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# General Acid Catalysis of Alcohol Heterolysis

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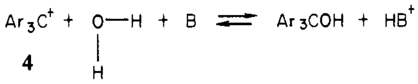
**Abstract:** The conversion of diferrocenylphenylmethanol (**5**) into its carbocation is general acid catalyzed in $H_2O$:$CH_3CN$, 1:1 w/w, and $\alpha = 0.88$. The corresponding reaction of tropyl alcohol is also general acid catalyzed, and $\alpha = 0.71$ and 0.90 in water and $H_2O$:$CH_3CN$, 1:1 w/w, respectively. However, the hydrogen ion catalyzed reactions have inverse solvent kinetic hydrogen isotope effects, and $k_{H_2O}/k_{D_2O} = 0.56$ for reaction of **5** in $H_2O(D_2O)$:$CH_3CN$. Consideration of the equilibrium constants for alcohol protonation suggests that acid-catalyzed conversion of alcohol into carbocation should go from stepwise to concerted as the stability of the carbocation is increased.

The acid-catalyzed conversion of alcohols into carbocations is often written in terms of Scheme I, where the alcohol (**1**) is in equilibrium with its conjugate acid (**2**).[2] The carbocation may react with water regenerating **1**, or give alkene, or rearrange giving products with a new carbon skeleton. There is considerable evidence for this general mechanism; viz., electron-releasing groups and steric crowding at the reaction center speed reaction; solvent hydrogen isotope effects, $k_{H_2O}/k_{D_2O}$, are inverse; and the reactions are typically catalyzed specifically by the hydrogen ion.

However there are problems, especially for alcohols which contain very strongly electron-releasing substitutents. The addition of water to triarylmethyl carbocations (**4**) is general base cata-lyzed,[3-5] so that the reverse reaction of the alcohol should be general acid catalyzed. The rates of forward and back reactions cannot in some cases be fitted to Scheme I, making reasonable estimates of the basicity of the alcohol, suggesting that the reactions must be concerted,[3b] despite the inverse solvent hydrogen isotope effect.[6,7] (These inverse isotope effects had been considered diagnostic of preequilibrium proton transfers, but is now evident that this view is incorrect.)



$$Ar_3C^+ + \underset{\displaystyle H}{\overset{}{O}}{-}H + B \rightleftharpoons Ar_3COH + HB^+$$

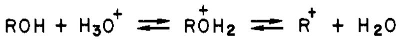
4

(a) Ar = $p$-$Me_2NC_6H_4$
(b) Ar = $p$-$MeOC_6H_4$ = An

Our aim was to examine a general acid catalyzed heterolysis of an alcohol, and to determine the solvent hydrogen isotope effect for its hydrogen ion catalyzed heterolysis. It is not easy to find a convenient system. For example, heterolysis of tri-$p$-anisylmethanol is not catalyzed by weak acid,[4-6] althought water addition to the carbocation is catalyzed by basic tertiary amines.[4,5] The reaction of water with cations such as Crystal Violet (**4a**) is general base catalyzed,[3] but this system is unsuitable because of protonation of the dimethylamino groups.

Ferrocenylmethanols are potentially useful substrates[7,8] because the rate constants are in a convenient range for measurement, and the more basic alcohols are converted into carbocations at pH ~4 (Scheme II). We used diferrocenylphenylmethanol (**5**), which reacts in acetonitrile–water, 1:1 w/w, with $k_f = 2.8 \times 10^{-4}$ s$^{-1}$ and $k_r = 4.35$ M$^{-1}$ s$^{-1}$.[8,9]

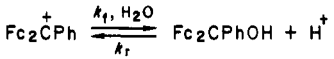
Scheme I



$$ROH + H_3O^+ \rightleftharpoons \overset{+}{R}OH_2 \rightleftharpoons R^+ + H_2O$$

1 2 3

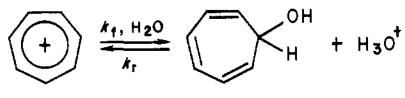
Scheme II



$$Fc_2\overset{+}{C}Ph \underset{k_r}{\overset{k_f,\ H_2O}{\rightleftharpoons}} Fc_2CPhOH + H^+$$

6 5

Scheme III



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Another potentially useful system is shown in Scheme III. The rate constants of water addition to tropylium ions (**7**) and of the reverse acid-catalyzed heterolysis of the alcohol (**8**) have been measured, although general base catalysis of water addition was not reported.[10]

Most of the systems studied to date involve formation or destruction of oxocarbocations, generated in most cases from acetals or orthoesters.[11-14] Some of these reactions follow a preassociation mechanism with no carbocation intermediate,[15] whereas with **5** and **8** the carbocation is observed directly.

## Experimental Section

**Materials and Kinetics.** The preparation of diferrocenylphenylmethanol (**5**) has been described.[7b] The other reagents were commercial samples and the purity of the acids was controlled by titration.

The reactions were followed spectrophotometrically.[7,10] The solvents were $H_2O$ or $H_2O$:MeCN, 1:1 w/w, or $D_2O$:MeCN made up to have the same mole:mole composition as the protio solvent.

**General Acid Catalysis.** The catalyzing acids were chosen so that the pH of the buffer was such that equilibrium is largely toward the cation:

$$ROH \underset{k_f}{\overset{k_r HA}{\rightleftharpoons}} R^+ + H_2O$$

The first-order rate constants, $k_\Psi$, for reaction in an acid, HA, are given by:

$$k_\Psi = k_f + k_r[HA] \qquad (1)$$

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[9] The first-order rate constant for addition of water to ferrocenylalkyl cations was designated $k_f$, and the second-order rate constant for acid heterolysis of the alcohol was designated $k_r$.[7,8]

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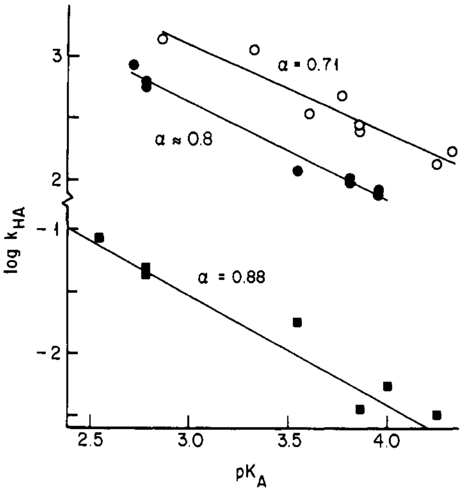

**Figure 1.** Brønsted plot for general acid catalysis of conversion of alcohols into carbocations at 25.0 °C: (○, ●) tropyl alcohol; (■) diferrocenylphenylmethanol. Open points refer to water, solid to $H_2O$:MeCN, 1:1 w/w.

There are specific salt effects upon water addition to carbocations and the reverse reaction,[4,5,7,16] and water addition may also be catalyzed by general bases.[3-5] The salt effects upon $k_f$ can be neglected, provided that $k_f$ makes a small contribution to $k_\Psi$, and we chose buffers accordingly.

The specific salt effects upon $k_r$ cannot be eliminated by working at constant ionic strength,[4,5,7,16] and to reduce them we used low [buffer], usually <0.05 M, but in a few cases we used 0.1 M buffer. There was no significant effect upon $k_{HA}$ with change in [buffer].

The second-order rate constant, $k_{HA}$, for reaction catalyzed by a weak acid HA can be calculated from

$$k_\Psi = k_H[H^+] + k_{HA}[HA] \qquad (2)$$

provided that $k_H[H^+]$ is constant, or can be estimated. For the weaker acids the contribution of the hydrogen ion reaction is small and constant and we can use

$$k_\Psi = \text{constant} + k_{HA}[HA] \qquad (2a)$$

and plot $k_\Psi$ against [HA]. However, for stronger acids we estimated $k_H[H^+]$ from the rate of reaction in HCl, and $[H^+]$ calculated from $pK_A$ and the buffer concentration. For reaction in water we used thermodynamic $pK_A$[17] and an activity correction using the Davis equation,[18] but for reactions in $H_2O$–MeCN we used $K_A$ values determined in this work. This approximation was reasonable because the acid dissociation constants are lower in $H_2O$–MeCN than in water. The two values of $k_{HA}$ agree for reactions catalyzed by the weaker acids, but for the stronger acids eq 2a overestimates $k_{HA}$ (Tables S1, S2, and S3, supplementary material).

Reaction of 7 with water in MeCN:$H_2O$, 1:1 w/w, was followed by mixing equal volumes of the cation in $10^{-3}$ M HCl with $10^{-3}$ M NaOH;[5] $k_f$ = 5.5 $s^{-1}$. We also mixed the cation in $10^{-3}$ M HCl with excess $NaHCO_3$ ($10^{-2}$, 1.5 × $10^{-2}$, and 2 × $10^{-2}$ M); $k_f$ = 7.1, 7.8, and 9.2 $s^{-1}$, respectively. The extrapolated $k_f$ agreed reasonably with that obtained by acid neutralization with NaOH.

**Dissociation Constants of the Weak Acids.** Acid dissociation constants, $K_A$, in acetonitrile:water, 1:1 w/w, were determined potentiometrically using a Thomas, high pH combination glass electrode. The response of the electrode was calibrated using HCl (0.005–0.03 M) in $H_2O$:MeCN, 1:1 w/w, and the weak acid was titrated against 0.1 M KOH. The acid dissociation constants were calculated by the method of Benet and Goyan.[19] (These values were similar to those estimated by the less accurate method of half-neutralization.)

Table I. Acid-Catalyzed Heterolysis of Diferrocenylphenyl Methanol[a]

| acid | $pK_A$ | $10^2k_{HA}$, $M^{-1}$ $s^{-1}$ [b] |
|---|---|---|
| HCl | | 435 |
| DCl | | 800 |
| maleic | 2.54 | 16.5 (20.7) |
| $CHCl_2CO_2H$ | 2.77 | 4.88 (7.1) |
| | | 4.40[c] (4.2) |
| $Me_3N^+CH_2CO_2H$ | 2.81 | 0 |
| $Et_2C(CO_2H)_2$ | 3.54 | 1.74 (1.74) |
| $CH_2(CN)CO_2H$ | 3.80 | 0.35 (0.35) |
| | | 0.35[c] (0.35) |
| 3,5-$(NO_2)_2C_6H_3CO_2H$ | 4.00 | 0.54 (0.54) |
| 2-$NO_2C_6H_4CO_2H$ | 4.25 | 0.37 (0.37) |

[a] In $H_2O$:MeCN, 1:1, w/w, at 25.0 °C. For the weak acids [acid]/[salt] = 1, except where specified. [b] Rate constants in parentheses are calculated using eq 2a. [c] [acid]/[salt] = 0.5.

Table II. Acid-Catalyzed Heterolysis of Tropyl Alcohol in Acetonitrile–Water[a]

| acid | $pK_A$ | $10^{-2}k_{HA}$, $M^{-1}$ $s^{-1}$ [b] |
|---|---|---|
| HCl | | 580 |
| $CHF_2CO_2H$ | 2.72 | 8.9 (12) |
| $CHCl_2CO_2H$ | 2.77 | 6.5 (11) |
| | | 6.0[c] (7) |
| $Me_3N^+CH_2CO_2H$ | 2.81 | (0.6) |
| $Et_2C(CO_2H)_2$ | 3.54 | 2.3 (2.2) |
| $CH_2(CN)CO_2H$ | 3.80 | 1.3 (1.3) |
| | | 1.0[d] (1.3) |
| $CH_2(CO_2H)_2$ | 3.96 | 1.6 (1.7) |
| | | 1.7[d] (1.7) |

[a] In $H_2O$:MeCN, 1:1, w/w at 25.0 °C. For the weak acids [acid]/[salt] = 0.5, except where specified. [b] Rate constants in parentheses are calculated using eq 2. [c] [acid]/[salt] = 0.33. [d] [acid]/[salt] = 1.0.

Table III. Acid-Catalyzed Heterolysis of Tropyl Alcohol[a]

| acid | $pK_A$ | $10^{-2}k_{HA}$, $M^{-1}$ $s^{-1}$ [b] |
|---|---|---|
| HCl | | 1460 |
| $CH_2ClCO_2H$ | 2.86 | 14.0[c] |
| $OCH{\cdot}CO_2H$ | 3.32 | 10.6[c] (12.8) |
| $EtOCH_2CO_2H$ | 3.60 | 3.40 (3.40) |
| $HCO_2H$ | 3.77 | 4.80 (5.00) |
| $MeCH(OH)CO_2H$ | 3.86 | 2.80 (2.80) |
| | | 2.48[c] (2.60) |
| $CH_2{=}CHCO_2H$ | 4.25 | 1.36 (1.36) |
| $(CH_2)_3(CO_2H)_2$ | 4.34 | 3.48 (3.48) |

[a] In water at 25.0 °C. For the weak acids [acid]/[salt] = 1, except where specified. [b] Rate constants in parentheses were calculated using eq 2a. [c] [acid]/[salt] = 0.5.

The values of $pK_A$ in acetonitrile–water are given in Tables I and II. The solvent effect upon these constants depends upon the acid, and typically the more hydrophobic the acid the greater the solvent effect upon $pK_A$, because these acids are more stabilized, relative to the anion, by the use of less aqueous solvent.

**Dissociation Constants of the Tropylium Ion.** The acid dissociation constant, $K_{R^+}$, of the tropylium ion has been measured in water, and in $H_2O$:MeCN, 1:1. In water $pK_{R^+}$ = 4.75[20a] or 4.76.[10]

$$C_7H_7^+ + H_2O \xrightleftharpoons{K_{R^+}} C_7H_7OH + H^+$$

and in aqueous MeCN the apparent $pK_{R^+}$ = 4.01.[20b,21,22]

The $pK_{R^+}$ value in $H_2O$:MeCN, 1:1 w/w, is 4.02, measured in a dilute HCl, using the absorbance of the cation at 277 mm and the isosbestic point at 268 nm.[10] Our value agrees with that of Jutz and Voithenleitner.[20b] (The solvent effect upon $pK_{R^+}$ is similar to those for the tri-*p*-anisylmethyl and ferrocenylalkyl cations and is due largely to a decrease

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(21) The solvent was $H_2O$:MeCN, 1:1,[20b] but it was not specified as to volume or weight composition.

(22) In the mixed solvent the apparent constant is written as: $K_{R^+} = [C_7H_7OH][H^+]/[C_7H_7^+]$.

in activity coefficient of the alochol on addition of organic solvent.[7a])

The value of $pK_{R^+} = 4.18$ for **6** was determined from independently measured values of $k_f$ and $k_r$ in $H_2O$:MeCN 1:1 w/w.[7b]

## Results and Discussion

**General Acid Catalysis.** The second-order rate constants, $k_{HA}$, for conversion of alcohol into carbocation, are in Tables I, II, and III. The corresponding Brønsted plots are in Figure 1, and the value of $\alpha$ is 0.88 for reaction of **1**, and 0.71 and ca. 0.8 for reactions of **8** in water and $H_2O$:MeCN, 1:1 w/w, respectively. These $\alpha$ values are calculated using the least-squares treatment, with equal weight given to each data point, except that for (trimethylammonium)acetic acid. Statistical corrections were applied for reactions catalyzed by dibasic acids.[23] The large negative deviation of $k_{HA}$ for (trimethylammonium)acetic acid (Tables I and II) is almost certainly due to coulombic repulsions between the acid and the forming positive charge in the transition state.

The value of $\alpha$ for reaction of tropyl alcohol (**8**) is smaller in water than in $H_2O$–MeCN (Figure 1). This solvent effect can be rationalized in terms of the Hammond postulate.[24] Addition of acetonitrile to water increases the free energy of the final state (carbocation + carboxylate ion) relative to the initial state and moves the transition state toward the final state. These changes are evident from the increases of $pK_A$ and decreases of $pK_{R^+}$ on addition of organic solvent to water.

**Hydrogen Ion Catalyzed Reaction.** The second-order rate constant for acid-catalyzed heterolysis of tropyl alcohol (**8**) in aqueous HCl ($0.5–2 \times 10^{-3}$ M) of $1.46 \times 10^{5}$ $M^{-1}$ $s^{-1}$ at 25.0 °C. (Table III) agrees with that of $1.5 \times 10^{5}$ $M^{-1}$ $s^{-1}$ estimated indirectly at 23 °C by Ritchie and Fleischauer from $K_{R^+}$ and the first-order rate constant for reaction of the cation in water.[10] It is lower than the values given by Zuman and co-workers,[25] but is consistent with that of $6.6 \times 10^{4}$ $M^{-1}$ $s^{-1}$ at 12 °C given by Eigen.[26] The second-order rate constant in $H_2O$:MeCN 1:1 w/w, is $5.8 \times 10^{4}$ $M^{-1}$ $s^{-1}$ (calculated from $k_f$ and $K_{R^+}$; Experimental Section). This solvent effect, like that on $K_{R^+}$, can be ascribed to stabilization of the alcohol relative to transition state or carbocation. (The solvent effect upon $k_f$ is similar to those found for water addition to ferrocenylalkyl cations.[7a])

Because of the low solubility of diferrocenylphenylmethanol, its acid heterolysis was followed in $H_2O$:MeCN, 1:1 w/w, with HCl, and the second-order rate constant is 4.35 $M^{-1}$ $s^{-1}$ at 25.0 °C for $1–7 \times 10^{-3}$ M HCl. The rate constant for acid heterolysis of diferrocenylmethanol is $k_r = 37.2$ $M^{-1}$ $s^{-1}$, under the same conditions,[7a] so that the phenyl groups reduce the reactivity of the alcohol toward acid. This behavior contrasts with that of di- and triarylmethanol where typically a tertiary alcohol is much more reactive than a secondary. It is not unusual for reactions of ferrocenylmethanols,[7] and has been ascribed to steric inhibition of resonance in the transition state and hindered attainment of the conformation required for transition state formation.[27] Thus the -I effect of the phenyl group is dominant.

The second-order rate constants for the hydrogen ion catalyzed reactions of **5** and **8** deviate negatively from the Brønsted plot, as is often found.[29]

**Isotope Effects on Hydrogen Ion Catalysis.** The value of $k_{H_2O}/k_{D_2O}$ for reaction of $Fc_2CPhOH$ is 0.54 (Table I). Similar inverse solvent hydrogen isotope effects are found in other acid-catalyzed reactions of alcohols[6,7a] and related substrates,[30-34] but in some reactions the substrate cannot be in equilibrium with conjugate acid, and some reactions are catalyzed by general acids.[3b,24,30-33]

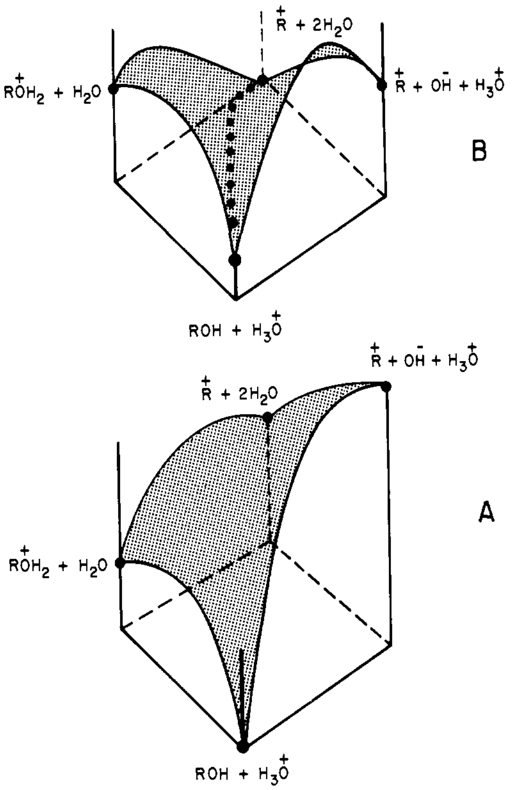
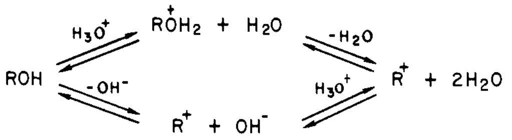


**Figure 2.** Qualitative three-dimensional free-energy diagrams for conversion of alcohols into carbocations.

Scheme IV



Relatively large, inverse, secondary solvent isotope effects are predicted for heterolysis catalyzed by lyonium ions,[30,34,35] and they may overcome any small primary isotope effect on the proton transfer. The secondary effects can be estimated either using fractionation factors[30,35] or in terms of changes in stretching frequencies due to differences in hydrogen bonding.[34]

Albery has pointed out that primary solvent kinetic isotope effects are often less informative mechanistically than secondary effects on proton transfers,[35] and small primary isotope effects are common in proton transfer between electronegative atoms. Analogy with hydrogen bonding suggests that the proton could be in a double potenital energy minimum,[30,34] and Swain and his co-workers set out this principle in terms of their "solvation rule".[36] There are other rationalizations of small primary isotope effects.[37,38]

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(38) Solvent hydrogen isotope effects are generally larger for general base as compared with nucleophilic catalysis, and appear to be mechanistically useful in these reactions.[39]

Table IV. Estimated Free Energies of Intermediate, Transition, and Final States[a]

| substrate | $pK_A$ | $pK_{R^+}$ | $R^+OH_2$ + $H_2O$ | $R^+$ + $OH^-$ + $H_3O^+$ | · $R^+$ + $2H_2O$ | $\Delta G^\ddagger$ |
|---|---|---|---|---|---|---|
| $C_7H_7OH$ | −7 | 4.8 | 9 | 12.5 | −6.5 | 10.5 |
| $(p\text{-}MeOC_6H_4)_3COH$ | −9 | 0.8 | 12 | 18 | −1 | 15 |
| $(p\text{-}MeOC_6H_4)$-PhCHOH | −8 | −5.7 | 11 | 27 | +8 | 21 |
| PhCHMeOH | −7 | −12 | 9 | 35 | +16 | 24.5 |

[a] Free energies of the intermediates are in kcal $mol^{-1}$ relative to the alcohol and hydrogen ion.

**Transition States of Alcohol Heterolysis.** Addition of water to preformed carbocations is general base catalyzed,[3-5] and we observe the predicted general acid catalysis of heterolysis of similar alcohols (Figure 1). The values of $\alpha$ suggest extensive, but incomplete, proton transfer to the hydroxyl group in the transition states for carbocation formation. These observations can be rationalized in terms of the Jencks–More O'Ferrall free energy diagrams[40] (Figure 2 and Scheme IV).

The free energies of the intermediate states in water can be estimated from $pK_{R^+}$ and $pK_A$ of protonated alcohol. The $pK_{R^+}$ values for many stable carbocations are known,[7,41] and can be estimated for triarylmethanols.[43]

$$R^+OH_2 + H_2O \overset{K_A}{\rightleftharpoons} ROH + H_3O^+$$

$$R^+ + 2H_2O \overset{K_R}{\rightleftharpoons} ROH + H_3O^+$$

We consider acid-catalyzed heterolysis of alcohols ranging from tropyl alcohol, which gives a relatively stable carbocation, to 1-phenylethanol. A ferrocenylmethanol such as **5** would be similar to tropyl alcohol with regard to the free energy difference between alcohol and carbocation. The $pK_{R^+}$ values for most of these alcohols are known, and we assume the $pK_A$ values shown in Table IV.[3b,42,43]

The value of $pK_{R^+}$ for 1-phenylethanol is not known, but we estimate it by comparing $\log k_r$ and $pK_{R^+}$ for some arylmethanols. Values of $k_f$ (and $k_r$) for water addition to triarylmethyl cations are known,[44] and $pK_{R^+}$ can be calculated from the linear relation between $\log k_r$ and $pK_{R^+}$ for several tertiary alcohols:[44]

$$\log k_r = 1.4 + 0.57 pK_{R^+} \tag{3}$$

Log $k_r$ for reaction of 1-phenylethanol in aqueous $HClO_4$ at 25 °C is ca. −5.7,[45] giving $pK_{R^+} \approx -12$. As a test of eq 3 we estimate $\log k_r \approx -1.85$ for *p*-methoxydiphenylmethanol in aqueous $HClO_4$ at 25 °C, which agrees with the observed value of −2.7 in dioxane-water, 40:60 v/v,[47,48] because $k_r$ decreases with decreasing water content of the solvent. In any event our conclusions do not depend on the precise values of $pK_A$ and $pK_{R^+}$.

We estimate the approximate free energies of the various states relative to the alcohol and hydrogen ion in water (Table IV), using eq 4, where $K$ is the appropriate equilibrium constant. (Because

$$\Delta G° = -RT \ln K \tag{4}$$

of the approximations $\Delta G°$ is rounded off.)

More O'Ferrall and Jencks pointed out that concerted reactions are preferred to stepwise reactions when the latter would involve formation of high-energy intermediates.[40] In the reactions in Table IV, $R^+ + OH^-$ represents in acid a high-energy intermediate. Protonated alcohol would be a relatively high-energy intermediate in heterolysis of $C_7H_7OH$ and $An_3COH$, which is consistent with these reactions being concerted, but as $pK_{R^+}$ becomes more and $pK_A$ less negative, the reaction path is more likely to involve protonated alcohol as an intermediate. These changes can also be seen in terms of the free energies of activation ($\Delta G^\ddagger$), and alcohol protonation (Table IV). Values of $\Delta G^\ddagger$ increase in the sequence $An_3COH$ < AnPhCHOH < PhCHMeOH, and for the two less reactive alcohols are larger than the free energies for protonation.

These comparisons suggest that protonation of the alcohol precedes the rate-limiting step in acid-catalyzed reactions of aliphatic alcohols, and of PhCHMeOH,and that water addition to the carbocations is not general base catalyzed. Nucleophilic attack upon relatively reactive carbocations formed in $S_N1$ reactions[49] and upon some intermediate and preformed oxocarbocations is in many cases diffusion controlled.[12,13] Thus mechanistic changes upon acid-catalyzed decomposition of alcohols parallel those upon acetal and orthoester hydrolysis[11,12] and acid dehydration of an intermediate carbinolamine.[14]

These mechanistic differences for acid-catalyzed conversion of alcohols into carbocations can readily be visualized in terms of three-dimensional energy diagrams[40] (Figure 2). In this figure, A represents reaction of an alcohol such as 1-phenylethanol, which is probably stepwise, with conjugate acid, $RO^+H_2$, in equilibrium with alcohol. In this system the free energy of the carbocation is considerably higher than that of the conjugate acid, but as the carbocation is stabilized by electron-releasing groups the situation can be represented by B. The reaction is concerted and the reaction coordinate is shown by the dotted line, as for reactions of tropyl alcohol or diferrocenylphenylmethanol.

These free energy diagrams (Figure 2) are oversimplified because they do not take into account the conformational requirements for stabilization of the transition state by charge delocalization. These conformational requirements are very stringent for reactions of diferrocenylphenylmethanol where the preferred conformations of the alcohol and carbocation are very different from that of the transition state.[7,28]

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**Supplementary Material Available:** Table S1, reaction of $Fc_2CPhOH$ in $MeCN{:}H_2O$, 1:1 w/w; Table S2, reaction of tropyl alcohol in $MeCN{:}H_2O$, 1:1 w/w; Table S3, reaction of tropyl alcohol in water (3 pages). Ordering information is given on any current masthead page.

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