126 °C (0.5 mmHg) [lit.[26] 150–160 °C (3 mmHg)]. Analysis of this material by HPLC showed a contaminant, corresponding to ~3% of the total absorbance at 278 nm, that was stable under solvolysis conditions and did not interfere with product analysis.

1-(4-(Dimethylamino)phenyl)ethyl 3,4-dichlorophenyl thioether was synthesized by reacting 1-(4-(dimethylamino)phenyl)ethyl alcohol (250 mg) with 3,4-dichlorothiophenol (1.0 mL) in 250 mL of 50% acetonitrile in water containing a final concentration of 50 mM acetate buffer ($[HA]/[A^-] = 9$). The reaction was monitored by HPLC and after 3 h, when all of the 1-phenylethyl alcohol had reacted, the reaction mixture

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(15) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 3288–3294.

(16) Frank, R. L.; Adams, C. E.; Allen, R. E.; Gander, R.; Smith, P. V. *J. Am. Chem. Soc.* **1946**, *68*, 1365–1369.

(17) Oelschlagar, H. *Arch. Pharm.* (*Weinheim, Ger.*) **1957**, *290*, 587–596; *Chem. Abstr.* **1958**, *52*, 8989.

(18) Synthesis of this compound in acetone and water was previously reported. Aaron, J.-J.; Dubois, J.-E.; Krausz, F.; Martin, R. *J. Org. Chem.* **1973**, *38*, 300–304.

(19) Shiner, V. J., Jr.; Buddenbaum, W. E.; Murr, B. L.; Lamaty, G. *J. Am. Chem. Soc.* **1968**, *90*, 418–426.

(20) Keeffe, J., Ph.D. Thesis, University of Washington, 1964.

(21) "Organic Syntheses"; Horning, E. L., Ed.; Wiley: New York, 1955; Collect. Vol. 3, p 696.

(22) Alexander, E. R.; Wildman, R. B. *J. Am. Chem. Soc.* **1948**, *70*, 1187–1189.

(23) Kochergin, P. M.; Blinova, L. S.; Titkova, R. M.; Karpov, G. A. *J. Org. Chem. USSR* **1971**, *7*, 2238–2242.

(24) McElvain, S. M. "The Characterization of Organic Compounds"; MacMillan: New York, 1953; p 198.

(25) Goering, H. L.; Briody, R. G.; Sandrock, G. *J. Am. Chem. Soc.* **1970**, *92*, 7401–7407.

(26) Based on solvolysis reaction conditions given in Okamoto, K.; Kinoshita, T.; Takemura, Y.; Yoneda, H. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1426–1433.

was extracted with 200 mL of petroleum ether. The organic layer was washed with 1.0 M NaOH and dried over $MgSO_4$. After removal of solvent by rotary evaporation, the residue was stored in 20 mL of acetonitrile at -15 °C. This material contained a contaminant, corresponding to ~5% of the absorbance at 260 nm, that was stable under solvolysis reaction conditions and did not interfere with product analysis.

[1-(4-Methylphenyl)ethyl]dimethylsulfonium bromide was synthesized from dimethyl sulfide and 1-(4-methylphenyl)ethyl bromide.[27]

1-(4-Methoxyphenyl)ethyl trifluoroethyl ether was synthesized by trifluoroethanolysis of 1-(4-methoxyphenyl)ethyl alcohol (2 mL) in 100 g of trifluoroethanol containing 15 μL of 2.0 M $HClO_4$. The reaction was shown by HPLC to be complete after 40 min at room temperature. The acid was then neutralized with triethylamine and trifluoroethanol was removed by rotary evaporation. 1-(4-(Dimethylamino)phenyl)ethyl methyl ether was synthesized by methanolysis of 100 mg of 1-(4-(dimethylamino)phenyl)ethyl alcohol in 500 mL of methanol containing 5 μL of 2 M $HClO_4$. The reaction was followed by HPLC and was complete after ~2 h at 50 °C. The acid was then neutralized with 10 μL of 1.0 M Na_2CO_3 and most of the methanol was removed by rotary evaporation. The resulting product was stored in ~2 mL of methanol.

1-(4-Nitrophenyl)ethyl tosylate was prepared by a published procedure.[28]

Solvolysis Reaction Procedures. Solvolysis reaction solutions were prepared to constant ionic strength by mixing measured volumes of water (at constant ionic strength of 1.0 maintained with $NaClO_4$) and organic solvent. Reaction mixtures were incubated at room temperature (22 ± 2 °C) when only the product composition was to be examined; product ratios were found to be constant over this small temperature range. Reactions were initiated by adding substrate in acetonitrile to give a usual final concentration of 0.5–2.0 mM. Lower concentrations of 1-(4-methoxyphenyl)ethyl derivatives were used for reactions in solvents of high trifluoroethanol content in order to maintain a >10-fold excess of azide over substrate. Lower concentrations of 1-(4-(dimethylamino)phenyl)ethyl 3,4-dichlorophenyl thioether (~0.1 mM) were used because of the large extinction coefficients for 1-(4-(dimethylamino)phenyl)ethyl derivatives.

The uncatalyzed reactions of substituted 1-phenylethyl benzoate esters and the acid-catalyzed reaction of 1-(4-methoxyphenyl)ethyl phenyl ether were monitored by HPLC for substrate disappearance as a function of time in order to determine the kinetic order of the reaction with respect to azide concentration. For reactions in which trapping by azide was efficient (>80% at 0.5 M azide) rates were measured for reaction at room temperature (22 ± 2 °C). A lower yield of azide adduct (~40% at 0.5 M azide) was obtained for the reaction of 1-(4-methylphenyl)ethyl pentafluorobenzoate and the reaction of this compound was followed at 25 ± 0.2 °C.

Product Analysis by Liquid Chromatography. Aliquots from the reaction mixtures (50–200 μL) were injected directly onto a Waters Associates reverse-phase 10-μm octadecylsilane chromatography column, which was pressurized inside a Waters Radial Compression Module. Separation of the components of the reaction mixture was accomplished by either isocratic or gradient elution with mixtures of $MeOH:H_2O$. 1-(4-(Dimethylamino)phenyl)ethyl derivatives were separated as the free base by elution with buffered $MeOH/H_2O$ solutions prepared by mixing MeOH with 20 mM Tris acetate in water, pH = 7.5. All compounds were observed to elute between 40:60 and 90:10 $MeOH:H_2O$. For a constant ring substituent the following order of elution was observed for the reaction components: phenol, 1-phenylethyl alcohol, 1-phenylethyl methyl ether, styrene ~ 1-phenylethyl azide adduct ~ 1-phenylethyl chloride, 1-phenylethyl trifluoroethyl ether, 1-phenylethyl phenyl ether ~ 1-phenylethyl benzoate ester. Unless otherwise stated, the products were cleanly separated. The charged compound, [1-(4-methylphenyl)ethyl]dimethylsulfonium bromide did not bind to the HPLC column at 50:50 $MeOH:H_2O$.

After separation by HPLC, products were detected by the UV absorbance at the following wavelengths (nm) for the different ring-substituted 1-phenylethyl derivatives: 4-$N(CH_3)_2$, 260; 4-OCH_3, 278; 3,4-di-OCH_3, 278; 3-Br, 4-OCH_3, 278; 3-NO_2, 4-OCH_3, 269; 4-SCH_3, 254; 4-OPh, 271; 4-CH_3, 263; 4-F, 263; 3-CH_3, 264; 3-OCH_3, 271; 3-Br, 267; 4-CN, 271; 4-NO_2, 277. Peak areas were obtained by electronic integration with a Waters Associates Model 730 Data Module.

In most cases solvolysis of 1-phenylethyl derivatives in 50:50 $TFE:H_2O$ gave only the two products corresponding to solvent addition. The 1-phenylethyl alcohol was identified as the earlier eluting peak by comparison with synthetic material. Product assignments for the 4-methoxy-, 4-methyl-, 4-fluoro-, and 3-methoxy-substituted compounds were confirmed by observing the change in peak ratios with changing trifluoroethanol composition of the solvent. In all cases the 1-phenylethyl alcohol eluted well before the trifluoroethyl ether.

Equimolar amounts of standard solutions of 1-(4-methoxyphenyl)ethyl alcohol and trifluoroethyl ether gave equal peak areas, within an experimental error of ±5%. In addition it was found that the total peak area of solvent adducts, at a constant substrate concentration, was independent of the solvent composition for the reactions of 1-(4-methylphenyl)ethyl chloride and 1-(4-fluorophenyl)ethyl chloride in mixed trifluoroethanol:water solvents, showing that the extinction coefficients of the water and trifluoroethanol adducts are identical. These compounds were examined because of the relatively small extinction coefficients and sharp UV maxima for the corresponding alcohols. Product concentration ratios for the solvent adducts were obtained directly from the ratios of the peak areas.

The product ratios were shown to be constant over several half-times during the solvolysis of 1-phenylethyl benzoate esters. The products are stable in solutions containing azide anion, but small changes in peak ratios were observed after longer times in unbuffered solutions, from acid-catalyzed equilibration of the solvent adducts. No change in the product ratios was observed for several hours after the reaction of 1-(4-methylphenyl)ethyl chloride. Product ratios were found to be constant for the first 10–20% of the reaction during the acid-catalyzed solvolysis of 1-(4-methoxyphenyl)ethyl phenyl ether.

HPLC analysis of the products of reaction of 1-phenylethyl derivatives in the presence of azide showed an additional peak which usually eluted just before the trifluoroethyl ether. This product was identified as the azide adduct because the observed peak areas showed the expected dependence on azide concentration (eq 3), when calculated as a fraction

$$\frac{[RN_3]}{[P_t]} = \frac{k_{az}[N_3^-]}{k_s + k_{az}[N_3^-]} \tag{3}$$

of the total reaction product, P_t. In all cases in which the azide adduct was free of substantial amounts of styrene (i.e., all except the reactions of 1-(4-methylphenyl)ethyl chloride and 1-(3-bromophenyl)ethyl chloride) the sum of the product peak areas was found to be independent of the azide concentration through azide concentrations which give at least 45% yield of azide adduct. This shows that the extinction coefficients of the azide and solvent adducts are the same, within experimental error.

The azide adduct formed from 1-(4-(dimethylamino)phenyl)ethyl alcohol was found to be too unstable to permit analysis by HPLC. Cleavage of the alcohol in the presence of azide followed by chromatography in the presence of methanol gave a new peak that was identified as the methyl ether; this peak was not observed if the reaction mixture was diluted into 1.0 M aqueous sodium carbonate prior to chromatography. The 1-(4-methoxyphenyl)ethyl azide adduct was prepared by reaction of the parent nitrobenzoate ester in 95% trifluoroethanol in water containing 0.05 M azide at 60 °C. After removal of trifluoroethanol by rotary evaporation the product was extracted into ether. Evaporation of the ether gave the azide adduct as an oil which was shown to be stable in 50:50 (v:v) trifluoroethanol:water for 5 h; it reacts very slowly at 60 °C.

Analysis by HPLC gave a clean separation of the azide adduct from other products in most reactions. However, the 1-(4-phenoxyphenyl)ethyl azide adduct coeluted with the trifluoroethyl ether. For reactions in azide solutions the contribution of the trifluoroethyl ether to the observed area of the azide adduct peak was estimated from the area of the 1-(4-phenoxyphenyl)ethyl alcohol peak and a value of 6 for the ratio of the water and trifluoroethanol adducts observed at zero azide concentration. It was shown for other substrates that the ratio of peak areas for the water and trifluoroethanol adducts is independent of the azide concentration.

Solvolysis of 1-(4-methylphenyl)ethyl derivatives and 1-(3-bromophenyl)ethyl derivatives gave styrene elimination products that coelute with the azide adduct.[29] The contribution of 4-methylstyrene to the observed area of the peak for the 1-(4-methylphenyl)ethyl azide adduct was estimated from the observed area of the peak and the fraction of styrene formation obtained for reaction in the absence of azide, with the assumption that styrene constituted a constant fraction of the total solvolysis products. Values for the peak area due to the azide adduct obtained by this method agreed with estimates based on the decrease in the areas of the solvent adduct peaks and with the value obtained after removal of 4-methylstyrene by treatment of 200 μL of the reaction mixture with 15 μL of mercaptoethanol for 2 h. This procedure was shown to remove 4-methylstyrene quantitatively from reaction mixtures that contained no azide. The size of the correction for 4-methylstyrene depended on the substrate leaving group and the solvent composition. For

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(27) Roe, F. L., Jr.; Saunders, W. H., Jr. *Tetrahedron* **1977**, *33*, 1581–1585.

(28) Phillips, J. *J. Chem. Soc.* **1923**, 44.

(29) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.*, following paper in this issue.

the reaction of 1-(4-methylphenyl)ethyl pentafluorobenzoate in 50:50 (v:v) trifluoroethanol:water, 4-methylstyrene constituted ~13% of the total observed absorbance at 263 nm and 50% of the observed azide adduct peak at 0.10 M azide or 20% at 0.50 M azide. For the reaction of 1-(4-methylphenyl)ethyl chloride in 50:50 (v:v) trifluoroethanol:water, 4-methylstyrene constituted only 2–3% of the total absorbance at 263 nm, so that at azide concentrations of ≥0.20 M, 4-methylstyrene constituted less than 10% of the observed azide adduct peak. The amount of 4-methylstyrene formed in the reaction of 1-(4-methylphenyl)ethyl chloride increased to ~10% of the total absorbance at 263 nm for reaction in 90:10 methanol:water and constituted between 60% of the area of the observed azide adduct peak at 0.04 M azide and 25% at 0.16 M azide.

The reaction of 1-(4-(dimethylamino)phenyl)ethyl 3,4-dichlorophenyl thioether in unbuffered trifluoroethanol:water solutions was slow due to a strong common ion effect of 3,4-dichlorobenzenethiolate anion. In the presence of an excess of added nucleophile the half-time of the reaction was ~10 min. The relationship between the observed peak ratios for the water and trifluoroethanol adducts at increasing total lyoxide concentration is given by eq 4. The observed ratio of trifluoroethyl ether to

$$\frac{[\mathrm{ROTFE}]}{[\mathrm{ROH}]} = \frac{k_{\mathrm{TFE}}[\mathrm{CF_3CH_2OH}] + k_{\mathrm{CF_3CH_2O^-}}[\mathrm{CF_3CH_2O^-}]}{k_{\mathrm{H_2O}}[\mathrm{H_2O}] + k_{\mathrm{OH^-}}[\mathrm{OH^-}]} \tag{4}$$

alcohol, [ROTFE]/[ROH], was directly proportional to the total concentration of base in the range 0.33–3.3 mM. This shows that at these concentrations of base the $k_{\mathrm{OH^-}}[\mathrm{OH^-}]$ term in eq 4 is negligible. The rate constant ratio $k_{\mathrm{CF_3CH_2O^-}}/k_{\mathrm{H_2O}}$ is essentially equal to $[\mathrm{ROTFE}][\mathrm{H_2O}]/[\mathrm{ROH}][\mathrm{CF_3CH_2O^-}]$, because the contribution of the k_{TFE} term to ROTFE formation is negligible at these base concentrations. The relative reactivities of trifluoroethoxide and methyl thioglycollate anions were obtained from product ratios determined in the presence of a 10- to 100-fold excess of trifluoroethoxide ion, which insured complete ionization of the thiol. Product ratios were constant with time, showing that the thiol adduct was stable.

The rate constants for the acid-catalyzed cleavage of substituted 1-phenylethyl alcohols were determined by measuring the initial rates of formation of the trifluoroethyl ether upon reaction in 50:50 trifluoroethanol:water (v:v) at 25 °C. The reactions were quenched by adding aliquots of the reaction mixture to equal or larger volumes containing ≥4-fold molar excess of sodium bicarbonate while mixing rapidly. The reactions were monitored by HPLC for the first 0.5–5% of the reaction. To correct for small differences in the sample injection volumes, the area of the trifluoroethyl ether peak was normalized by using the substrate as an internal standard. First-order rate constants were determined from plots of the normalized peak areas, A, against time according to $k = (\mathrm{d}A/\mathrm{d}t)/A_0$, in which A_0 is the area of the substrate peak. Apparent second-order rate constants, k_{h}, were obtained from plots of k against acid concentration. Rate constants for acid-catalyzed C–O cleavage, k_{H}, were obtained by correcting for regeneration of alcohol from reaction of the carbocation with water according to eq 5, in which the partitioning

$$k_{\mathrm{H}} = k_{\mathrm{h}}\left(1 + \frac{k_{\mathrm{H_2O}}[\mathrm{H_2O}]}{k_{\mathrm{TFE}}[\mathrm{TFE}]}\right) \tag{5}$$

ratio $k_{\mathrm{H_2O}}/k_{\mathrm{TFE}}$ was measured by generation of the carbocation from other 1-phenylethyl derivatives as described in the text. The peak areas for the trifluoroethyl ether formed from 1-(4-phenoxyphenyl)ethyl alcohol were corrected for a trace impurity present in the alcohol which coeluted with the ether and was shown to be stable to acid.

The pK_a of N-protonated 1-(4-(dimethylamino)phenyl)ethyl alcohol in 50:50 TFE:H$_2$O at ionic strength 0.5 (NaNO$_3$) was determined spectrophotometrically at 248 nm in buffers of 4-morpholinoethanesulfonic acid. After standardization of the pH meter with water, solutions of 0.001–0.05 M hydrochloric acid in this solvent were found to follow the relationship $-\log [\mathrm{H^+}] = (0.98 \pm 0.02)\ \mathrm{pH\ (obsd)} + 0.44$.

Results

Figure 1 shows that the rate of the disappearance of 1-(4-methoxyphenyl)ethyl 4-nitrobenzoate in 50:50 (v:v) trifluoroethanol:water is independent of the concentration of azide ion in the range 0–0.5 M. The time course for reaction of all six mixtures is fitted by a single first-order rate constant; i.e., the reaction is zero order with respect to azide. At the highest azide concentration 98% of the product was the azide adduct. Similarly, the observed rate constant for the acid-catalyzed cleavage of 1-(4-methoxyphenyl)ethyl phenyl ether was found to increase less than 20% as the concentration of azide buffer ($[\mathrm{HN_3}]/[\mathrm{N_3^-}] = 11.2$) was increased from 0.05 to 0.50 M. This is much less than the increase of >3-fold that would be required if the reaction were first order in azide, based on the observed increase in the yield of the azide adduct from 32% to 82% of the total reaction products.

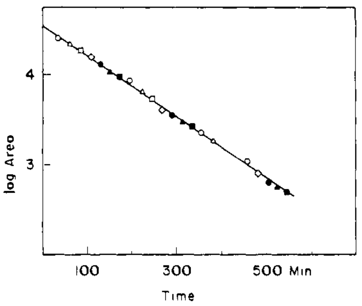

Figure 1. Dependence on azide concentration of the rate of solvolysis of 1-(4-methoxyphenyl)ethyl 4-nitrobenzoate in 50:50 TFE:H$_2$O (v:v) at 22 ± 2 °C and $\mu = 0.50$ maintained with NaClO$_4$. The reaction mixtures contained equal substrate concentrations and the following azide concentrations: ○, 0.50 M; △, 0.25 M; □, 0.050 M; ●, 0.025 M; ▲, 0.0125 M; ■, 0 M. The y axis shows the integrated area of the substrate peak observed after separation of reaction components by HPLC.

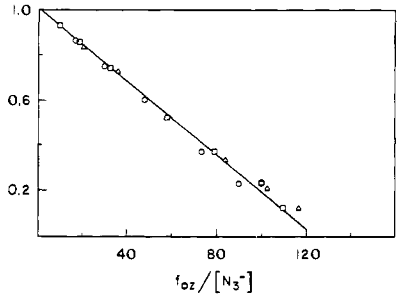

Figure 2. Linearized plot[30] of the dependence upon azide concentration of the fraction of product as the azide adduct, f_{az}, for the solvolysis of 1-(4-methoxyphenyl)ethyl derivatives under the conditions described for Figure 1. Key: ○, 1-(4-methoxyphenyl)ethyl 4-nitrobenzoate; △, 1-(4-methoxyphenyl)ethyl phenyl ether, $[\mathrm{HN_3}]/[\mathrm{N_3^-}] = 11.2$; □, same, $[\mathrm{HN_3}]/[\mathrm{N_3^-}] = 4.4$.

Figure 2 shows that the dependence of the yield of azide adduct, f_{az}, on the concentration of azide anion is the same for 1-(4-methoxyphenyl)ethyl derivatives with different leaving groups. The data for the 4-nitrobenzoate ester are shown by circles, and the data for the acid-catalyzed reaction of the phenyl ether are shown by triangles and squares at two different buffer ratios. The linear plot is based on a rearranged form of eq 3.[30] These results show that the ratio of the rate constants for reaction with solvent and with azide is independent of the concentration of azide ion.

Experiments similar to that shown in Figure 1 demonstrated a zero-order dependence of the rate on azide concentration for the reactions of 1-(4-(methylthio)phenyl)ethyl 3,5-dinitrobenzoate, 1-(3-bromo-4-methoxyphenyl)ethyl pentafluorobenzoate, and 1-(4-methylphenyl)ethyl pentafluorobenzoate; a 10% decrease in the rate constant for the last compound was observed with an increase in the concentration of azide anion from 0 to 0.5 M.[31]

Zero-order kinetics with respect to the concentration of azide ion was also observed for the reactions of 1-(4-methylphenyl)ethyl chloride in mixed methanol:water and acetonitrile:water solvents.[31] The reaction of this compound in 50:50 (v:v) trifluoroethanol:water is also expected to be zero-order in azide, since the second-order reaction with azide of 1-(4-fluorophenyl)ethyl and 1-(3-methoxyphenyl)ethyl chlorides is not faster relative to solvolysis in 50:50 (v:v) trifluoroethanol:water than in the above solvents.[31] The values of k_{obsd} for the reaction of 1-(3-nitro-4-methoxyphenyl)ethyl chloride in 20% acetonitrile in water (v/v) increase 20% as the azide anion concentration is increased from 0 to 0.48 M.[31] This small increase in rate accounts for only 30% of the observed formation of azide adduct. A decrease in the yields of both azide

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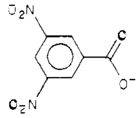
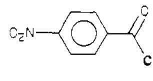
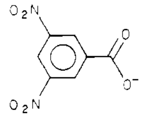
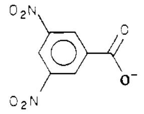
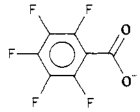
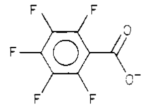
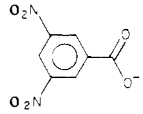
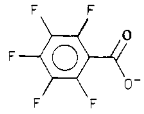
[30] Plowman, K. M. "Enzyme Kinetics"; McGraw Hill: New York, 1972; p 19.

[31] Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.*, third of four papers in this issue.

Table I. Partitioning Rate Constant Ratios for the Reactions of Azide Ion and Solvent with 1-(4-Substituted-phenyl)ethyl Derivatives and 1-(3-Substituted-4-methoxyphenyl)ethyl Derivatives in 50:50 TFE:H_2O (v:v)[a]

ring substituent	leaving group Y	k_{az}/k_{TFE}	k_{az}/k_{H_2O}	k_{az}/k_s, M^{-1} [b]
4-OCH_3	PhOH[c]	6850	3600	115
4-OCH_3		6200	3300	105
4-OCH_3	 [d]	6200	3300	105
4-SCH_3	 [d]	6100	3600	113
4-OPh	 [d]	770	520	16
3,4-di-CH_3	 [d]	48	41	1.3
4-CH_3	 [d]	38	42	1.1
4-CH_3	Cl^- [d]	52	40	1.2
3-OCH_3, 4-OCH_3	 [d]	6800	4200	130
3-Br, 4-OCH_3	 [d]	710	385	12.1
3-NO_2, 4-OCH_3	Cl^- [d]	150	60	1.9

[a] At 22 ± 2 °C with $\mu = 0.50$ maintained with $NaClO_4$. [b] Calculated treating k_s as a first-order rate constant. [c] For $[HN_3]/[N_3^-] = 11.2$ and 4.4. Average of values obtained for 5 concentrations of azide buffer (0.025–0.5 M) at each buffer ratio. [d] Average of values obtained for at least 5 different azide concentrations.

and solvolysis products in the presence of mercaptoethanol, a trapping reagent, provides evidence that azide adduct is formed from the 1-(3-nitro-4-methoxyphenyl)ethyl carbocation.[31]

Azide selectivities with respect to water, trifluoroethanol, and solvent for the trapping of substituted 1-phenylethyl carbocations are tabulated in Table I. The selectivities for azide, water, and trifluoroethanol are dimensionless on the basis of molar concentrations and the second-order rate constants k_{az}, k_{H_2O}, and k_{TFE}, respectively, whereas those for solvent are M^{-1} on the basis of pseudo-first-order rate constants for reaction with solvent, k_s.

It was not possible to obtain azide selectivity values directly for the 1-(4-(dimethylamino)phenyl)ethyl carbocation because of decomposition of the azide adduct on the chromatography column. The reactivity of thiolate anions toward carbocations is similar to that of azide[32] and the $k_{CH_3OCOCH_2S^-}/k_s$ value reported in Table II provides an estimate for the azide selectivity toward the 1-(4-(dimethylamino)phenyl)ethyl carbocation. The thiolate selectivities were obtained from experimentally determined values for $k_{RS^-}/k_{CF_3CH_2O^-}$, $k_{CF_3CH_2O^-}/k_{H_2O}$, and k_{H_2O}/k_{TFE}. The procedure for obtaining the first two values is described in the Experimental Section, while the method used to obtain k_{H_2O}/k_{TFE} is described in the following paper.[29]

Table II. Nucleophilic Selectivities for Reactions of the 1-(4-(Dimethylamino)phenyl)ethyl Carbocation in 50:50 TFE:H_2O (v:v)[a]

$k_{CF_3CH_2O^-}/k_{H_2O}$ [b]	2.2×10^5
$k_{CH_3OCOCH_2S^-}/k_{CF_3CH_2O^-}$ [c]	350
k_{H_2O}/k_{TFE} [d]	3
$k_{CH_3OCOCH_2S^-}/k_{TFE}$ [e]	2.3×10^8 [f]
$k_{CH_3OCOCH_2S^-}/k_s$ [g]	$2.5 \times 10^6\ M^{-1}$ [f]

[a] At 22 ± 2 °C, and $\mu = 0.50$ maintained with $NaClO_4$. Rate constant ratios are calculated from the ratios of product and reactant concentrations. [b] For the uncatalyzed reaction of 1-(4-(dimethylamino)phenyl)ethyl 3,4-dichlorophenyl thioether. Average values at 4 trifluoroethanol concentrations from 3×10^{-4} M to 3×10^{-3} M. [c] Average of values at $[RS^-] = 4.0 \times 10^{-4}$ M and 4 trifluoroethoxide concentrations from 1.3×10^{-2} M to 1.3×10^{-1} M. [d] For the acid-catalyzed reaction of 1-(4-(dimethylamino)phenyl)ethyl methyl ether. [e] Obtained by combining the above values. [f] Estimated error ±20%. [g] Calculated by using a pseudo-first-order rate constant (k_S, s^{-1}) for the solvent reaction.

Specific salt effects on the partitioning of the 1-(4-methoxyphenyl)ethyl carbocation between azide and solvent in 50:50 (v:v) trifluoroethanol:water and 100% water are shown in Table III. The effect of changing solvent composition on the partitioning of the 1-(4-methoxyphenyl)ethyl carbocation in a series of 50:50 (v:v) aqueous:organic solvents is shown in Table IV.

The effects of changing methanol:water (v:v) and trifluoroethanol:water solvent composition on the partitioning of the 1-(4-methoxyphenyl)ethyl and the 1-(4-methylphenyl)ethyl carbocations between azide and solvent are shown in Table V. The latter cation was generated by solvolysis of 1-(4-methylphenyl)ethyl chloride. The 1-(4-methoxyphenyl)ethyl carbocation was generated by solvolysis of the chloroacetate derivative in solvents containing >60% water and from 4-nitrobenzoate or 3,5-dinitrobenzoate esters in solvents of ≤60% water. Identical azide selectivities were obtained for reactions of the chloroacetate and the 3,5-dinitrobenzoate esters in 30:70 methanol:water and for reactions of the 4-nitrobenzoate and the 3,5-dinitrobenzoate esters in a number of methanol:water and trifluoroethanol:water mixtures.

The solvolysis of 1-(4-methoxyphenyl)ethyl 3,5-dinitrobenzoate ester in solvents of high methanol composition that contained azide gave small amounts of attack at the ester carbonyl group. This was indicated by the detection of methyl 3,5-dinitrobenzoate upon product analysis by HPLC and by a decrease in the apparent k_{MeOH}/k_{H_2O} values from 6 to 4 for reaction in 80:20 (v:v) methanol:water as the concentration of sodium azide was increased from 0 to 0.04 M, showing that 4% of the total product (or 33% of the 1-(4-methoxyphenyl)ethyl alcohol) formed in the presence of azide in this solvent is derived from base-catalyzed hydrolysis at the carbonyl group.[33] Addition at the carbonyl group was more pronounced when the reaction was carried out in the presence of sodium propionate. Values of k_{az}/k_{H_2O} corrected for addition at the carbonyl group are listed in parentheses in Table V, on the basis of observed values of k_{az}/k_{MeOH} and values of k_{MeOH}/k_{H_2O}

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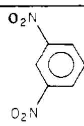
(32) (a) A value of $k_{az} = 5 \times 10^6\ M^{-1}\ s^{-1}$ for reaction of the trianisylmethyl carbocation was reported by Bunton, C. A.; Huang, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 3536–3544. (b) A value of k_{RS^-} of $7 \times 10^7\ M^{-1}\ s^{-1}$ for reaction of $HOCH_2CH_2S^-$ with the same carbocation was reported by Ritchie, C. D.; Gandler, J. *J. Am. Chem. Soc.* **1979**, *101*, 7318–7323.

(33) A 2-fold excess of diisopropylethylamine was found to catalyze addition of solvent at the acyl group for the reaction of 2-cyclohexenyl 3,5-dinitrobenzoate in 60% aqueous acetone. Kantner, S. S.; Humski, K.; Goering, H. L. *J. Am. Chem. Soc.* **1982**, *104*, 1693–1697.

Table III. Salt Effects on the Partitioning of the 1-(4-Methoxyphenyl)ethyl Carbocation between Azide Ion and Solvent[a]

solvent, 100% H_2O;[b] leaving group, $ClCH_2CO_2^-$			solvent, 50/50 TFE/H_2O (v:v); leaving group, 			
salt[c]	k_{az}/k_{H_2O}	k_{az}/k_s, M^{-1} [d]	salt[e]	k_{az}/k_{H_2O}	k_{az}/k_{TFE}	k_{az}/k_s, M^{-1} [d]
none	3500	63	none	5200	11900	169
1.0 M $NaClO_4$	2720	49	0.5 M $NaClO_4$	3300	6200	105
1.0 M NaCl	2120	38	0.5 M NaCl	3110	5570	98
1.0 M NaBr	2880	52	0.5 M NaBr	3250	6170	104
1.0 M NaI	3720	67	0.5 M NaI	3630	7005	116

[a] At 22 ± 2 °C. Rate constant ratios are calculated from the ratios of product and reactant concentrations. [b] Containing 1% CH_3CN. [c] $[NaN_3] = 0.01$ M. [d] Calculated by using a pseudo-first-order rate constant, $k_S(s^{-1})$, for the solvent reaction. [e] $[NaN_3] = 0.005$ M.

Table IV. Solvent Effects on the Partitioning of the 1-(4-Methoxyphenyl)ethyl Carbocation between Azide Ion and Solvent[a]

solvent, v:v	k_{az}/k_{H_2O}	k_{az}/k_{ROH}	k_{az}/k_S,[b] M^{-1}
50:50 TFE:H_2O[c]	3300	6200	105
50:50 MeOH:H_2O	950	110	7.1
50:50 EtOH:H_2O	570	100	7.5
50:50 CH_3OEtOH:H_2O	430	150	9.3
50:50 HOEtOH:H_2O	560	90	6.8
50:50 CH_3COCH_3:H_2O	470		17
50:50 CH_3CN:H_2O	860		31
50:50 $HCON(CH_3)_2$:H_2O	260		9.4
50:50 $CH_3S(O)CH_3$:H_2O	220		7.9

[a] At 22 ± 2 °C and $\mu = 0.50$ maintained with $NaClO_4$. The cation was generated by the solvolysis of 1-(4-methoxyphenyl)ethyl *p*-nitrobenzoate. [b] Calculated by using a pseudo-first-order rate constant, k_S (s^{-1}), for the solvent reaction. [c] Identical values, within experimental error, were obtained for 1-(4-methoxyphenyl)ethyl derivatives with phenol and 3,5-dinitrobenzoate leaving groups (Table I).

that were determined in unbuffered solutions. Values of k_{MeOH}/k_{H_2O} are 10–20% higher for the acid-catalyzed reaction of 1-(4-methoxyphenyl)ethyl phenyl ether than for the reaction of the 3,5-dinitrobenzoate ester at zero azide concentration, when the reactions are carried out in solvents of high methanol composition. This difference may also reflect 1–2% of solvent addition at the carbonyl group.

Rate constants, k_H, were determined for the acid-catalyzed cleavage to the corresponding carbocation of 1-phenylethyl alcohols with electron-donating substituents at the 4-position by measuring the initial rates of formation of the trifluoroethyl ether in 50:50 trifluoroethanol:water, as described in the Experimental Section. These rate constants were corrected for the partitioning of the carbocation between trifluoroethanol and water (Table I). Rate constants for the acid-catalyzed cleavage of 1-(4-(dimethylamino)phenyl)ethyl alcohol were measured at three values of pH << pK_a and were calculated from the relationship $k_h = k_{obsd}[SH^+]/[S][H^+] = k_{obsd}/K_a$, in which SH^+ is the N-protonated substrate, using a measured value of pK_a = 5.51. The observed rate constants were found to be independent of acid concentration under these conditions, as expected when the reactive form of the substrate is completely protonated. Second-order rate constants determined at pH values up to 6 were found to agree with those determined in acid solution, but rate constants at lower acid concentrations were larger and variable for reasons that are not understood. The results are summarized in Table VI.

These rate constants are combined with values of k_{H_2O} to give the dimensionless equilibrium constants for carbocation formation from the corresponding 1-phenylethyl alcohols shown in Table VII (eq 2). Values of K_R (M) for carbocation formation may be obtained from $K_R = [HOH]/K_{eq}$ and the concentration of water, 27.8 M. Table VII also shows values of k_H obtained from extrapolation of the Hammett correlation of these data, as described below, and additional values of K_{eq} for compounds with larger values of σ.

Discussion

The large negative values of ρ^+ for the solvolysis of substituted 1-phenylethyl derivatives[12,34,35] and the near limiting α and β secondary deuterium isotope effects on the solvolysis rates of 1-phenylethyl chlorides[19] demonstrate a carbocation-like transition state for these reactions. Scrambling of ^{18}O label in unreacted ring-substituted 1-phenylethyl 4-nitrobenzoates[25] and partial racemization of unreacted 1-phenylethyl chloride[36] and alcohol[37] during the course of solvolysis or exchange with water could occur through the reversible formation of an unstable carbocation intermediate. Trapping with azide and almost complete racemization have demonstrated the formation of an intermediate with a significant lifetime during the solvolysis of 1-(4-methoxyphenyl)ethyl 4-nitrobenzoate in 90% acetone.[25]

Classical evidence for an S_N1 reaction mechanism is presented in Figures 1 and 2. Despite the fact that product analysis shows a much greater reactivity of azide ion than of solvent (k_{az}/k_s = 105 M^{-1}) toward 1-(4-methoxyphenyl)ethyl 4-nitrobenzoate in 50:50 TFE:H2O (v:v), azide has no effect on the observed reaction rate under conditions in which up to 98% of the product is the azide adduct; i.e., the reaction is zero order with respect to azide. This demonstrates that the azide ion reacts with an intermediate after the rate-limiting step.

The intermediate that reacts with azide and solvent might be either a carbocation–leaving group ion pair that is formed in an irreversible step or the free carbocation. Figure 2 shows that identical values of k_{az}/k_s are obtained for the reaction of 1-(4-methoxyphenyl)ethyl 4-nitrobenzoate and for the acid-catalyzed reaction of 1-(4-methoxyphenyl)ethyl phenyl ether, in which phenol is the leaving group. The absence of an effect of the structure or charge of the leaving group on the partitioning of the carbocation intermediate[38] suggests that it is a free, diffusionally equilibrated carbocation. Reactions of 1-(4-methylphenyl)ethyl derivatives in this solvent that do proceed through the ion pair show significant differences in selectivity with leaving groups of different structure and charge.[29]

The large values of k_{az}/k_s for reactions of 1-(4-methoxyphenyl)ethyl derivatives provide further evidence for the formation of a free, solvent-equilibrated carbocation. Reaction of 1-(4-methoxyphenyl)ethyl chloroacetate in water gives equal amounts of azide and solvent adducts at 0.02 M N_3^-, so that $k_{az} = 50\ k_s$ (Table V). The first-order rate constant for diffusional separation of the ion pair, k_{-d}, must be at least as large as k_{az}, because association constants for ion pair formation in water are small,[39] $K_{as} = k_d/k_{-d} \leq 1.0\ M^{-1}$, and k_{az} cannot be larger than k_d, the rate constant for diffusion-controlled formation of the ion pair.

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(34) Hill, E. A.; Gross, M. L.; Stasiewicz, M.; Manion, M. *J. Am. Chem. Soc.* **1969**, *91*, 7381–7392.

(35) Noyce, D. S.; Virgilio, J. A. *J. Org. Chem.* **1972**, *37*, 2643–2647.

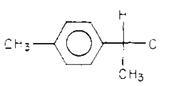
(36) Shiner, V. J., Jr.; Hartshorn, S. R.; Vogel, P. C. *J. Org. Chem.* **1973**, *38*, 3604–3610.

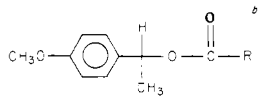
(37) Grunwald, E.; Heller, A.; Klein, F. S. *J. Chem. Soc.* **1957**, 2604–2613.

(38) McLennan, D. J.; Martin, P. L. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1099–1105.

(39) Davies, C. W. "Ion Association"; Butterworth & Co.: London, 1962; pp 77–87.

Table V. Effect of Changing Solvent Composition on the Partitioning of 1-(4-Methylphenyl)ethyl Chloride and 1-(4-Methoxyphenyl)ethyl Derivatives[a]





solvent,[c] % TFE v/v	k_{az}/k_{H_2O}[d]	k_{az}/k_{TFE}[d]	k_{az}/k_s, M^{-1} [e]	% TFE,[f] v/v	k_{az}/k_{H_2O}[d]	k_{az}/k_{TFE}[d]	k_{az}/k_{MeOH}[d,g]	k_{az}/k_{AcO^-}[d,h]	k_{az}/k_s, M^{-1} [e]
				20	2640			60	58
				30	2670		113	57	67
				40	3020	5 200	128	54	83
50	38	51	1.2	50	3070	5 900	129	58	98
60	38	57	1.4	60	3470	7 600	148	59	133
70	37	64	1.7	70	3910	10 200	184	69	195
80	41	75	2.4	80	4790	15 300	225	71	330
90	44	88	3.8	90	6060	23 900	300	78	700
97	45	101	5.9						

solvent, % MeOH v/v	k_{az}/k_{MeOH}[d]	k_{az}/k_{H_2O}[d]	k_{az}/k_s, M^{-1} [e]	% MeOH,[i] v/v	k_{az}/k_{H_2O}[d]	k_{az}/k_{MeOH}[d]	k_{az}/k_s, M^{-1} [e]	k_{MeOH}/k_{H_2O}[d,j,k]
				0^l	2720		49	
				10^l	2680	260	36	10.3
				20^l	2260	213	23	10.6
				$30^{l,m}$	1870	170	15	11.0
				40^m	1300	140	10	9.3
50^n	27	66	1.1	50^m	1000	111	7.2	9.0
60^o	29	65	1.2	60^m	720 $(840)^p$	104	5.8	7.7 (8.3) 7.1^k
70^q	34	68	1.3	70^m	540 $(660)^p$	95	4.7	5.7 (7.0) 7.5^k
80^r	43	75	1.6	80^m	350 $(540)^p$	90	4.0	3.9 (6.0) 7.1^k
90^s	56	91	2.1					

[a] At 22 ± 2 °C. Solutions were prepared by mixing the aqueous solution ($\mu = 1.0$ maintained by $NaClO_4$) with a specified volume of the organic cosolvent. [b] Average of values obtained with $4\text{-}NO_2PhCO_2^-$ and $3,5\text{-di-}NO_2PhCO_2^-$ leaving groups. [c] A single azide concentration, equal to the fraction (v) of water times 0.5 M, was used for each solvent composition. [d] Ratio of second-order rate constants. [e] Calculated by using a pseudo-first-order rate constant, k_s (s^{-1}), for the solvent reaction. [f] A single azide concentration, equal to the fraction (v) of water times 0.02 M, was used for each solvent composition. [g] Trifluoroethanol was replaced by methanol. The ratio of TFE:MeOH (v:v) was 25. [h] $[AcO^-]:[N_3^-] = 25$. [i] A single azide concentration, equal to the fraction (v) of water times 0.20 M, was used for each solvent composition. [j] Values in parentheses are for reactions in the absence of azide. [k] The indicated values are for the acid-catalyzed reaction of 1-(4-methoxyphenyl)ethyl phenyl ether. [l] $R = CH_2Cl$. [m] $R = 3,5\text{-di-}NO_2Ph$. [n] Average of values at 0.1, 0.2, 0.3, and 0.4 M $[N_3^-]$. [o] Average of values at 0.08, 0.16, 0.24, and 0.32 M $[N_3^-]$. [p] Calculated from the observed k_{az}/k_{MeOH} values and k_{MeOH}/k_{H_2O} values determined in the absence of azide (footnote *j*, see text). [q] Average of values at 0.06, 0.12. 0.18, and 0.24 M $[N_3^-]$. [r] Average of values at 0.04, 0.08, 0.12, and 0.16 M $[N_3^-]$. [s] $\mu = 0.20$. Average of values at 0.04, 0.08, 0.12. and 0.16 M $[N_3^-]$.

Table VI. Rate Constants for the Acid-Catalyzed Cleavage of Ring-Substituted 1-Phenylethyl Alcohols[a]

substituent	$[H^+]$, M	number of runs	k_H, M^{-1} s^{-1}
$4\text{-}N(CH_3)_2$[b]	0.0083-0.033	3	680
$4\text{-}OCH_3$	0.0008-0.005	6	1.1×10^{-1}
$4\text{-}SCH_3$	0.017-0.067	4	7.6×10^{-3}
4-OPh	0.025-0.050	4	8.4×10^{-3}
$3\text{-Br}, 4\text{-}OCH_3$	0.0003-0.0083	4	2.6×10^{-3}
$4\text{-}CH_3$	0.083-0.33	4	8.4×10^{-4}
$3\text{-}NO_2, 4\text{-}OCH_3$	0.083-0.50	5	2.1×10^{-5}

[a] In 50:50 TFE:H_2O (v:v) at 25 °C, ionic strength at 0.5 maintained with $NaClO_4$, except for the 4-(dimethylamino) compound. [b] Ionic strength maintained at 0.5 with $NaNO_3$.

Therefore, both k_{az} and k_{-d} must be at least 50 times larger than k_s and the ion pair will be largely dissociated before significant reaction with solvent or azide occurs.

The conclusion that the rate constants for the reactions of azide with substituted 1-phenylethyl carbocations are diffusion limited[13] is supported by the following experimental evidence.

(1) The observed azide selectivities show a very large dependence on carbocation stability, in contrast with the almost constant selectivities observed for reactions of nucleophiles toward triarylmethyl carbocations and other electrophiles of widely varying reactivity that follow the N^+ scale of nucleophilic reactivity.[40,41] The values of $k_{az}/k_s = N^+ = \sim 10^6$ M^{-1} for activation-limited reactions of azide ion[32a,40] may be compared with values of k_{az}/k_s that range from 1.1 to 130 M^{-1} for the reactions of azide ion with substituted 1-phenylethyl carbocations (Table I). The large slope of −4.5 for a plot of log k_{az}/k_s against σ^+ (see below) is consistent with $\rho^+ = 0$ for the diffusion-controlled reaction of azide and $\rho^+ = 4.5$ for the reaction with solvent. Such a large difference in selectivity is inconsistent with activation-limited reactions of azide ion with the carbocation.

(2) The ratio $k_{az}/k_{RSH} = 3.3 \pm 0.3$ for the reaction of propanethiol with the 1-(4-methoxyphenyl)ethyl carbocation[13,29] is 10^6 times smaller than the k_{az}/k_{RSH} ratio for the reactions of azide ion and mercaptoethanol with the trianisylmethyl cation.[42] The lack of selectivity of the former cation towards nucleophiles of vastly differing reactivities suggests that azide is reacting by an encounter-limited process.

(3) A rate constant of 5×10^6 M^{-1} s^{-1} has been reported for the reaction of azide ion with the trianisylmethyl carbocation.[32a]

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(40) Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1972**, *94*, 4966-4971.

(41) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348-354.

(42) Based on rate constants of 3.3 M^{-1} s^{-1} for the reaction of mercaptoethanol and 5×10^6 M^{-1} s^{-1} for the reaction of azide ion with trianisylmethyl carbocation.[32]

Table VII. Rate and Equilibrium Constants for the Reactions of Substituted 1-Phenylethyl Carbocations[a]

substituent	k_{TFE},[b] $M^{-1}\ s^{-1}$	k_{H_2O},[b] $M^{-1}\ s^{-1}$	k_s, s^{-1}	k_H,[c] $M^{-1}\ s^{-1}$	$K_{eq}^{H_2O}$ [d]
4-$N(CH_3)_2$[e]	22	65	2×10^3	680	10
4-OCH_3	8×10^5	1.5×10^6	5×10^7	1.1×10^{-1}	7.3×10^{-8}
4-OCH_3, 3-OCH_3	7×10^5	1.2×10^6	4×10^7		
4-OCH_3, 3-Br	7×10^6	1.3×10^7	4×10^8	2.6×10^{-3}	2.0×10^{-10}
4-OCH_3, 3-NO_2	3.3×10^7	8×10^7	3×10^9	2.1×10^{-5}	2.6×10^{-13}
4-SCH_3	8×10^5	1.4×10^6	4×10^7	7.6×10^{-3}	5.4×10^{-9}
4-OPh	6×10^6	1.0×10^7	3×10^8	8.4×10^{-3}	8.4×10^{-10}
4-CH_3	1.0×10^8	1.3×10^8	4×10^9	8.4×10^{-4}	6.5×10^{-12}
4-F[f]	5×10^8	7×10^8	2×10^{10} [g]	6×10^{-5}	9×10^{-14}
H[f]	3×10^9	3×10^9	1×10^{11} [g]	3×10^{-5}	1×10^{-14}
3-OCH_3[f]	6×10^9	7×10^9	2×10^{11} [g]	8×10^{-6}	1×10^{-15}
3-Br[f]	3×10^{10}	4×10^{10}	1×10^{12} [g]	4×10^{-7}	1×10^{-17}
4-CN[f]	1×10^{11}	2×10^{11}	6×10^{12} [g]	2×10^{-8}	1×10^{-19}
4-NO_2[f]	2×10^{11}	4×10^{11}	1×10^{13} [g]	5×10^{-9}	1×10^{-20}

[a] In 50:50 (v:v) TFE:H_2O at ~25 °C and $\mu = 0.5$ maintained with $NaClO_4$. [b] Obtained by combining the azide:solvent selectivity values (Table I) with an estimated value of $5 \times 10^9\ M^{-1}\ s^{-1}$ for the diffusional reaction of azide. [c] Rate constant for the acid-catalyzed conversion of 1-phenylethyl alcohol to the carbocation. [d] k_H/k_{H_2O}. Values of K_R (M) are given by $K_R = [H_2O]/K_{eq} = 27.8/K_{eq}$. [e] Based on a value of $k_{RS^-} = 5 \times 10^9\ M^{-1}\ s^{-1}$ for the reaction with methyl mercaptoacetate (Table II). [f] Values obtained by extrapolation of the structure-reactivity relationships established for stable carbocations. [g] $k_s = 6.94(k_{TFE}) + 27.75(k_{H_2O})$.

A further increase in k_{az} of $>10^4$ for reaction of the 1-(4-methoxyphenyl)ethyl carbocation is expected, since the more modest change in substrate to the 4-methoxyphenyldiphenylmethyl carbocation is expected[43,44] to increase k_{az} by 10^2.

Rate constants between 10^9 and $10^{10}\ M^{-1}\ s^{-1}$ have been reported for reactions in hydroxylic solvents that appear to be diffusion limited.[45,46] Combining a value[8] of $5 \times 10^9\ M^{-1}\ s^{-1}$ for k_{az} with the experimentally determined values of k_{az}/k_s gives the rate constants for reaction of solvent with 1-phenylethyl carbocations, k_s, shown in the upper part of Table VII. The thiolate selectivity of $k_{RS^-}/k_s = 2.5 \times 10^6\ M^{-1}$ for the reaction of the 1-(4-(dimethylamino)phenyl)ethyl carbocation (Table II) is close to the N^+ value for this ion, so that the k_s value for this cation is an upper limit; k_s will be smaller if the reaction of RS^- is slower than diffusion controlled. There is a small uncertainty in the values of k_s for the 1-(3-nitro-4-methoxyphenyl)ethyl and 1-(4-methylphenyl)ethyl cations because some of the reaction with the highly reactive cations may occur with an ion pair before diffusion away of the leaving group. A correction for reaction with the ion pair increases the estimated value of k_s from 4×10^9 to 6×10^9 s^{-1} for the 1-(4-methylphenyl)ethyl cation; the correction will be smaller for the 4-methoxy-3-nitro compound, which has a larger value of k_{az}/k_s.[29] It has been shown that a sulfonate ion has little or no effect upon the reactivity of a cation in a carbocation-sulfonate ion pair.[47]

Diffusion-controlled trapping of carbocations by strong nucleophiles provides an explanation for a number of examples of changing selectivity with varying reactivity.[7,15,48,49] Diffusion-controlled trapping of a carbocation intermediate has been used as a "clock" to determine the lifetimes of $ArC(CH_3)OCH_3^+$ oxocarbonium ions, with sulfite ions as the trapping reagent.[8]

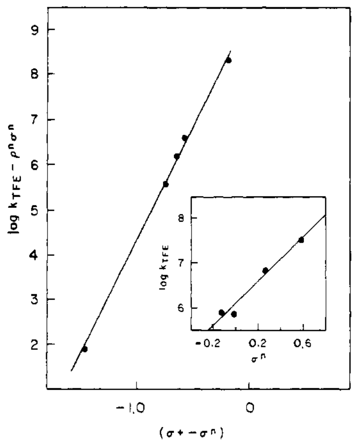

Figure 3. Hammett plot to evaluate ρ^r for the reaction of substituted 1-phenylethyl carbocations with trifluoroethanol. The y axis gives log k_{TFE} values, corrected for the contribution of inductive substituent interaction, and the x axis gives the resonance substituent constant ($\sigma^+ - \sigma^n$). Inset: Hammett plot to evaluate ρ^n. Log k_{TFE} values for the reaction of 1-(3-substituted-4-methoxyphenyl)ethyl carbocations are plotted against $\sum\sigma^n$ values of the 3- and 4-substituents.

Diffusion-controlled trapping with azide is the probable explanation for the decrease in selectivity with increasing reactivity of benzhydryl carbocations in the following series: 4,4'-dimethoxybenzhydryl mesitoate in methanol,[50] $k_{az}/k_{MeOH} = 20000$; 4,4'-dimethylbenzhydryl chloride in 90:10 to 50:50 (v:v) water:acetone,[49,51] $k_{az}/k_{H_2O} = 210$–1050; and benzhydryl chloride in 90% aqueous acetone,[49,52] $k_{az}/k_{H_2O} = 50$–100. There is evidence that these substrates react by an S_N1 mechanism with a carbocation intermediate,[53] so that the decreasing azide selectivities reflect increasing k_s values for the reaction of substituted benzhydryl carbocations. Structure–reactivity relationships for a heterogeneous series of alkyl and aryl chlorides show decreasing azide selectivity with decreasing reactivity, which presumably corresponds to increasing reactivity of the carbocation intermediate, as reported by several workers[54] and reexamined by Ta-

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[43] The substitution of two phenyl groups for two anisyl groups causes k_s to increase by 10^2.[44] A similar increase in k_{az} is expected, since for substituted triarylmethyl cations k_{az}/k_s is nearly constant.[32a,40]

[44] Diffenbach, R. A.; Sano, K.; Taft, R. W. *J. Am. Chem. Soc.* **1966**, *88*, 4747–4749.

[45] Rate constants have been reported of $10^{10}\ M^{-1}\ s^{-1}$ for diffusion-controlled reactions of anions with carbocations in methanol:dimethyl sulfoxide[40] and $10^9\ M^{-1}\ s^{-1}$ for thermodynamically favorable proton transfers between acidic and basic solutes in water: Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1–19. Benzyl cation and triethylamine react with a rate constant of $2 \times 10^9\ M^{-1}\ s^{-1}$ in dichloroethane; however, reactions with anions have rate constants of 3–$8 \times 10^{10}\ M^{-1}\ s^{-1}$, presumably because of electrostatic attraction in this solvent.[46]

[46] Sujdak, R. J.; Jones, R. L.; Dorfman, L. M. *J. Am. Chem. Soc.* **1976**, *98*, 4875–4879.

[47] Ritchie, C. D.; Hofelich, T. C. *J. Am. Chem. Soc.* **1980**, *102*, 7039–7044.

[48] Kemp, D. S.; Casey, M. L. *J. Am. Chem. Soc.* **1973**, *95*, 6670–6680. Rappoport, Z. *Tetrahedron Lett.* **1979**, 2559–2562. Rappoport, Z.; Apeloig, Y.; Greenblatt, J. *J. Am. Chem. Soc.* **1980**, *102*, 3837–3848.

[49] Ta-Shma, R.; Rappoport, Z. *Tetrahedron Lett.* **1982**, *23*, 781–784; *J. Am. Chem. Soc.* **1983**, *105*, 6082–6095.

[50] Ritchie, C. D. *J. Am. Chem. Soc.* **1971**, *93*, 7324–7325.

[51] Hawdon, A. R.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1952**, 2499–2504.

[52] Church, M. G.; Hughes, E. D., Ingold, C. K. *J. Chem. Soc.* **1940**, 966–970. Kovacevic, D.; Majerski, Z.; Borcic, S.; Sunko, D. E. *Tetrahedron* **1972**, *28*, 2469–2477. McLennan, D. J. *J. Chem. Soc., Perkin Trans. 2* **1974**, 481–485.

[53] A common ion rate depression has been observed for the solvolysis of substituted benzhydryl chlorides (Bailey, T. H.; Fox, J. R.; Jackson, E.; Kohnstam, G.; Queen, A. *Chem. Commun.* **1966**, 122–123) and the reaction of 4,4'-dimethoxybenzhydryl mesitoate is zero order in added azide.[50]

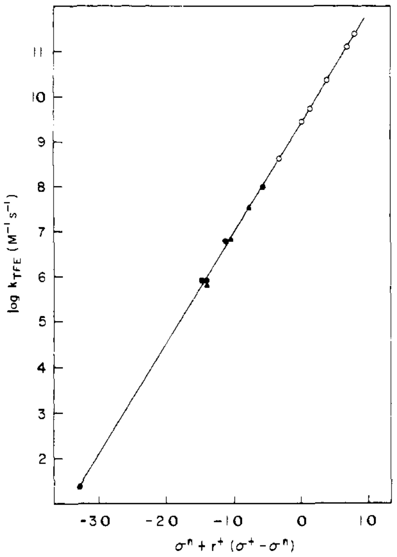

Figure 4. Yukawa–Tsuno plot (eq 6) for the reactions of ring-substituted 1-phenylethyl carbocations with trifluoroethanol in 50:50 trifluoroethanol:water. The triangles are rate constants for 1-(3-X-4-methoxyphenyl)ethyl carbocations. The open circles are extrapolated rate constants for the hypothetical reactions of less stable 1-phenylethyl carbocations with trifluoroethanol.

Shma and Rappoport.[49] The data for these substrates are also consistent with an S_N1 solvolysis mechanism and an intermediate that reacts at the diffusional limit with azide ion.[49]

Structure–Reactivity Relationships. Second-order rate constants for the reactions of substituted 1-phenylethyl carbocations with trifluoroethanol, k_{TFE}, and water, k_{H_2O}, as well as the first-order rate constants for their reactions with solvent, k_s, are summarized in the upper part of Table VII for the compounds with electron-donating substituents. These rate constants are all based on the value of $k_{az} = 5 \times 10^9$ M^{-1} s^{-1} for the diffusion-controlled reaction with azide ion. A Hammett correlation[55] of log (k_{az}/k_s) gives $\rho^+ = -4.5$, which corresponds to $\rho^+ = 4.5$ for k_s; ρ^+ for k_{H_2O} is also 4.5. The values of log k_{TFE} follow a Hammett correlation with $\rho^+ = 4.8$ (correlation coefficient = 0.992, not shown). However, the slope of the correlation for the 4-substituted compounds depends mainly on the amount of electron donation by resonance, because the values of σ^n are similar for these compounds. The much smaller value of $\rho^n = 2.5$ for the reactions of meta-substituted 1-(4-methoxyphenyl)ethyl carbocations with trifluoroethanol, shown in the inset to Figure 3, indicates that resonance effects make a major contribution to the observed structure–reactivity behavior, even larger than is accounted for by the ρ^+ correlation.

A separation of the polar and resonance effects according to the Yukawa–Tsuno treatment of eq 6[56] was obtained by subtracting the polar contribution, $\rho^n\sigma^n$, from log k_{TFE} and plotting against $(\sigma^+ - \sigma^n)$, as shown in Figure 3. This gives a slope of $\rho^r = \rho^n r^+ = 5.2$. A correlation of the data for all of the compounds in this series according to eq 6 gives a good fit (correlation coefficient = 0.998) with $\rho^n = 2.5$, $\rho^r = 5.2$, and $r^+ = 2.1$, as shown by the solid symbols in Figure 4. The two-parameter equation accounts for the almost identical values of k_{TFE} for the 4-OCH_3- and 4-SCH_3-substituted compounds; the ρ^+ correlation predicts a 6-fold larger rate constant for the 4-OCH_3 compound. A similar analysis for k_{H_2O} gives $\rho^n = 2.7$, $\rho^r = 4.9$, and $r^+ = 1.8$ (not shown). The open symbols in Figure 4 represent an extrapolation of the correlation to less stable carbocations. The apparent rate constants from this and similar extrapolations for k_{H_2O} and k_s are summarized in the bottom part of Table VII.

$$\log (k/k_0) = \rho^n[\sigma^n + r^+(\sigma^+ - \sigma^n)] \qquad (6)$$

The rate constants for the acid-catalyzed cleavage of substituted 1-phenylethyl alcohols to form the corresponding carbocations (k_H, eq 2, Table VI) were treated similarly. The data give a fair correlation with σ^+ and a value of $\rho^+ = -4.5$ (correlation coefficient = 0.994). This may be compared with values of $\rho^+ = -5.5$, -5.7, and -5.1 for the solvolysis of substituted 1-phenylethyl chlorides (80% aqueous acetone),[12] 1-phenylethyl acetates (30% aqueous ethanol),[34] and 1-phenylethyl diphenylphosphinates (80% ethanol–water, 75 °C),[35] respectively.[57] Separation of the substituent effects into polar and resonance contributions gives a good fit with values of $\rho^n = -4.9$, $\rho^r = -4.4$, and $r^+ = 0.9$ (correlation coefficient = 0.996).

The rate constants for the acid-catalyzed cleavage of the 4-OCH_3- and 4-SCH_3-substituted compounds differ by 14-fold, in contrast to the almost identical rate constants for reactions of the corresponding cations in the opposite direction (Tables I and VII). This is a consequence of the differing polar and resonance contributions of the 4-OCH_3 and 4-SCH_3 substituents and the smaller contribution of resonance to k_H than to k_{H_2O}. Comparison of the effects of these two substituents provides a simple method for estimating the relative importance of polar and resonance substituent effects that complements the r^+ parameter. The observed rate constant ratio of 14 suggests a somewhat smaller contribution of resonance than the r^+ value of 0.9, which corresponds to a ratio of 8 for the 4-OCH_3 and 4-SCH_3 compounds.

The rate constants k_H and k_{H_2O} refer to the same reaction in two directions (eq 2). The equilibrium constants for carbocation formation from the 1-phenylethyl alcohols are given by $K_{eq} = k_H/k_{H_2O}$ and range from 10 for the 1-(4-(dimethylamino)phenyl)ethyl cation to 3×10^{-13} for the 1-(3-nitro-4-methoxyphenyl)ethyl cation (Table VII). The carbocation of the dimethylamino compound does not accumulate because the nitrogen atom is protonated in acid solution; the value of K'_{eq} for the pH-independent dissociation of the protonated species is $K_aK_{eq} = 10^{-5.5} \times 10 = 10^{-4.5}$. Extrapolation to the 1-(4-nitrophenyl)ethyl compound gives $K_{eq} = 10^{-20}$. The effects of substituents on the equilibrium constants, obtained from the ρ values for the forward and reverse rate constants according to $\rho_{eq} = \rho_f - \rho_r$, are $\rho^+_{eq} = -9.0$, $\rho^n_{eq} = -7.6$, $\rho^r_{eq} = -9.3$, and $r^+_{eq} = 1.2$.

Comparison of the ρ^n and ρ^r values for k_H and K_{eq} shows that the transition state for the acid-catalyzed "solvolysis" of 1-phenylethyl alcohols is 64% of the way toward the carbocation with respect to charge development, as measured by the effects of polar substituents, and 47% of the way toward the carbocation with respect to the development of resonance delocalization, as measured by effects of electron-donating 4-substituents. These comparisons may also be expressed in terms of the normalized parameters $\rho^n_{nor} = 0.64$ and $\rho^r_{nor} = 0.47$ for k_H in the cleavage direction, and $\rho^n_{nor} = 0.36$ and $\rho^r_{nor} = 0.53$ for the attack of water on the carbocation, k_{H_2O}. These values show that the transition state, although it has a large amount of carbocationic character,[58] is still far from the limiting structure of a carbocation, especially with respect to the development of resonance delocalization of charge. Stated another way, the carbocation shows a surprisingly large selectivity and undergoes a considerable amount of bond formation before reaching the transition state, in spite of its low stability.

The conclusion that there is 64% charge development in the transition state for reactions of substituted 1-phenylethyl derivatives falls within the range of several less direct estimations that have been reported for other substrates. A comparison of the enthalpy change for carbocation formation at low temperature with Gibbs energies of activation for solvolysis in ethanol gives

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(54) Sneen, R. A.; Carter, J. V.; Kay, P. S. *J. Am. Chem. Soc.* **1966**, *88*, 2594–2595. Raber, D. J.; Harris, J. M.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 4821–4828.

(55) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley: New York, 1975; pp 55–78.

(56) Yukawa, Y.; Tsuno, Y.; Sawada, M. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2274–2286.

(57) A less negative value of $\rho^+ = -3.7$ has been reported for the acid-catalyzed cleavage of 1-phenylethyl alcohols in two different solvents, using a limited number of normalized rate constants. Gillen, C. J.; Knipe, A. C.; Watts, W. E. *Tetrahedron Lett.* **1981**, *22*, 597–600.

(58) Arnett, E. M.; Petro, C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 522–526.

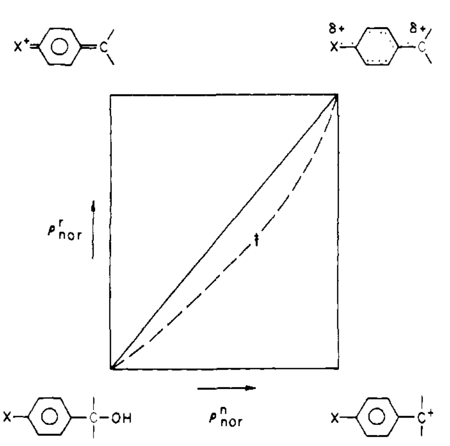


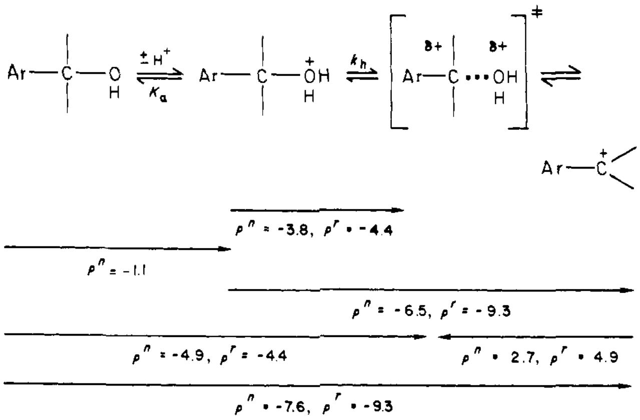
Figure 5. Structure–reactivity contour diagram to show the effects of polar, ρ^n, and resonance, ρ^r, substituent effects on the formation of substituted 1-phenylethyl carbocations, starting with the protonated alcohol. The x axis is taken to be a measure of C–O bond cleavage and the y axis a measure of the development of resonance delocalization of positive charge. The straight line shows a balanced reaction coordinate. The dashed line passes through the observed transition state with a lag in the development of resonance delocalization.

estimates of 75–89% development of positive charge in the transition state compared to the carbocation.[59] A comparison of the effects of substituents at five positions on the solvolysis of 1-naphthylethyl chlorides, on protodetritiation rates of naphthylene derivatives, and on ^{13}C chemical shifts upon ionization gives estimates of 47–51% charge development in the transition state for solvolysis of the chlorides.[60] A logarithmic correlation of the rate and equilibrium constants for the addition of water to substituted trityl cations can be fit by two parallel lines of slope 0.4 or, with some scatter, a single line of slope 0.7.[44,59]

There is a considerably larger relative contribution of resonance when the transition state is reached by reaction of solvent with the carbocation than when it is reached by departure of a leaving group from a 1-phenylethyl derivative in the solvolysis direction. This is apparent in the r^+ values of 2.1 and 1.8 for k_{TFE} and k_{H_2O}, compared with the value of 0.9 for k_H. This means that there is an *imbalance* in the expression of polar and resonance substituent effects. The imbalance corresponds to a relatively small expression of the resonance effect in the initial stages of bond cleavage for the solvolysis reaction and a relatively larger expression in the final stages of the reaction, after the transition state has been reached. In the reverse direction there is a relatively large loss of resonance as the transition state is reached for the attack of solvent on the carbocation and a proportionally smaller loss as bond formation is completed. The same sort of imbalance or lag in the expression of electron delocalization by resonance is well known for the deprotonation of nitroalkanes,[61,62] and also occurs in additions to nitrostilbenes.[63]

The imbalance may be described by the energy contour diagram[64,65] of Figure 5, in which the x and y axes describe the polar and resonance effects that are represented by ρ^n and ρ^r, respectively. A balanced reaction would follow the path shown by the diagonal solid line and would exhibit the same ratio of polar and resonance effects in the transition state and product. The observed structure–reactivity parameters correspond to a transition state on the dashed reaction path, in which the amount of electron delocalization is relatively small in the transition state compared with the products. The normalized structure–reactivity parameter ρ^n_{nor} = 0.64 places the transition state two-thirds of the way along the x axis for C–O bond cleavage and the value of ρ^r_{nor} = 0.47 places it halfway along the y axis for resonance delocalization of the positive charge into the phenyl ring.

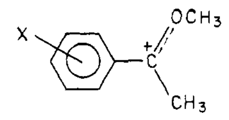
Scheme I



The imbalance or lag in the development of resonance delocalization may be attributed to two factors. First, the observed value of ρ^n = −4.9 for the acid-catalyzed cleavage of 1-phenylethyl alcohols may be corrected for protonation of the alcohol, using ρ^n = −1.1 for the protonation of substituted benzylamines (Scheme I).[66] This gives ρ^n = −3.8 and r^+ = 1.13 for k_H, and ρ^n = −6.5 and r^+ = 1.4 for equilibrium formation of the carbocation, starting with the protonated alcohol. The normalized parameter for k_H is then ρ^n_{nor} = 0.58, which is somewhat closer to the value of ρ^r_{nor} = 0.47. This corrected value of r^+ = 1.13 is close to the value of r^+ = 1.15 for the solvolysis of 1-phenylethyl chlorides.[12]

The second, and probably more important, explanation for this kind of imbalance is Kresge's proposal,[62,64] for the nitroalkane anomaly, that the fraction of electron delocalization itself depends upon the fraction of bond cleavage; a fraction of a fraction gives a smaller fraction. If the corrected value of ρ^n_{nor} = 0.58 corresponds to 58% bond cleavage and development of positive charge at C-1 (in the absence of resonance delocalization) and also to 58% rehybridization and delocalization of this charge, then the observed delocalization will be (0.58)(0.58) = 0.34 of the maximum. This is more than is needed to account for the observed value of ρ^r_{nor} = 0.47. Although the quantitative relationship is crude, it is reasonable that there should be a relationship of this kind between the fraction of bond cleavage and the rehybridization at the C-1 atom that makes resonance delocalization possible in the ionization of nitroalkanes, the solvolysis of 1-phenylethyl derivatives, and similar reactions.

The large difference between the value of ρ^r_{eq} = −9.3 for the equilibrium formation of 1-phenylethyl cations and ρ^r_{eq} = −2.2 for the corresponding reaction[8] with a methoxy group in the 1-position, to give the methoxyethyl cation **1**, provides a striking example of "resonance saturation" or "competing resonance".[56,67] Delocalization of positive charge onto the oxygen atom of **1** decreases the electron demand from the substituted benzene ring. The somewhat smaller difference in the values of ρ^n_{eq} = −7.6 and of ρ^n_{eq} = −2.5 respectively in the two reaction series reflects the same decrease in the charge density on the 1-carbon atom of **1**. The same effect provides an explanation for the progressively less



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(59) Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2889–2895.

(60) Forsyth, D. A.; Estes, M. R.; Lucas, P. *J. Org. Chem.* **1982**, *47*, 4379–4380.

(61) Bordwell, F. G.; Boyle, W. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3907–3911.

(62) Kresge, A. J. *Can. J. Chem.* **1974**, *52*, 1897–1903.

(63) Bernasconi, C. F.; Murray, C. J.; Fox, J. P.; Carre, D. J., personal communication.

(64) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948–7960.

(65) Jensen, J. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 1476–1488.

(66) Blackwell, L. F.; Fischer, A.; Miller, I. J.; Topsom, R. D.; Vaughan, J. *J. Chem. Soc.* **1964**, 3588–3591. Resonance with the reaction center is not expected to be significant for this protonation step.

(67) Winstein, S.; Morse, B. K.; Grunwald, E.; Schreiber, K. C.; Corse, J. *J. Am. Chem. Soc.* **1952**, *74*, 1113–1120. Loudon, G. M.; Berke, C. *J. Am. Chem. Soc.* **1974**, *96*, 4508–4517.

negative values of ρ for the hydrolysis of substituted benzaldehyde acetals,[68] $\rho = -3.3$, acetophenone ketals,[8] $\rho = -2.0$, and benzoate ortho esters,[69] $\rho = -1.2$.

The values of $\rho^n = 1.6$ and $\rho^r = 1.6$ for the reaction of **1** with water are also smaller than the corresponding values of $\rho^n = 2.7$ and $\rho^r = 4.9$ for the same reaction of 1-phenylethyl carbocations. However, the normalized values, based on equilibrium values of ρ for the protonated substrates, are $\rho^n_{nor} = 0.61$ and 0.42, and $\rho^r_{nor} = 0.73$ and 0.53 respectively for the two reactions.[8] This suggests that the fraction of bond formation in the transition state is *larger* for the slightly less reactive oxocarbonium ions, **1**, than for 1-phenylethyl carbocations, in spite of the smaller absolute values of ρ for the reactions of **1**. These comparisons illustrate the importance of using normalized rather than absolute ρ values in order to estimate the amount of bond formation or cleavage in the transition states of reactions of this kind.

There is an analogous decrease in the absolute value of ρ for the equilibrium formation of carbocations from monosubstituted 1-phenylethyl alcohols, $\rho^+ = -9.0$, benzhydryl alcohols,[70] $\rho^+ = -5.6$, and triarylcarbinols,[70] $\rho^+ = -3.8$, because of competing resonance. However, the ρ^+ values are similar, -9.0, -11.4, and -11.9, for the three series if the same substituent is added to each of the phenyl groups in each system. Approximately the same total charge is "seen" by the substituents upon ionization if the charge is divided between two or three phenyl groups, when the substituents are present on all of the phenyl groups.

The competition of resonance and polar substituent effects leads to a crossover of the relative reactivities of **1** and 1-phenylethyl carbocations. Electron donation from the 1-methoxy substituent of **1** normally decreases its rate constant for reaction with water compared with the corresponding 1-phenylethyl carbocations. However, extrapolation of the Hammett plot[8] for **1** gives a rate constant of $k_{H_2O} = 5 \times 10^3$ $M^{-1}\,s^{-1}$ for the 4-dimethylamino-substituted compound that is $\sim$10 times larger than $k_{H_2O} = 65$ $M^{-1}\,s^{-1}$ for the 1-(4-(dimethylamino)phenyl)ethyl cation. (The latter reaction is in 50:50 trifluoroethanol:water rather than water, but the effect of solvent on k_s is small; see below.) The large delocalization of charge from the 1-carbon atom by the dimethylamino group decreases the relative importance of electron donation from the methoxy group to the point that the electron-withdrawing polar effect of the oxygen atom becomes more important than electron donation by resonance, so that there is a net destabilization of the carbocation. The same kind of behavior has been observed for the addition of alkoxy substituents in the acid-catalyzed cleavage of acetals and ortho esters.[8,71]

Solvent and Salt Effects. The data reported in Tables III–V allow an evaluation of several of the many effects that solvents and salts can exert on the stability of carbocations.[5,72] We conclude that solvent and salt effects from stabilization or destabilization of the positive charge of the cation, per se, are small for the range of variation examined here. The most important effects of solvent on cation stability arise from (1) the nucleophilic reactivity of solvent components, (2) specific solvent effects on this nucleophilic reactivity, and (3) the molarity of the nucleophilic solvents.

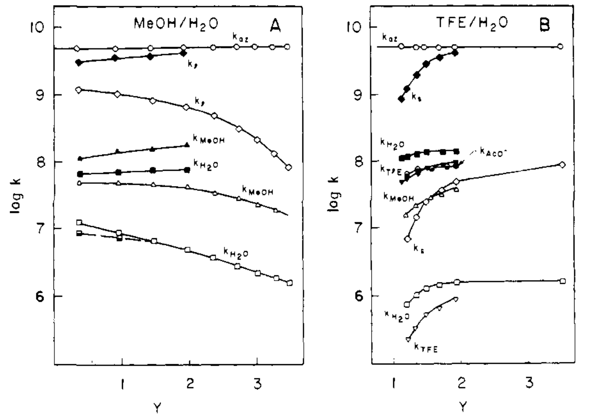

Figure 6. Dependence of nucleophilic reactivity on solvent composition for the reactions of the 1-(4-methylphenyl)ethyl carbocation (closed symbols) and 1-(4-methoxyphenyl)ethyl carbocation (open symbols) in mixed MeOH–H$_2$O and TFE–H$_2$O solvents, assuming a constant value of $k_{az} = 5 \times 10^9$ $M^{-1}\,s^{-1}$. (A) MeOH–H$_2$O; (B) TFE:H$_2$O: ♦, ◊, k_s (s^{-1}); ▲, △, k_{MeOH} ($M^{-1}\,s^{-1}$); ▼, ▽, k_{TFE} ($M^{-1}\,s^{-1}$); ■, □, k_{H_2O} ($M^{-1}\,s^{-1}$). ◪, k_{H_2O} values corrected for water addition at the carbonyl group as described in the text; ◒, k_{AcO^-} ($M^{-1}\,s^{-1}$).

Rate constants for the reactions of 1-(4-methoxyphenyl)ethyl and 1-(4-methylphenyl)ethyl cations with solvent (k_s) and with solvent components in methanol:water and trifluoroethanol:water mixtures are shown in Figure 6, based on observed product ratios (Table V) and an assumed value of $k_{az} = 5 \times 10^9$ $M^{-1}\,s^{-1}$. This value will not be constant in all of the solvent mixtures because of differences in viscosity and, possibly, other properties of the solvent that influence the diffusion coefficient of azide. The viscosities of the solvent and salt mixtures were not determined, but the differences are not expected to have a large effect on the rate constants. The viscosity of water–methanol mixtures passes through a maximum value of 1.8 in 50% methanol;[73] this change may contribute to the slight curvature of the lines in Figure 6A but will not alter the relative rate constants of the hydroxylic nucleophiles or the conclusions. The rate constants in Figure 6 are plotted against the Y values of the solvent mixtures, based on the solvolysis of tert-butyl chloride,[74] which are often taken to be a measure of the "ionizing power" of the medium.

(1) Nucleophilic Reactivity of the Solvent. This is the single most important factor that determines carbocation stability; it accounts for most of the change in the values of k_s for the solvent ranges shown in Figure 6. Methanol is approximately 10-fold more reactive than water and 100-fold more reactive than trifluoroethanol with the 1-(4-methoxyphenyl)ethyl carbocation (open symbols).

The sensitivity of the carbocation to the nucleophilic reactivity of alcohols and water decreases with decreasing stability of the cation, as is apparent for the 4-methyl compound in Figure 6 (closed symbols) and for a larger series of cations and alcohols described elsewhere.[29]

(2) Solvent Effects on Nucleophilic Reactivity. An important contributing factor to the low reactivity of solutions containing a high concentration of trifluoroethanol is a decrease in the nucleophilic reactivity of trifluoroethanol and other nucleophiles, which presumably involves hydrogen bonding.[72,75-77] The electron-withdrawing trifluoromethyl group of trifluoroethanol can decrease the reactivity of a nucleophile, N, by strengthening a hydrogen bond to the lone pair electrons of N, **2**, and by weakening

$N\cdots HOCH_2CF_3$

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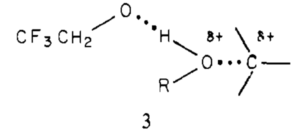

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the solvation of the developing positive charge on a hydroxylic nucleophile in the transition state through hydrogen bonding to the solvent, **3**. Trifluoroethanol itself as a nucleophile should be

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(68) Dunlap, R. B.; Ghanim, G. A.; Cordes, E. H. *J. Phys. Chem.* **1970**, *73*, 1898–1901.

(69) Bull, H. G.; Koehler, T. C.; Pletcher, T. C.; Ortiz, J. J.; Cordes, E. H. *J. Am. Chem. Soc.* **1971**, *93*, 3002–3011.

(70) Deno, N. C.; Evans, W. L. *J. Am. Chem. Soc.* **1957**, *79*, 5804–5807.

(71) Bunton, C. A.; De Wolfe, R. H. *J. Org. Chem.* **1965**, *30*, 1371–1375. Cordes, E. H.; Bull, H. G. *Chem. Rev.* **1974**, *74*, 581–603.

(72) Rappoport, Z.; Kaspi, J. *J. Am. Chem. Soc.* **1974**, *96*, 4518–4530.

(73) "Handbook of Chemistry and Physics", Weast, R. C., Ed.; CRC Press Inc.: Boca Raton, FL, 1979; p D246 and D239.

(74) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2770–2777. Shiner, V. J., Jr.; Dowd, W.; Fisher, R. D.; Hartshorn, S. R.; Kessick, M. A.; Milakofsky, L.; Rapp, M. W. *J. Am. Chem. Soc.* **1969**, *91*, 4838–4843.

(75) Kaspi, J.; Rappoport, Z. *Tetrahedron Lett.* **1977**, 2035–2038.

(76) Raber, D. J.; Neal, W. C., Jr.; Dukes, M. D.; Harris, J. M.; Mount, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 8137–8146.

(77) Kaspi, J.; Rappoport, Z. *J. Am. Chem. Soc.* **1980**, *102*, 3829–3837 and references therein.

particularly sensitive to the second of these effects because its high acidity favors such solvation and base catalysis in its nucleophilic reactions.[72,77,78] The larger decrease in k_{TFE} compared with k_{H_2O}, k_{MeOH}, and k_{AcO^-} with increasing trifluoroethanol concentration (Figure 6B)[77] suggests that this is the more important of the two effects. It also accounts for the nonlinear decrease in the reactivity of alcohols with changing solvent composition, which becomes significant only above ~50% trifluoroethanol as the concentration of water is significantly reduced (Figure 6).[10,75,77] This decrease is consistent with the larger reactivity of alcohol dimers than of monomers in dichloroethane.[46]

There is little, if any, decrease in the rate constant for the reaction of water with the 1-(4-methylphenyl)ethyl carbocation at high trifluoroethanol concentration (Figure 6B, solid squares). This is another reflection of the decreased selectivity of this highly reactive cation, which is discussed in the following paper.[29]

(3) Molarity of Nucleophilic Solvents. The replacement of water by bulkier alcohols decreases the total molarity of hydroxylic nucleophiles in the solvent and causes a significant change in the ratio k_s/k_{ROH}. For trifluoroethanol–water this decrease reaches a factor of 4 in pure trifluoroethanol.

(4) Ion-Solvating Ability. The data in Tables IV and V and Figure 6 show that there is surprisingly little dependence of the lifetime of these carbocations on the ion-solvating ability or dielectric constant of the solvent. The rate constants for reaction of the 1-(4-methoxyphenyl)ethyl carbocation with methanol and with water increase only 3- to 6-fold over a range of 3 units of the Y scale of solvent ionizing power (Figure 6A). There is an even smaller sensitivity of k_s and k_{H_2O} to solvent ionizing power or dielectric constant over most of the range of trifluoroethanol–water mixtures and k_{MeOH} is actually larger in 50% trifluoroethanol than in 10% methanol (Figure 6). A solvent effect on carbocation reactivity may account for the value of $k_{az}/k_{H_2O} = 560$ for ethylene glycol/water, which is about twice as high as the expected value from $k_{az}/k_{H_2O} = 1000$ for methanol:water, and the 4-fold decrease in k_{az} that is expected from the relative viscosities of the two mixtures (Tables IV and V).[73] There is also only a small difference between the values of $k_{az}/k_{H_2O} = 200$ for the reaction of 1-(4-methoxyphenyl)ethyl 4-nitrobenzoate with tetrabutylammonium azide in 90:10 (v/v) acetone:water at 78.6 °C[25] and $k_{az}/k_{H_2O} = 470$ for reaction of the same compound with sodium azide in 50:50 acetone:water at room temperature (Table IV).

There is also very little effect of salts, which might be expected to stabilize cations, on carbocation stability. The ratios of k_{az} to k_s, k_{H_2O}, and k_{TFE} change by less than 2-fold as the ionic strength is increased from 0.01 to 1.0 in water or from 0.005 to 0.5 in 50:50 trifluoroethanol:water, as shown in Table III. The small increase in the ratio at low ionic strength, compared with most of the salt solutions, might be explained by an electrostatic effect on the diffusional combination of azide anion with the carbocation.[45] There is a small specific salt effect that increases the ratios in the order $Cl^- < ClO_4^- < Br^- < I^-$ and might be attributed to salting in (or less salting out) of the carbocation that decreases its reactivity in the presence of the larger, "softer" anions. Perchlorate anion is known to decrease the reactivity of trianisylmethyl cation.[32a] There is also little or no effect of salts on the relative reactivities of water and trifluoroethanol; there may be an increase of 20% in k_{TFE}/k_{H_2O} at ionic strength 0.5 (Table III). This is in contrast to poorer ionizing solvents, in which ions can increase the reactivity of trifluoroethanol compared with other hydroxylic nucleophiles.[77,78] These results are consistent with the small effect of a sulfonate ion in an intramolecular ion pair.[47]

Thus, solvent ionizing power, as measured by the Y scale or dielectric constant, and electrostatic effects of added salts are among the least important factors that influence carbocation stability under the conditions examined here. This is consistent with the conclusion that the Y scale represents, in large part, the effect of solvent on the solvation of anionic leaving groups in the transition states of solvolysis reactions.[79] The comparatively small effects of both solvents and salts would be unlikely to cause a major change in reaction mechanism by changing the lifetime of the carbocation over the range of variation examined here.[5]

Registry No. 4-$CH_3OC_6H_4CH(CH_3)OPh$, 88563-46-6; 3,5-$(O_2N)_2C_6H_3COOCH(CH_3)C_6H_4OCH_3$-4, 88563-47-7; 4-$O_2NC_6H_4COOCH(CH_3)C_6H_4OCH_3$-4, 58287-11-9; 3,5-$(O_2N)_2C_6H_3COOCH(CH_3)C_6H_4SCH_3$-4, 88563-48-8; 3,5-$(O_2N)_2C_6H_3COOCH(CH_3)C_6H_4OPh$-4, 88563-49-9; $C_6F_6COOCH(CH_3)C_6H_3(CH_3)_2$-3,4, 88563-50-2; $C_6F_6COOCH(CH_3)C_6H_4CH_3$-4, 88563-51-3; 4-$CH_3C_6H_4CHClCH_3$, 2362-36-9; 3,5-$O_2NC_6H_3COOCH(CH_3)C_6H_3(OCH_3)_2$-3,4, 88563-52-4; $C_6F_6COOCH(CH_3)C_6H_3$-3-Br-4-OCH_3, 88563-53-5; 3-NO_2-4-$CH_3OC_6H_3CHClCH_3$, 88563-54-6; N_3^-, 14343692; 4-$(CH_3)_2NC_6H_4C^+HCH_3$, 82414-94-6; 4-$CH_3OC_6H_4C^+HCH_3$, 18207-33-5; 3,4-$(CH_3O)C_6H_3C^+HCH_3$, 88563-55-7; 3-Br-4-$CH_3OC_6H_3C^+HCH_3$, 88510-80-9; 3-NO_2-4-$CH_3OC_6H_3C^+HCH_3$, 88510-81-0; 4-$CH_3SC_6H_4C^+HCH_3$, 82414-95-7; 4-$PhOC_6H_4C^+HCH_3$, 82414-96-8; 4-$CH_3C_6H_4C^+HCH_3$, 31042-87-2; 4-$FC_6H_4C^+HCH_3$, 31067-69-3; PhC^+HCH_3, 25414-93-1; 3-$CH_3OC_6H_4C^+HCH_3$, 82414-97-9; 3-$BrC_6H_4C^+HCH_3$, 82414-98-0; 4-$NCC_6H_4C^+HCH_3$, 82414-99-1; 4-$O_2NC_6H_4C^+HCH_3$, 82415-00-7.

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(78) Funderburk, L. H.; Aldwin, L.; Jencks, W. P. *J. Am. Chem. Soc.* **1978**, *100*, 5444–5459. Sinnott, M. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 2026–2032.

(79) Parker, A. J.; Mayer, U.; Schmid, R.; Gutmann, V. *J. Org. Chem.* **1978**, *43*, 1843–1854. Luton, P. R.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2*, **1979**, 1507–1511. Abraham, M. H.; Taft, R. W.; Kamlet, M. J. *J. Org. Chem.* **1981**, *46*, 3053–3056.