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A Comparison of Substituent Effects on the Stability of α,α-Dimethylbenzyl Carbocations in Aqueous Solution and in the Gas Phase: How Significant Is Nucleophilic Solvation?

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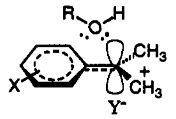
Abstract: Rate and equilibrium constants for conversion of ring-substituted cumyl alcohols in acidic solutions of 50:50 (v/v) trifluoroethanol/water ($I = 0.50$, $NaClO_4$) to an equilibrium mixture of the corresponding cumyl alcohol, cumyl trifluoroethyl ether, and α-methylstyrene and the fractional yields of cumyl trifluoroethyl ether obtained from partitioning of the cumyl carbocation intermediates of these reactions between capture by water and by trifluoroethanol have been determined. These data and estimates of absolute rate constants for the reaction of ring-substituted cumyl carbocations with water in 50:50 (v/v) trifluoroethanol/water[30] have been used to calculate equilibrium constants K_R and K_P respectively for conversion of ring-substituted cumyl carbocations to the corresponding cumyl alcohols and α-methylstyrenes and the changes in Gibbs free energy $(\Delta G_X)_{sol}$ for deprotonation of ring-substituted cumyl carbocations by α-methylstyrene. A plot of $(\Delta G_X)_{sol}$ against $(\Delta G_X)_{gas}$ for the corresponding reactions in the gas phase is linear with a slope of 0.70, in contrast to the previously reported unitary slopes of correlations of substituent effects on carbocation stability in solution and in the gas phase. We conclude that there is a modest increase in the stabilization of ring-substituted cumyl carbocations by solvation as their stability is decreased, but that this is much smaller than the change in stabilization by solvation with the changing stability of pyridinium and anilinium ions. The possible relevance of these data to the stabilization of carbocations by nucleophilic solvation is discussed.

Introduction

There is compelling evidence for concerted bimolecular solvolysis reactions at aliphatic carbon. These reactions proceed through a transition state that is stabilized relative to that for stepwise solvolysis by partial bonding of the solvent to the aliphatic carbon, so as to avoid the formation of highly unstable carbocation reaction intermediates.[2–5] It has also been proposed, based upon changes in linear free energy correlations of the effect of changing solvent nucleophilicity on solvolytic reactivity, that the transition state for *stepwise* ionization reactions to form carbocation intermediates may be stabilized by interactions with nucleophilic solvents.[6–10] Presumably, this is a Lewis acid–base interaction between a nonbonding electron pair of the solvent and the developing *p* orbital at the reaction transition state that is partially expressed at the transition state for heterolytic bond cleavage and fully expressed as nucleophilic solvation of the carbocation reaction intermediate (e.g., **1**).

There have been several experimental and theoretical studies directed toward understanding the magnitude and nature of the interactions between solvent and carbocations.[11–19] The results of these studies show that carbocations are strongly stabilized by solvation; however, they provide no evidence for stabilization of carbocations by the Lewis acid–base-type interaction illustrated by **1**.[11–19] For instance, the slope of a plot of the changes in Gibbs free energy for formation of carbocations from the corresponding alcohols in water against those for a similar reaction in the gas phase is *not significantly different from 1.0* for data that include the strongly resonance-stabilized tropylium and α-methylbenzhydryl carbocations and the more weakly stabilized cumyl carbocation.[17,18] A unitary slope has also been reported for a plot of the enthalpy of formation of a variety of secondary and tertiary carbocations (as ion pairs with SbF_5Cl^-) from the respective chlorides in SO_2ClF against the enthalpy for their formation from the corresponding alkanes in the gas phase (hydride affinity).[14]



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An increase in stabilization of a carbocation by nucleophilic solvation with increasing thermodynamic driving force for its

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reaction with nucleophilic reagents would be reflected by a slope of less than unity for plots of Gibbs free energy changes for reaction of the carbocations in aqueous solution against those for reaction in the gas phase: the observation of unitary slopes for these plots shows that stabilization of carbocations by solvation by the nucleophilic solvent water or by SO_2ClF remains constant as the carbocation is destabilized.[14,17,18] This is inconsistent with nucleophilic solvation of carbocations by water, because the strength of such an interaction should increase with increasing reactivity of the carbocation as a Lewis acid in the same manner that the strength of solvation by hydrogen bonding increases with increasing acidity of the hydrogen bond donor.[20,21] This should hold both for destabilization of carbocations by decreasing resonance electron donation from the ring substituent, because this frees the partially occupied orbital at the benzylic carbon to interact more strongly with the Lewis base (see **1**), and for their destabilization by polar electron-withdrawing substituents, because the polar interaction between the ring substituent and the positive charge will be attenuated by the change from a vacuum to a solvent of high dielectric constant.[22]

The results of theoretical calculations also suggest that the total stabilization of carbocations by solvation is constant and independent of carbocation stability.[19]

The interpretation of the earlier correlation[18] of Gibbs free energy changes for formation of carbocations in water and in the gas phase is not definitive, because this correlation is dominated by data for strongly resonance-stabilized carbocations and it does not clearly span a range of substrates over which a change from an unassisted to a solvent-assisted stepwise solvolysis reaction has been proposed to occur. This change in mechanism has been proposed to occur for the solvolyses of ring-substituted cumyl derivatives as the ring substituent is changed from strongly electron-donating to strongly electron-withdrawing.[9,10] If the transition states for these reactions are subject to increasing stabilization by nucleophilic solvation with increasing reactivity of the cumyl carbocation intermediates. then this effect should also be observed as a corresponding increase in the nucleophilic solvation of the fully-formed carbocations (**1**).

We report here equilibrium constants for formation of ring-substituted cumyl carbocations from the respective α-methylstyrenes in a largely aqueous solvent of 50:50 (v/v) trifluoroethanol/water and a comparison of these data with results from earlier studies on the relative stabilities of cumyl carbocations in the gas phase.[23] The correlation of the Gibbs free energy changes for formation of the cumyl carbocations in solution and in the gas phase is linear with a slope of 0.70. These data show that there is an increase in stabilization of ring-substituted cumyl carbocations by solvation with decreasing carbocation stability, part of which might be due to specific nucleophilic solvation.

Experimental Section

Materials. Inorganic acids and salts were reagent grade and were used without further purification. Chemicals for organic syntheses. 2-phenyl-2-propanol. α-methylstyrene, *p*-toluenesulfonic acid, 2,2,2-trifluoroethanol. and solvents for column chromatography were purchased from Aldrich and were used without further purification. The methanol for HPLC analyses (HPLC grade) was purchased from Fisher. and the water used for product and kinetic studies was distilled and then passed through a Milli-Q water purification system.

Organic Syntheses. ^1H NMR spectra at 200 MHz and ^{13}C NMR spectra at 75 MHz were recorded on Varian spectrometers using $CDCl_3$ as solvent.

Ring-substituted cumyl alcohols were prepared by reaction of the corresponding ethyl benzoates with methyl magnesium iodide in dry ether at 0 °C.[24] and ring-substituted α-methylstyrenes were prepared either by dehydration of the alcohol using *p*-toluenesulfonic acid as a catalyst[25] or by a Wittig reaction of the corresponding acetophenone with the anion of methyltriphenylphosphonium bromide.

Ring-substituted cumyl methyl ethers were synthesized by adaptation of the procedure for preparation of the unsubstituted cumyl methyl ether.[26] The ring-substituted cumyl alcohols (200 mg) were dissolved in 40 mL of methanol containing a specified amount of *p*-toluenesulfonic acid and the progress of the reaction was monitored by HPLC. After conversion of 50–80% of the alcohol to the methyl ether. and before the formation of a significant amount of α-methylstyrene. the reactions were quenched by the addition of a 10% excess of solid sodium acetate. and the methanol was evaporated. The residue was dissolved in ethyl ether which was then washed with brine and saturated $NaHCO_3$, dried with $MgSO_4$. and evaporated. Purification by column chromatography over 75 g of silica gel. eluting with 10% ethyl acetate/hexanes. gave the cumyl methyl ethers as colorless oils in greater than 99% purity. as determined by HPLC.

4-Methoxycumyl methyl ether was prepared in 75% yield using 1 mM *p*-toluenesulfonic acid and a 1 h reaction time at room temperature. ^1H NMR δ 1.55 (6H. s. CH_3). 3.08 (3H, s. CH_3O). 3.85 (3H. s. CH_3OAr), 6.9, 7.4 (4H, A_2B_2, $J = 9$ Hz, C_6H_4). ^{13}C NMR δ 159.18. 138.53. 127.59. 114.00 (Ar). 76.72 ($C(CH_3)_2$). 28.17 ($C(CH_3)_2$). 50.70 (OCH_3). 55.46 ($ArOCH_3$). Exact mass calcd for $C_{11}H_{16}O_2$, 180.1150: found. 180.1136. Anal. ($C_{11}H_{16}O_2$) C. H.

4-Methylthiocumyl methyl ether was prepared in 70% yield using 0.3 mM *p*-toluenesulfonic acid and a 1 h reaction time at room temperature. ^1H NMR δ 1.55 (6H. s. CH_3). 2.53 (3H. s, CH_3S), 3.10 (3H. s. CH_3O). 7.29 (4H. m. C_6H_4). ^{13}C NMR δ 143.60. 137.40. 127.12. 126.98 (Ar), 76.84 ($C(CH_3)_2$). 28.07 ($C(CH_3)_2$), 50.85 (OCH_3). 16.05 ($ArSCH_3$). Exact mass calcd for $C_{11}H_{16}OS$, 196.0922; found, 196.0934.

4-Methylcumyl methyl ether was prepared in 58% yield using 1 mM *p*-toluenesulfonic acid and a 2 h reaction time at room temperature. ^1H NMR δ 1.51 (6H. s, CH_3). 2.33 (3H. s. CH_3). 3.04 (3H, s. CH_3O), 7.2. 7.3 (4H. A_2B_2. $J = 8$ Hz. C_6H_4). ^{13}C NMR δ 143.57, 136.97. 129.50. 126.38 (Ar). 76.98 ($C(CH_3)_2$). 28.21 ($C(CH_3)_2$). 50.83 (OCH_3), 21.16 ($ArCH_3$). Exact ($M^+ - 15$) calcd for $C_{10}H_{13}O$, 149.0966; found, 149.0946. Anal. ($C_{11}H_{16}O$) C. H.

4-Fluorocumyl methyl ether was prepared in 51% yield using 1 mM *p*-toluenesulfonic acid and a 50 h reaction time at room temperature. ^1H NMR δ 1.49 (6H. s, CH_3). 3.03 (3H, s, CH_3O). 7.0–7.4 (4H. m. C_6H_4). ^{13}C NMR δ 162.46. 142.38. 128.00. 115.35 (Ar), 76.64 ($C(CH_3)_2$). 28.08 ($C(CH_3)_2$). 50.62 (OCH_3). Exact ($M^+ - 15$) calcd for $C_9H_{10}OF$. 153.0716: found, 153.0702. Anal. ($C_{10}H_{13}OF$) C, H.

3-Methoxycumyl methyl ether was prepared in 37% yield using 1 mM *p*-toluenesulfonic acid and a 20 h reaction time at room temperature. ^1H NMR δ 1.50 (6H. s. CH_3). 3.06 (3H, s. CH_3O). 3.80 (3H, s. CH_3OAr). 7.0–7.3 (4H, m. C_6H_4). ^{13}C NMR δ 160.40. 148.48. 129.74. 118.77. 112.42. 112.45 (Ar). 77.08 ($C(CH_3)_2$). 28.14 ($C(CH_3)_2$), 50.91 (OCH_3), 55.39 ($ArOCH_3$). Exact mass calcd for $C_{11}H_{16}O_2$, 180.1150: found, 180.1142.

3-Fluorocumyl methyl ether was prepared in 52% yield using 1 mM *p*-toluenesulfonic acid and a 2 h reaction time in refluxing methanol. ^1H NMR δ 1.49 (6H. s. CH_3). 3.06 (3 H. s. CH_3O). 6.9–7.3 (4H. m. C_6H_4). ^{13}C NMR δ 163.73, 149.78, 130.22. 121.87, 114.15. 113.44 (Ar), 76.85 ($C(CH_3)_2$), 27.99 ($C(CH_3)_2$), 50.90 (OCH_3). Exact ($M^+ - 15$) calcd for $C_9H_{10}OF$. 153.0716; found 153.0703.

HPLC Product Analyses. The cumyl trifluoroethyl ether products of the solvolyses of the corresponding cumyl alcohols or cumyl methyl ethers were identified as described in previous work.[27-29] The α-methylstyrene products of elimination reactions were identified by showing that their retention times are identical with those of authentic samples.

Unless stated otherwise, the reactants and products were cleanly separated by HPLC as described previously[27-29] and were detected by their UV absorbance at the following wavelengths. which are λ_{max}. or close to λ_{max}. for the corresponding ring-substituted cumyl alcohols: 4-methoxycumyl derivatives, 273 nm: 4-methylthiocumyl derivatives. 260 nm ($\lambda_{max} = 255$ nm): 4-methylcumyl derivatives, 263 nm; 4-fluorocumyl

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derivatives, 264 nm; cumyl derivatives. 258 nm: 3-methoxycumyl derivatives. 272 nm: 3-fluorocumyl derivatives. 268 nm (λ_{max} = 262 nm). The following ratios of extinction coefficients ($\epsilon_{alk}/\epsilon_{ROH}$) for ring-substituted α-methylstyrenes and the corresponding cumyl alcohols were determined at the above wavelengths by UV spectroscopy (ring substituent. $\epsilon_{alk}/\epsilon_{ROH}$): 4-MeO. 3.9: 4-MeS. 0.59: 4-Me. 23; 4-F. 3.6; 4-H. 34;[26] 3-MeO. 0.93; 3-F. 2.9. The extinction coefficients of the ring-substituted cumyl alcohols at the above wavelengths were shown to be identical with those of the corresponding cumyl trifluoroethyl ethers by the observation of equal and opposite changes in the areas (normalized using an internal injection standard) of the growing peak for the trifluoroethyl ether and the shrinking peak for the cumyl alcohol during the acid-catalyzed conversion of the alcohols to the trifluoroethyl ethers.

Product Studies. The reactions of ring-substituted cumyl methyl ethers at 22 ± 2 °C were initiated by injection of 30 μL of a solution of substrate (0.1–0.2 M) in acetonitrile into 3.0 mL of 50:50 (v/v) trifluoroethanol/water (I = 0.50. $NaClO_4$) containing the following concentrations of perchloric acid: 4-methoxycumyl methyl ether. 5 × 10^{-4} M; 4-methylthiocumyl methyl ether. 5 × 10^{-4} M; 4-methylcumyl methyl ether. 0.005 M; 4-fluorocumyl methyl ether, 0.25 M: 3-methoxycumyl methyl ether, 0.25 M: 3-fluorocumyl methyl ether. 0.25 M. The reaction products were analyzed by HPLC at least twice during the first 20% of the reaction of the methyl ether. and the product ratios were found to be constant during this time. The fractional yield of the trifluoroethanol adduct (f_{ROTFE}) was determined using eq 1. where A_{ROH} and A_{ROTFE} are the peak areas for the water and trifluoroethanol adducts, respectively, obtained from HPLC analysis. The yields of ring-substituted α-methylstyrenes obtained from deprotonation of the corresponding ring-substituted cumyl carbocations were less than 1%.

$$f_{ROTFE} = A_{ROTFE}/(A_{ROTFE} + A_{ROH}) \qquad (1)$$

Acid-catalyzed equilibration of ring-substituted cumyl alcohols. trifluoroethyl ethers. and α-methylstyrenes at 22 ± 2 °C was initiated by injection of 30 μL of a solution of substrate (0.1–0.2 M) in acetonitrile into 3.0 mL of 50:50 (v/v) trifluoroethanol/water (I = 0.50, $NaClO_4$) containing perchloric acid and a stable internal injection standard. The relative concentrations of the reaction products were determined by HPLC analysis. Chemical equilibrium was first established between the ring-substituted cumyl alcohol [ROH] and trifluoroethyl ether [ROTFE]. and at very long times (*ca.* 3 days) equilibrium was established between the solvent adducts and the α-methylstyrenes. The ratios of the equilibrium concentrations of the ring-substituted cumyl alcohols and trifluoroethyl ethers were calculated directly from the ratio of peak areas obtained from HPLC analysis ($[ROH]_{eq}/[ROTFE]_{eq} = (A_\infty)_{ROH}/(A_\infty)_{ROTFE}$). because the two adducts have identical extinction coefficients at the wavelengths used for HPLC analysis. The ratios of the equilibrium concentrations of the ring-substituted α-methylstyrenes and the corresponding cumyl alcohols were determined from the ratio of peak areas obtained from HPLC analysis ($(A_\infty)_{alk}/(A_\infty)_{ROH}$) and the ratio of the extinction coefficients of these products at the wavelengths used for HPLC analysis (eq 2).

$$[\text{alkene}]_{eq}/[ROH]_{eq} = [(A_\infty)_{alk}/(A_\infty)_{ROH}][\epsilon_{ROH}/\epsilon_{alk}] \qquad (2)$$

Equilibrium constants for interconversion of the solvent adducts (K_{TFE}. Scheme 1) and the cumyl alcohol and α-methylstyrene (K_{alk}. Scheme 3) were calculated from eqs 3 and 4. respectively.

$$K_{TFE} = [ROTFE]_{eq}[HOH]/[ROH]_{eq}[CF_3CH_2OH] \qquad (3)$$

$$K_{alk} = [\text{alkene}]_{eq}/[ROH]_{eq} \qquad (4)$$

Kinetic Studies. The acid-catalyzed reactions of ring-substituted cumyl alcohols at 25 °C were initiated by injection of 30 μL of a solution of substrate (0.1–0.2 M) in acetonitrile into 3.0 mL of 50:50 (v/v) trifluoroethanol/water (I = 0.50. $NaClO_4$) containing perchloric acid and a stable internal injection standard. The conversion of the alcohol into the trifluoroethyl ether was followed by monitoring the appearance of the ether by HPLC. Pseudo-first-order rate constants. k_{obsd} (s^{-1}). were obtained as the slopes of semilogarithmic plots of $(A_\infty)_{ROTFE} - A_{ROTFE}$ against time. where $(A_\infty)_{ROTFE}$ is the area of the peak for the trifluoroethyl ether at chemical equilibrium between the alcohol and the trifluoroethyl ether. The endpoint $(A_\infty)_{ROTFE}$ was stable on the time scale for interconversion of the cumyl alcohol and trifluoroethyl ether. However, a decrease in the concentration of both solvent adducts was observed as equilibrium was established with the α-methylstyrene over a much longer time scale.

Table 1. Rate and Equilibrium Constants for Reactions of Ring-Substituted Cumyl Alcohols in Acidic Solutions of 50:50 (v/v) Trifluoroethanol/Water at 25 °C (I = 0.50, $NaClO_4$)

ring substituent	K_{TFE}[a]	f_{ROTFE}[b]	$(k_H)_{obsd}$[c,d] ($M^{-1}\ s^{-1}$)	k_H[e] ($M^{-1}\ s^{-1}$)
4-MeO	1.04	0.08	1.78	11.3
4-MeS	1.01	0.10	0.22	1.1
4-Me	0.66	0.11	0.16	0.58
4-F	0.68	0.11	7.9 × 10^{-3}	0.029
4-H	0.68	0.16[f]		7.3 × 10^{-3} [f]
3-MeO	0.93	0.20	2.8 × 10^{-3}	6.7 × 10^{-3}
3-F	0.86	0.18	1.2 × 10^{-4}	3.1 × 10^{-4}

[a] Equilibrium constants for acid-catalyzed interconversion of the ring-substituted cumyl alcohol and trifluoroethyl ether. [b] Fractional yield of the trifluoroethyl ether from reaction of the corresponding methyl ether in 50:50 (v/v) trifluoroethanol/water at 25 °C (I = 0.50. $NaClO_4$). [c] Second-order rate constant for acid-catalyzed conversion of the ring-substituted cumyl alcohol to an equilibrium mixture of the cumyl alcohol and trifluoroethyl ether. [d] The slope of a four-point plot of k_{obsd} against $[H^+]$. [e] Second-order rate constants for acid-catalyzed conversion of ring-substituted cumyl alcohols to cumyl carbocations. [f] Data from ref 26.

Observed second-order rate constants, $(k_H)_{obsd}$ ($M^{-1}\ s^{-1}$). for conversion of the cumyl alcohols to an equilibrium mixture of the alcohol and trifluoroethyl ether were determined as the slopes of four-point plots of k_{obsd} against $[H^+]$ using the following ranges of $[HClO_4]$: 4-methoxycumyl alcohol, 5 × 10^{-4} – 5 × 10^{-3} M: 4-methylthiocumyl alcohol and 4-methylcumyl alcohol. 0.005–0.05 M: 4-fluorocumyl alcohol. 3-methoxycumyl alcohol, and 3-fluorocumyl alcohol. 0.05–0.50 M.

Results

Observed second-order rate constants, $(k_H)_{obsd}$ ($M^{-1}\ s^{-1}$), for the acid-catalyzed conversion of ring-substituted cumyl alcohols to an equilibrium mixture of the alcohol and trifluoroethyl ether in 50:50 (v/v) trifluoroethanol/water at 25 °C (I = 0.50, $NaClO_4$) are reported in Table 1.

Scheme 1

$$\mathrm{ROH} \underset{(k_H)_{HOH}[H^+]}{\overset{(k_H)_{TFE}[H^+]}{\rightleftharpoons}} \mathrm{ROTFE}$$

$$(k_H)_{TFE} = (k_H)_{obsd}K_{TFE}/(1 + K_{TFE}) \qquad (5)$$

Equilibrium constants. K_{TFE} (Scheme 1), for the acid-catalyzed interconversion of ring-substituted cumyl alcohols and trifluoroethyl ethers in 50:50 (v/v) trifluoroethanol/water at 25 °C (I = 0.50, $NaClO_4$), determined by HPLC analysis of product concentrations at chemical equilibrium, are reported in Table 1. Second-order rate constants, $(k_H)_{TFE}$ ($M^{-1}\ s^{-1}$, not listed), for conversion of ring-substituted cumyl alcohols to the corresponding trifluoroethyl ethers (Scheme 1) were calculated from the values of $(k_H)_{obsd}$ and K_{TFE} using eq 5.

The significance of the net rate constant $(k_H)_{TFE}$ for conversion of ring-substituted cumyl alcohols to the corresponding cumyl trifluoroethyl ethers depends upon the mechanism for this reaction.

Scheme 2

$$\mathrm{ROH} \underset{k_{HOH}[HOH]}{\overset{k_H[H^+]}{\rightleftharpoons}} R^+ \xrightarrow{k_{TFE}[CF_3CH_2OH]} \mathrm{ROTFE}$$

$$k_H = (k_H)_{TFE}(1/f_{ROTFE}) \qquad (6)$$

In 50:50 (v/v) trifluoroethanol/water the solvolysis reactions of ring-substituted cumyl benzoates and chlorides proceed by a stepwise mechanism through liberated carbocation intermedi-

Table 2. Kinetic and Thermodynamic Data for the Formation and Reaction of Ring-Substituted Cumyl Carbocations in Acidic Solutions of 50:50 (v/v) Trifluoroethanol/Water[a]

ring substituent	k_{HOH} (M^{-1} s^{-1})	K_{alk}[c]	K_R[d] (M)	K_P[e] (M)	$(\Delta G_X)_{sol}$[f] (kcal/mol)	$(\Delta G_X)_{gas}$[g] (kcal/mol)
4-MeO	3.4×10^5 [b]	0.13	8.4×10^5	1.1×10^5	8.5	10.5
4-MeS	7.5×10^5 [b]	0.11	1.9×10^7	2.1×10^6	6.8	10.0
4-Me	3.2×10^7 [b]	0.092	1.5×10^9	1.4×10^8	4.3	4.1
4-F	1.4×10^8 [b]	0.087	1.3×10^{11}	1.1×10^{10}	1.7	–0.1
4-H	5.0×10^8 [h]	0.11	1.9×10^{12} [i]	2.1×10^{11}	0	0
3-MeO	1.1×10^9 [h]	0.083	4.6×10^{12}	3.8×10^{11}	–0.3	2.1
3-F	4.3×10^9 [h]	0.077	3.9×10^{14}	3.0×10^{13}	–2.9	–5.1

[a] At 25 °C ($I = 0.50$. $NaClO_4$). [b] Estimated second-order rate constant for reaction of the cumyl carbocation with water. see text. [c] Equilibrium constants for conversion of ring-substituted cumyl alcohols to the corresponding α-methylstyrenes in the presence of 0.50 M $HClO_4$. [d] $K_R = (k_{HOH}/k_H)$ 27.8 M. [e] $K_P = K_R K_{alk}$. [f] $(\Delta G_X)_{sol} = -RT \ln[(K_P)_X/(K_P)_H]$. [g] Data from ref 23. [h] Extrapolated from a Yukawa–Tsuno correlation of the data for the less reactive carbocations. see text. [i] Data from ref 26.

ates.[30] and the same mechanism is assumed here for the acid-catalyzed solvolyses of ring-substituted cumyl alcohols (Scheme 2). A more detailed justification for this assumption is given in the Discussion. Equation 6, derived for Scheme 2. defines the relationship between the experimental second-order rate constants (k_H)TFE (M^{-1} s^{-1}) and the second-order rate constants k_H (M^{-1} s^{-1}) for acid-catalyzed cleavage of ring-substituted cumyl alcohols to form the corresponding cumyl carbocations. The rate constant for ionization of these substrates is larger than $(k_H)_{TFE}$, because most ionization steps are nonproductive and lead not to the formation of trifluoroethyl ether (k_{TFE}, Scheme 2) but to regeneration of the substrate by capture of the cumyl carbocation by water (k_{HOH}). The fraction of the intermediate that reacts with trifluoroethanol in 50:50 (v/v) trifluoroethanol/water (f_{ROTFE}, Table 1) was determined as the fractional yield of the trifluoroethyl ether obtained in the perchloric acid-catalyzed reactions of ring-substituted cumyl methyl ethers in this solvent (eq 1). Values of k_H (M^{-1} s^{-1}, Scheme 2), calculated from $(k_H)_{TFE}$ and f_{ROTFE} using eq 6, are reported in Table 1. The data for the formation of the unsubstituted cumyl carbocation were taken from earlier work.[26]

Equilibrium is established between ring-substituted cumyl alcohols and the corresponding trifluoroethyl ethers in acidic solutions of 50:50 (v/v) trifluoroethanol/water before accumulation of a significant amount of the α-methylstyrene: a much longer period of time is required for the solvent adducts to reach equilibrium with the alkene. Equilibrium constants K_{alk} (Scheme 3) for conversion of ring-substituted cumyl alcohols to the corresponding α-methylstyrenes in 50:50 (v/v) trifluoroethanol/water containing 0.50 M $HClO_4$ were calculated from the ratio of the concentrations of these compounds at chemical equilibrium (eq 4) and are listed in Table 2.

Discussion

Reaction Mechanism. In acidic solutions of 50:50 (v/v) trifluoroethanol/water ($I = 0.50$, $NaClO_4$), ring-substituted cumyl alcohols are readily converted to an equilibrium mixture of the alcohol and the corresponding trifluoroethyl ether. The following observations from earlier work provide good evidence that this reaction proceeds by a stepwise mechanism through ring-substituted cumyl carbocation intermediates.

(1) A stepwise mechanism through the 1-phenylethyl carbocation intermediate has been observed for acid-catalyzed exchange of $H_2{}^{18}O$ into enantiomerically pure 1-phenylethyl alcohol.[31,32] The stepwise mechanism is even more favorable for the reaction of cumyl alcohol. because of the greater stability of the cumyl carbocation reaction intermediate and the greater steric hindrance to the concerted bimolecular substitution reaction.

(2) The nucleophilic substitution reactions of azide ion with ring-substituted cumyl 4-nitrobenzoates, 3,5-dinitrobenzoates, pentafluorobenzoates, and chlorides to form the corresponding azide ion adducts are zero order in the concentration of azide ion.[30] This is classical evidence for a two-step reaction mechanism through a carbocation intermediate. The same mechanism should be followed for the acid-catalyzed solvolyses of cumyl alcohols, because the driving force for a concerted reaction is considerably smaller for solvent, which is weakly nucleophilic, than for the strong nucleophile azide ion.

Only very small yields of ring-substituted α-methylstyrenes (<1%) are obtained from deprotonation of the cumyl carbocation intermediates of acid-catalyzed solvolysis of the corresponding methyl ethers in 50:50 (v/v) trifluoroethanol/water. but much larger yields are obtained at chemical equilibrium. This shows that only part of the difference in the kinetic barriers for the reaction of water with cumyl carbocations as a nucleophile and as a Bronsted base can be accounted for by a difference in the thermodynamic driving force for these reactions, and that there must also be a larger intrinsic kinetic barrier to the latter reaction. The observation that equilibrium *between* solvent adducts to ring-substituted cumyl carbocations is established much more rapidly than equilibrium of the solvent adducts with the corresponding α-methylstyrenes is also consistent with a relatively large intrinsic kinetic barrier for proton transfer reactions at the α-carbon compared with the barrier to nucleophilic addition/cleavage reactions at the benzylic carbon. We are uncertain of the explanation for this difference in intrinsic kinetic barriers.

Rate and Equilibrium Constants. The methods for determination of the equilibrium constants for the reactions of ring-substituted cumyl carbocations in solution are similar to those reported in earlier work for the reactions of ring-substituted 1-phenylethyl carbocations[27] and for the reactions of benzyl, benzhydryl, and fluorenyl carbocations.[26]

(1) Second-order rate constants. k_H (M^{-1} s^{-1}, Table 1), for specific acid-catalyzed cleavage of cumyl alcohols to form the corresponding cumyl carbocations were determined by first measuring the observed second-order rate constants, $(k_H)_{obsd}$ (M^{-1} s^{-1}), for nucleophilic substitution by trifluoroethanol at the cumyl alcohols and then correcting these data for (a) the fraction of cumyl alcohol that remains at chemical equilibrium (eq 5. Scheme 1) and (b) the fraction of times that carbocation formation generates the trifluoroethanol adduct (f_{ROTFE}, eq 6, Scheme 2). The size of this correction changes by only 2.5-fold on moving from the most reactive to the least reactive ring-substituted cumyl alcohol (Table 1).

(2) Second-order rate constants. k_{HOH} (M^{-1} s^{-1}). for reaction of ring-substituted cumyl carbocations with water in the mixed solvent of 50:50 (v/v) trifluoroethanol/water, calculated from data reported previously.[30] are given in Table 2. Most of these rate constants were determined from product rate constant ratios k_{az}/k_{HOH} (M^{-1}) for partitioning of carbocations between capture by azide ion and by water[30] and $k_{az} = 5 \times 10^9$ M^{-1} s^{-1} for the

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(30) Richard, J. P.; Amyes, T. L.; Vontor, T. *J. Am. Chem. Soc.* **1991**, *113*, 5871–5873.

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

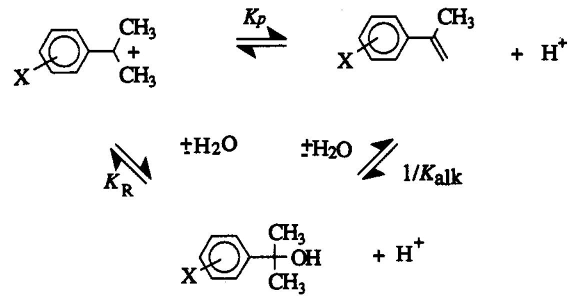
(32) Merritt, M. V.; Bell, S. J.; Cheon, H.-J.; Darlington, J. A.; Dugger, T. L.; Elliot, N. B.; Fairbrother, G. L.; Melendez, C. S.; Smith, E. V.; Swartz, P. L. *J. Am. Chem. Soc.* **1990**, *112*. 3560–3566.

diffusion-limited reaction of azide ion.[27,33,34] A value of k_{az} = 3.9 × 10^9 M^{-1} s^{-1} has been determined in 98:2 (v/v) trifluoroethanol/water by direct measurement of the decay of the 4-methoxycumyl carbocation generated by photoprotonation of 4-methoxy-α-methylstyrene.[35] The difference between this value of k_{az} for reaction of the 4-methoxycumyl carbocation and k_{az} = (5–6) × 10^9 M^{-1} s^{-1} determined for reaction of a variety of more unstable α-substituted 4-methoxybenzyl carbocations in 98:2 (v/v) trifluoroethanol/water[35] is consistent with a small chemical barrier for capture of the former carbocation by azide ion. The value of k_{HOH} (M^{-1} s^{-1}) for reaction of the 4-methoxycumyl carbocation (Table II) was therefore calculated using the slightly smaller value of k_{az} = 3.9 × 10^9 M^{-1} s^{-1}. Rate constants k_{HOH} (M^{-1} s^{-1}) for reaction of the 4-H-, 3-MeO-, and 3-F-substituted cumyl carbocations were determined by extrapolation of a fit of the data in Table 2 for the less reactive carbocations to the Yukawa–Tsuno equation.[36] The magnitude of the extrapolation (1.4 log units) is significantly smaller than the range of values of k_{HOH} covered by the original correlation (2.5 log units).

(3) Equilibrium constants K_R (Scheme 3, Table 2) for reaction of ring-substituted cumyl carbocations with water were calculated using eq 7. where 27.8 M is the concentration of water in 50:50 (v/v) trifluoroethanol/water.

$$K_R = (k_{HOH}/k_H)27.8\ M \qquad (7)$$

Scheme 3



$$K_P = K_R K_{alk} \qquad (8)$$

$$(\Delta G_X)_{sol} = -RT\ln[(K_P)_X/(K_P)_H] \qquad (9)$$

(4) Equilibrium constants K_{alk} (Scheme 3, Table 2) for interconversion of ring-substituted α-methylstyrenes and cumyl alcohols in acidic solutions of 50:50 (v/v) trifluoroethanol/water were determined from the ratio of the concentrations of the alkene and alcohol at chemical equilibrium (eq 4). The value of K_{alk} = 0.13 for formation of 4-methoxy-α-methylstyrene in 50:50 (v/v) trifluoroethanol/water is close to the earlier reported value of 0.09 for reaction in 4.8% sulfuric acid in water.[24]

(5) Equilibrium constants K_P (Scheme 3, Table 2) for proton transfer from ring-substituted cumyl carbocations to water to form the corresponding α-methylstyrenes were calculated from the values of K_R and K_{alk} using eq 8. Gibbs free energy changes [$(\Delta G_X)_{sol}$, Scheme 4] for proton transfer from ring-substituted cumyl carbocations ($XC_6H_4C(CH_3)_2^+$) to α-methylstyrene were calculated using eq 9. The Gibbs free energy changes for these reactions in the gas phase [$(\Delta G_X)_{gas}$]. determined by measurement of the relative concentrations of $XC_6H_4C(CH_3)_2^+$ and $C_6H_5C(CH_3)_2^+$ at chemical equilibrium with the corresponding α-methylstyrenes by pulsed ion cyclotron resonance mass spectrometry,[23] are given in Table 2.

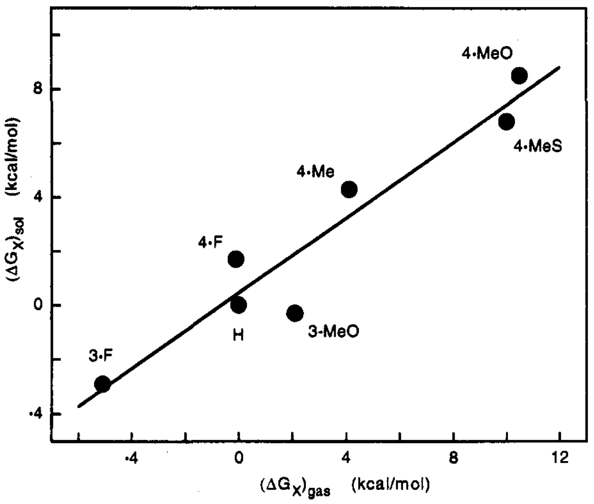


Figure 1. Correlation of the Gibbs free energies for deprotonation of ring-substituted cumyl carbocations by α-methylstyrene in the gas phase with those for the same reaction in 50:50 (v/v) trifluoroethanol/water.

Substituent Effects on Cumyl Carbocation Stability in the Gas Phase and in Solution. The derived Gibbs free energy changes for proton transfer from ring-substituted cumyl carbocations to α-methylstyrene in the largely aqueous (80 mol %) solvent of 50:50 (v/v) trifluoroethanol/water [$(\Delta G_X)_{sol}$, eq 9] are plotted in Figure 1 against the free energy changes for the same reaction in the gas phase [$(\Delta G_X)_{gas}$]. The slope of the correlation in Figure 1 will lie between zero and 1.0, provided the substituent effects are dominated by interactions between the ring substituent X and the delocalized positive charge, because this interaction is maximal in a vacuum with a dielectric constant of 1.0, and it will be attenuated in solvents of higher dielectric constant. The observed slope of 0.70 shows that 70% of the gas-phase-substituent effects are maintained for the reaction in 50:50 (v/v) trifluoroethanol/water and is consistent with a significant attenuation of these substituent effects by solvation. We prefer the plot in Figure 1 to one which reverses the labels of the x- and y-axes [a plot of $(\Delta G_X)_{gas}$ against $(\Delta G_X)_{sol}$],[17,18] because the slope in Figure 1 provides a direct measure of the fractional attenuation by solvent of the gas-phase-substituent effects.

Data for the effect of changing ring substituent on the stability of cumyl carbocations in the gas phase show a good fit to Hammett substiuent constants σ^+;[23b] and the correlation between gas phase and solution date (Figure 1) requires that the solution reactions also correlate with σ^+.

The 3-MeO substituent for which σ = 0.12 is expected to destabilize the unsubstituted cumyl carbocation toward proton transfer to α-methylstyrene. This substituent causes weak destabilization of the cumyl carbocation in solution, but in the gas phase it stabilizes the cation by 2.1 kcal/mol relative to α-methylstyrene (Table 2), so that the point for the 3-MeO substituent shows a significant negative deviation from the correlation line in Figure 1. The cause for this deviation is not understood. but it may be unrelated to solvent attenuation of gas-phase-substituent effects (see below). Such attenuation would reduce the magnitude of the 3-MeO-substituent effect. but it should not cause the effect of the 3-MeO substituent to change from carbocation-stabilizing compared with 4-H in the gas phase to carbocation-destabilizing in solution.[37]

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(33) McClelland, R. A.; Kanagasabapathy, V. M.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 6913–6914.

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(35) McClelland, R. A.; Cozens, F. L.; Steenken, S.; Amyes, T. L.; Richard, J. P. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1717–1722.

(36) The values of k_{HOH} for the 4-MeO; 4-MeS; 4-Me-, and 4-F-substituted cumyl carbocations given in Table 2 together with that for the 4-phenoxycumyl carbocation (k_{HOH} = 2.1 × 10^6 M^{-1} s^{-1})[30] show a good fit (r = 0.999) to the Yukawa–Tsuno equation [Yukawa, Y.; Tsuno, Y.; Sawada, M. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2274–2286] with values of ρ^n = 2.7 and r^+ = 1.6. These parameters are similar to the values of ρ^n = 2.7 and r^+ = 1.8 determined for the capture of ring-substituted 1-phenylethyl carbocations by 50:50 (v/v) trifluoroethanol/water.[27]

(37) The slope of the linear correlation in Figure 1 changes slightly from 0.70 to 0.68 if data for the 3-MeO-substituted cumyl carbocation are omitted.

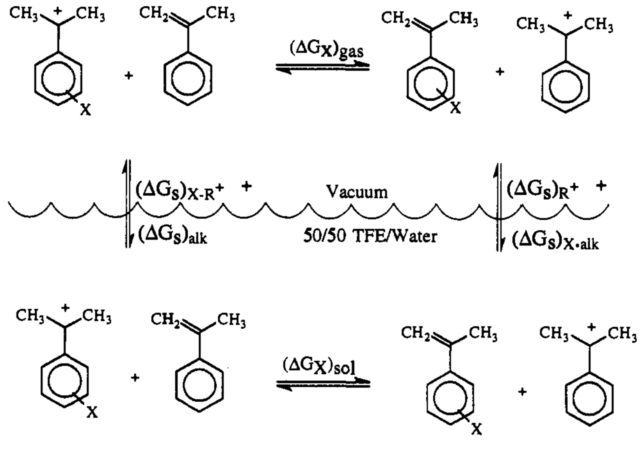
Comparison with Earlier Data. The correlation of enthalpies of formation of carbocations from neutral chloride adducts in SO_2ClF against the enthalpies for carbocation formation from alkanes in the gas phase has a slope of about 1. Several systematic deviations from this correlation were noted, but these were not sufficiently large as to affect the conclusion that "*in solvents of sufficiently low nucleophilicity there is very little differential solvation of carbonium ions or their ion pairs*".[14] The correlation of free energies of formation of carbocations from the corresponding alcohols in the nucleophilic solvent water against free energies for their formation in the gas phase by proton transfer between the hexamethyl cyclohexadienyl carbocation and the corresponding alkenes has a slope of 0.83, but it was concluded that this "*is not significantly different from unity in view of uncertainties in acidity function behavior (for the solution reactions)*".[18]

By contrast, the slope of 0.70 for the plot in Figure 1 of data for reaction of ring-substituted cumyl carbocations is significantly different from 1.0. even after consideration of the cumulative experimental errors in the calculation of the equilibrium constants K_P for the solution reaction.[38] The greatest uncertainty in this analysis lies in the values of k_{HOH} ($M^{-1}\,s^{-1}$) for reaction of unstable cumyl carbocations with water. obtained by extrapolation of the linear Yukawa–Tsuno relationship of data for the more stable carbocations.[36] These and the derived values of K_P are upper limits. because the true values of k_{HOH} for addition of water to the more reactive carbocations could show a negative deviation from the Yukawa–Tsuno relationship due to a Hammond-type shift to an earlier reaction transition state.[39] Such an error would lead to a *decrease* in the slope of the correlation shown in Figure 1. We conclude that the substituent effects on the relative stability of cumyl carbocations are significantly smaller in 50:50 (v/v) trifluoroethanol/water than in the gas phase.

These results are consistent with modest attenuation by solvent of gas-phase-substituent effects on carbocation stability: and they suggest that the difference between the slope of 1.0 reported earlier for the correlation of *enthalpies* for carbocation formation in SO_2ClF[14] and the slope of 0.83 for the correlation of *Gibbs free energies* of carbocation formation in water[18] is significant. This difference may reflect a large contribution of an entropic term to differential carbocation solvation due (possibly) to the tendency of charge-dipole interactions between carbocations and solvent to increase solvent order in the first few solvation spheres, and/or to the relatively poor solvation of carbocations by the weakly nucleophilic solvent SO_2ClF.[44] In conclusion, our results do not conflict with earlier conclusions that interactions between carbocations and solvent are weak but. rather. show that such interactions are not insignificant.

Solvent Effects on Cumyl Carbocation Stability. Equation 10 derived for Scheme 4 gives the relationship between the difference in the effect of ring substituents X on the change in Gibbs free energy for proton transfer between cumyl carbocations and α-methylstyrene in 50:50 (v/v) trifluoroethanol/water and in the gas phase $[(\Delta G_X)_{gas} - (\Delta G_X)_{sol}]$ and the effect of X on the solubility of the reactants and products in aqueous trifluoroethanol. The larger substituent effects on ΔG_X for the gas phase than for the solution reaction ($|(\Delta G_X)_{gas} - (\Delta G_X)_{sol}| > 0$) are due primarily to changes in the solubility of the charged cumyl carbocations $[(\Delta G_S)_{X\text{-}R^+} - (\Delta G_S)_{R^+})]$, rather than the solubility of the α-methylstyrenes. This is because interactions of the polar solvent with charged carbocations are much stronger than those with neutral molecules, so that the changes in these interactions with changing ring substituent should also be largest when the substituent is attached to a charged ion. Furthermore, specific solvation of a substituent at α-methylstyrene will only result in a solvent-perturbation of the equilibrium in Scheme 4 when there is a *change* in the solvation of the substituent at the cumyl carbocation. This is unlikely unless positive charge is delocalized onto the ring substituent at the cation, in which case the solvent perturbation of the equilibrium (Scheme 4) will again be dominated by the substituent effect on the solubility of the charged ion.

Scheme 4



$$(\Delta G_X)_{gas} - (\Delta G_X)_{sol} = = [(\Delta G_S)_{X\text{-}R^+} - (\Delta G_S)_{R^+})] + [(\Delta G_S)_{alk} - (\Delta G_S)_{X\text{-}alk})] \quad (10)$$

The correlation in Figure 1 includes data for a substituent which destablilizes the cumyl carbocation by field and/or inductive effects (3-F: $[(\Delta G_X)_{gas} - (\Delta G_X)_{sol}] \approx [(\Delta G_S)_{X\text{-}R^+} - (\Delta G_S)_{R^+})] \approx -2.2$ kcal/mol, Table 2) and for substituents that stabilize the cumyl carbocation by a resonance effect (4-MeS and 4-MeO: $[(\Delta G_X)_{gas} - (\Delta G_X)_{sol}] \approx [(\Delta G_S)_{X\text{-}R^+} - (\Delta G_S)_{R^+})] \approx 3.2$ and 2.0 kcal/mol, respectively). The solvent attenuation of these polar and resonance substituent effects may be due to the effect of the change from a vacuum to a solvent of high dielectric constant and/or to the effect of nucleophilic solvation (see **1**).

(1) The polar effect of the electron-withdrawing 3-F substituent favors transfer of the 3-fluorocumyl carbocation from the gas phase to aqueous trifluoroethanol relative to transfer of the cumyl carbocation. This must be due, in part. to reduction in the destabilizing electrostatic interactions between the positive charge at the benzylic position of the carbocation and the positive end of the dipole of the 3-F substituent upon transfer to the solvent of high dielectric constant. However, these interactions might also be relieved by nucleophilic solvation (see **1**), or by the formation of a hydrogen bond between solvent and a hydrogen on the α-methyl group of the carbocation. Both of these would lead to the transfer of charge density onto solvent and thus to increased separation of the interacting charge and dipole.

(2) The resonance electron-donating 4-MeO and 4-MeS substituents cause transfer of these resonance-stabilized cumyl carbocations from the gas phase to aqueous trifluoroethanol to become unfavorable relative to the transfer of the cumyl carbocation, because of solvent attenuation of the resonance substituent effect. This may be due to the tendency of charge-dipole interactions between the carbocation and solvent to favor localization of positive charge at the benzylic carbon and hence to attenuate charge delocalization onto the aromatic ring substituent, to nucleophilic solvation at the benzylic carbon (see **1**) which would cause a decrease in the stabilization of the

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(38) Equilibrium constants K_P were calculated from eq 13.

$$K_P = \frac{K_{alk} f_{ROTFE}(1 + K_{TFE}) k_{HOH}(27.8\ M)}{(k_H)_{obsd} K_{TFE}} \quad (13)$$

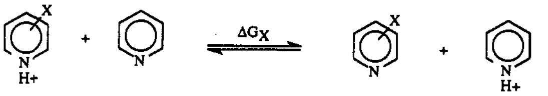
The estimated cumulative error in K_P is ±120% assuming liberal errors of ±20% for each of the experimental values in eq 13. By contrast, an error of >2500% in the individual values of K_P would be required to obtain a unitary slope for the plot in Figure 1.

(39) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334–338.

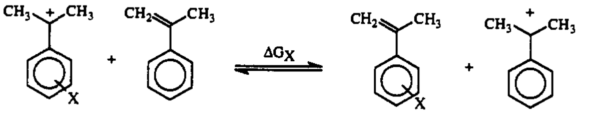
carbocation by electron donation from the ring substituent, or to other effects.

Our data do not permit a detailed analysis of the relative contributions of the effects of decreased polar interactions and substrate polarizability in a solvent of high dielectric constant and of nucleophilic solvation to the observed attenuation of the effects of ring substituents on the stability of cumyl carbocations in aqueous trifluoroethanol. However, a comparison of the gas phase and solution substituent effects on the relative stability of these cumyl carbocations with similar data for the deprotonation of ring-substituted pyridinium and anilinium ions shows that the Lewis base-type interaction (nucleophilic solvation) of solvent with cumyl carbocations is considerably weaker than the Brønsted base-type interaction (solvation by hydrogen bonding) of solvent with pyridinium and anilinium ions.

(1) The plot of $(\Delta G_X)_{sol}$ for deprotonation of ring-substituted pyridinium ions by pyridine (eq 11) in solution against $(\Delta G_X)_{gas}$ for the same reaction in the gas phase has a slope of 0.40 which is much smaller than the slope of 0.70 for the corresponding plot for deprotonation of ring-substituted cumyl carbocations by α-methylstyrene (eq 12).[40,41]



(11)



(12)

(2) Proton transfer between the 3-fluorocumyl carbocation and α-methylstyrene is more favorable by 2.2 kcal/mol in the gas phase than in aqueous trifluoroethanol (Table 2), but proton transfer between the 3-fluoroanilinium ion and aniline is only 1.4 kcal/mol more favorable in the gas phase than in water.[41]

A simple explanation for the larger solvent attenuation of substituent effects on proton transfer between nitrogen acids and bases than of those on proton transfer between carbon acids and bases is that it reflects the greater covalent character, and the resulting transfer of charge onto solvent, for hydrogen bonds between solvent and pyridinium and anilinium ions than of nucleophilic solvation of carbocations (see **1**). This is consistent with earlier conclusions that solvation of carbocations is weaker than solvation of Brønsted acids in which an acidic proton forms a hydrogen bond to solvent.

Water acts as a donor and acceptor, respectively, in hydrogen bonds with pyridine and the pyridinium ions. Both types of hydrogen bonds should contribute to the large solvent attenuation of substituent effects on deprotonation of ring-substituted pyridinium ions (eq 11), because each acts to reduce the magnitude of polar substituent effects by decreasing the change in effective charge that interacts with the ring substituent on moving from the substituted pyridinium ion (reactant) to the neutral free base (product).

Effect of Nucleophilic Solvation on Organic Reactivity. The total change in $(\Delta G_X)_{gas}$ on moving from strongly electron-donating to strongly electron-withdrawing substituents is (4–5) kcal/mol larger than the change in $(\Delta G_X)_{sol}$ over the same range of substituents (Table 2). This shows that there is a (4–5) kcal/mol increase in the stabilization of the carbocations by solvation with decreasing carbocation stability, assuming that the substituent effects on the solubility of ring-substituted α-methylstyrenes are negligible (see above). These data are consistent with the proposal that nucleophilic solvation (see **1**) provides increasing stabilization of the transition state for solvolysis of ring-substituted cumyl derivatives as the ring substituent is changed from strongly electron-donating to electron-withdrawing.[9,10] However, part of all of the (4–5) kcal/mol change in the stabilization provided by solvation may be due simply to the attenuation of polar substituent effects by the solvent of high dielectric constant, in which case stabilization of these carbocations by nucleophilic solvation would be very weak. Furthermore, it is unclear whether the observed deviations from linear free energy relationships for the solvolysis reactions of ring-substituted cumyl derivatives[9,10] are in fact due to nucleophilic assistance to ionization of the substrates, because there is no assistance to ionization of these substrates by the very strong nucleophiles azide ion and 1-propanethiol.[30]

The results of this work and (to the best of our knowledge) all previous experimental investigations of substituent effects on carbocation stability in the gas phase and in solution show that Lewis base-type stabilization of carbocations by nucleophilic solvation is much weaker than the solvation of Brønsted acids and bases by formation of hydrogen bonds between electronegative atoms. Therefore, while the fraction of the total (*ca.* 50 kcal/mol)[17] solvation energy of carbocations due to Lewis acid–base-type interactions with nucleophilic solvent remains to be determined, there is good evidence that this interaction is considerably weaker than hydrogen bonds between water and ammonium ion protons, which have been estimated to be stabilizing by *ca.* 7 kcal/mol per hydrogen bond for the ammonium and methyl ammonium ions.[42,43] Further experimental and theoretical studies directed toward determination of the absolute strength of Lewis acid–base interaction (**1**) between nucleophilic solvent and carbocations are needed.

Acknowledgment. The support of this work by Grant GM 39754 from the National Institutes of Health is gratefully acknowledged.

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