h. 9-Arylxanthenols. These were prepared in a manner analogous to the triarylcarbinols by reaction of the appropriate aryl Grignard reagent with xanthen-9-one (Eastman, white label). Due to the low solubility of xanthenone in THF, the solid was usually added directly to the Grignard solution, and the resulting suspension was stirred overnight followed by the usual work-up procedure. Yields were generally 50–75%. The melting points of xanthenols with the following substituents agreed with those reported in the literature: 9-phenyl,[53,54] 9-o-tolyl,[55] 9-m-tolyl,[56] 9-p-tolyl,[57] 9-p-anisyl,[58] and 9-(p-trifluoromethyl)phenyl.[24] 9-(2,6-Dimethylphenyl)xanthenol was purified by chromatography on a silica gel column or by recrystallization from methylene chloride–petroleum ether and had mp 185–186.5° (red-brown melt). *Anal.* Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 82.92; H, 6.14. 9-(o-Trifluoromethylphenyl)xanthenol was not characterized but converted to the methyl ether.

i. 9-Phenylxanthyl chloride[57] was prepared by the method of Schoepfle.[59]

j. 9-Arylxanthyl Ethers. The ethers were all prepared from the 9-arylxanthenols by the following general method. To approximately 3 g of carbinol dissolved in a minimal amount of methylene chloride was added 6 ml of trifluoroacetic acid. The resulting red-brown solution of carbonium ion was added slowly to approximately 150 ml of the appropriate alcohol, and the color was discharged by neutralization with a concentrated alcoholic solution of sodium hydroxide. After 30 min the solution was poured into ice water, and the 9-arylxanthyl ethers separated either as oils or solids. Solids were recovered by filtration and recrystallized from the appropriate alcohol. Oils were extracted into diethyl ether and after removal of solvent, solids were obtained which were recrystallized from the appropriate alcohol. Melting points were in agreement with those found in the literature for methyl ethers of 9-phenyl-[54] and 9-p-anisylxanthenols,[58] and for 9-phenylxanthyl ethyl ether.[54] Methyl ethers of other 9-arylxanthenol derivatives had the following physical properties: 9-o-methyl, mp 115.5–116.5°, 9-p-trifluoromethyl, mp 72–73.5° (*Anal.* Calcd for $C_{21}H_{15}O_2F_3$: C, 70.78; H, 4.24; F, 16.00. Found: C, 70.02; H, 4.20; F, 15.68), and 9-o-trifluoromethyl, a light tan crystalline solid, mp 133–134.5° (*Anal.* Calcd for $C_{21}H_{15}O_2F_3$: C, 70.78; H, 4.24; F, 16.00. Found: C, 70.65; H, 4.41; F, 15.99). 9-Phenylxanthyl isopropyl ether had mp 101–102°.

k. 9-Arylxanthyl Cations. Tetrafluoroborate salts of all 9-arylxanthyl derivatives listed in Tables II and V were prepared and isolated by the method used for trityl fluoroborates[52] using purified carbinols or ethers as precursors. The yellow salts were reprecipitated from methylene chloride–petroleum ether mixtures.

l. Triphenylcyclopropenyl Compounds. Previously described methods were used for preparation of 1,2,3-triphenylcyclopropenium bromide,[60] tert-butyl ether,[60] and methyl ether.[61] 1,2,3-Triphenylcyclopropenyl isopropyl ether was prepared in a manner analogous to that of the methyl ether and was a white solid with mp 98–100°. Triphenylcyclopropenium tetrafluoroborate was prepared from the bromide. (*Anal.* Calcd for $C_{21}H_{15}BF_4$: C, 71.21; H, 4.27; F, 21.46. Found: C, 71.29; H, 4.41; F, 21.88.)

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The Basicity of Ethanol. An Acidity Function for Alcohols

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Contribution from the Department of Chemistry, University of Saskatchewan Regina Campus, Regina, Canada. Received January 12, 1971

Abstract: Chemical shift data have been used to determine the basicity of ethanol in sulfuric acid solutions. This technique indicates that ethanol is one-half protonated in approximately 70% H_2SO_4 ($H_0 = -5.9$) and that the protonated species has a relatively high demand for solvation by water. Application of the Bunnett–Olsen equation gives the pK_{BH^+} to be -1.94. Since the protonation equilibrium spans a substantial range of acid concentrations it is possible to obtain an alcohol acidity function (H_{ROH}) from 33 to 94% H_2SO_4 using but a single indicator. The H_{ROH} function increases much less rapidly with increasing acid concentration than for any other known acidity function.

The basicity of aliphatic alcohols is an important topic that has been discussed in several previous papers.[1–4] A knowledge of the pK_{BH^+} values is essential to an understanding of the numerous reactions of these compounds that are subject to acid catalysis or inhibition and thus has application to both organic and biochemical processes. However, before quantitative estimates of basicity can be made, two requirements must be met: (i) it must be possible to measure the extent of protona-

tion in solutions of varying acid concentration and (ii) a suitable function defining the acidity of the solution at each acid concentration should be available.

If these two requirements are met it is then possible to estimate pK_{BH^+} values for alcohols by use of eq 1, where H_{ROH} is an acidity function describing the protonation of alcohols.[5,6] Unfortunately, no such alcohol acidity

$$\log \{ROH_2^+\}/\{ROH\} = -H_{ROH} + pK_{BH^+} \quad (1)$$

function has previously been available. However, Yates and McClelland[7] have shown that most known

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acidity functions are approximately linear in H_0[8] and it is not an unreasonable assumption that the H_{ROH} acidity function would also conform to this pattern. Hence eq 1 could be rewritten in the form of eq 2. Furthermore,

$$\log \{\text{ROH}_2^+\}/\{\text{ROH}\} = -mH_0 + pK_{\text{BH}^+} \quad (2)$$

thermore, the work of Weston, et al.,[1] indicates that the protonation of methanol and 2-propanol can be described by this equation with the value of m being approximately 0.2–0.3. Values of m of less than unity have also been obtained for other oxygen bases such as amides,[11] ketones,[12-15] phosphine oxides,[16] sulfoxides,[17] and carboxylic acids and esters.[18] These observations suggest that the increase in solvation which takes place when oxygen bases protonate is greater than that accompanying the protonation of amines (which were used as indicators in the development of the H_0 function); i.e., the protonation equilibria for oxygen bases respond less readily to increases in the concentration of mineral acid since each increase in acid concentration is necessarily accompanied by a decrease in the amount of water available to solvate the protonated species.[6]

If experience continues to indicate that plots of $\log \{\text{BH}^+\}/\{\text{B}\}$ correlate reasonably well with H_0 it might be useful to define the basicity of all weakly basic compounds in this way. The apparent pK_{BH^+} values would then indicate the acidity (on the H_0 scale) at which the base was half-protonated and the slope would be a measure of the relative solvation requirements of the reaction. It should be noted, however, that while this procedure has been used by several authors to produce usable and interesting results it suffers from the fact that the apparent pK_{BH^+} values do not have thermodynamic significance. Clearly, the pK_{BH^+} values as defined by eq 2 are equal to the product of the slope times the acidity at the point where the value of the ratio $\{\text{BH}^+\}/\{\text{B}\}$ is unity. On the other hand, the accuracy of a pK_{BH^+} value obtained from the product (mH_0) would be limited by any nonlinearity between acidity functions, and while this may be small in the region 20–100% H_2SO_4 it often becomes significant in more dilute solutions.[9]

As an alternative to this procedure Bunnett and Olsen[19] have pointed out that plots of $(H_x + \log \{\text{H}^+\})$ against $(H_0 + \log \{\text{H}^+\})$ are more nearly linear than the corresponding plots of H_x vs. H_0, and that an advantage

can consequently be derived from the use of such composite functions in the estimation of pK_{BH^+} values of weak organic bases.[9] From the linear free energy relationship derived by these authors (eq 3) it can be seen that a plot of $\log (\{\text{BH}^+\}/\{\text{B}\}) + H_0$ against $(H_0 + \log \{\text{H}^+\})$ should be linear with a slope of ϕ and an inter-

$$\log (\{\text{BH}^+\}/\{\text{B}\}) + H_0 =$$
$$\phi(H_0 + \log \{\text{H}^+\}) + pK_{\text{BH}^+} \quad (3)$$

cept equal to pK_{BH^+}. It has been shown that the term $(1 - \phi)$ is then analogous to the slope (m) of eq 2.[15] Furthermore the intercepts of these plots should give pK_{BH^+} values of thermodynamic significance since in very dilute solutions H_0 and $-\log \{\text{H}^+\}$ become equal, thus causing the first term on the right of eq 3 to disappear and leaving the left side equal to $\log \{\text{BH}^+\}/\{\text{B}\}$ $\{\text{H}^+\}$. Landini, et al.,[17] have recently applied this procedure to a study of the protonation of sulfoxides with good results.

Assuming that an acidity function can be approximated it is still necessary to find a method for detecting the degree of protonation at various acidities. Since aliphatic alcohols lack an ultraviolet spectral band which could be used for this purpose (as has often been done with other compounds) attempts have been made to use less common methods. For example, Arnett and coworkers,[4] using heats of protonation in fluorosulfuric acid, have recently estimated that ethanol is one-half protonated at an acidity of -5.1 on the H_0 scale. The validity of this method of estimating basicities rests on the observation that there is an empirical relationship between the point of half-protonation and the heat liberated when the base is dissolved in fluorosulfuric acid. Although the apparent pK_{BH^+} values thus obtained are not thermodynamically significant, they can be used to compare directly the relative basicities of compounds with widely different structures.

The use of Raman band intensities as measurements of the extent of protonation of methanol and 2-propanol has been investigated by Deno and Wisotsky[20] and by Weston, et al.[1] Their results also indicate that these alcohols are one-half protonated at acidities of approximately -5 on the H_0 scale.

Other less direct methods such as the use of rate data for reactions which presumably proceed via protonated alcohols[21-23] or solvent extraction techniques[24,25] give pK_{BH^+} values that are somewhat more positive. However such estimates are of dubious reliability, as has been discussed at length by other authors.[1,3]

The use of nmr chemical shifts is an attractive method because the measurements involve only molecules in their ground states, thus avoiding the necessity of considering excited states. Although chemical shifts were once thought to be subject to unusual solvent effects this fear has been obviated by the observation that chemical shift data can be used to obtain reliable pK_{BH^+} values for anines,[26] amides,[16] ketones,[16,13]

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(26) E. Grunwald, A. Loewenstein, and S. Meiboom, J. Chem. Phys., 27, 641 (1957).

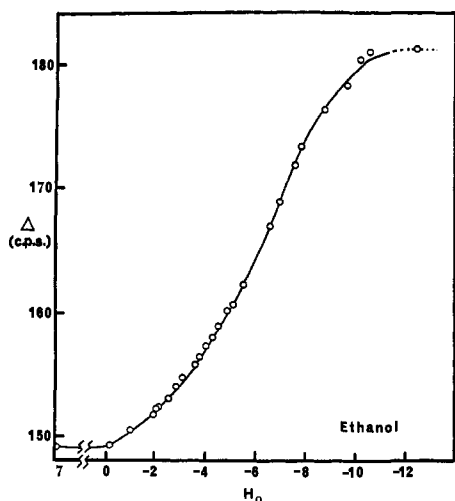Figure 1. Titration curve for the protonation of ethanol.

phosphine oxides,[16] phosphine sulfides,[16] sulfoxides,[17,27] and carboxylic acids.[28,29]

In particular it should be noted that chemical shifts have been found to give values almost identical with those obtained from the use of ultraviolet–visible spectroscopy for amides,[16] ketones,[13,16] and sulfoxides[17] when both methods have been applied to the same compounds. In attempting to use chemical shifts to study the protonation of alcohols we have found that it is not solvent effects but the relatively high concentrations required to obtain a clearly defined signal and the tendency of protonated alcohols to undergo chemical reactions (probably formation of sulfate esters) in highly concentrated sulfuric acid solutions that define the limitations of this method. Nevertheless by keeping the temperature low (0°) and taking spectra quickly it is possible to obtain good estimates of the chemical shifts for 0.035 M solutions of ethanol up to 98.5% H_2SO_4.

As a further precaution against solvent effects we have adopted the procedure first described by Edward, et al.,[2] in which the difference between the chemical shifts of the α- and β-hydrogens (Δ) is taken as a measure of the extent of protonation. This method rests on the assumption that the chemical shifts of the α-hydrogens will be more greatly affected by protonation than those of the β-hydrogens and it has the added advantage that since all the atoms in a simple small molecule would be in approximately the same environment any solvent effects should be minimized.

Experimental Section

All spectra were obtained on an A60A Varian spectrophotometer fitted with a constant-temperature probe which was held at 0°. Each measurement was made by first adding 0.10 ml of alcohol to 5.0 ml of cold standardized acid, transferring a small portion to a precooled nmr tube, and then recording the spectrum using side band techniques to minimize errors in the calibration of the instrument. This procedure worked very well from 0 to 93.7% H_2SO_4; however, at acid concentrations greater than 93.7% it was not possible to use the side band technique because the alcohol underwent a chemical reaction to give equilibrium amounts of a product (probably the sulfate ester)[2] having a spectrum which

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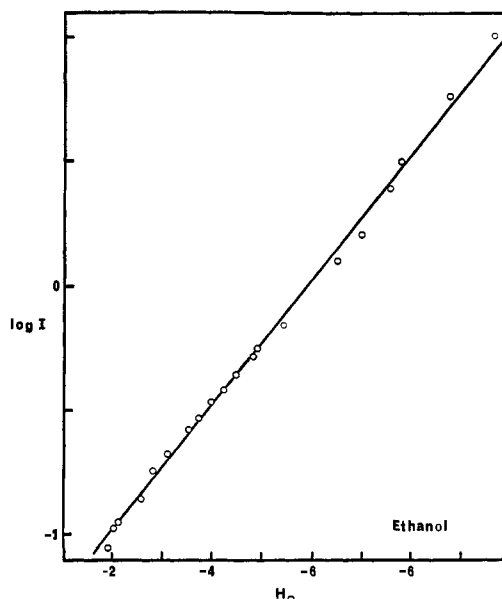(29) J. Siigur, T. Pehk, U. Haldna, and E. Lippmaa, Reakts. Sposobnost. Org. Soedin., 7, 179 (1970).

Figure 2. Plot of log I against H_0; slope $= -0.25$; intercept $= -5.88 \pm 0.14$; correlation coefficient $= 0.997$.

overlapped with that of the alcohol. However, by working quickly at low temperatures we were able to obtain reliable estimates of Δ (within ± 0.4 cps) up to 98.5% H_2SO_4.

The acid solutions were standardized by titrating weighed amounts of each sulfuric acid solution with standardized sodium hydroxide solutions. The H_0 values used up to 99.44% H_2SO_4 are those reported by Jorgenson and Hartter.[10] The acidity of the solution containing 100.1% H_2SO_4 was estimated by combining the data of Brand, et al.,[30] for the protonation of aromatic nitro compounds with those reported by Jorgenson and Hartter for the protonation of primary aromatic amines. While it is obvious that this procedure might lead to quite serious errors in the exact acidity values of these solutions, it should not introduce an appreciable error into our work since this highly acidic solution was used only to obtain Δ for the fully protonated alcohol. Furthermore, since the signal indicates the presence of a large amount of sulfate ester at this acidity little reliance can be place on this point.

Statistical analysis of the data was accomplished with the aid of an IBM 360 computer.

Results and Discussion

The values of Δ obtained for ethanol dissolved in different concentrations of H_2SO_4 are listed in Table I. The ratio $\{ROH_2^+\}/\{ROH\}$ which we have designated as I (in conformity with the suggestions of Bunnett and Olsen[19]) was then calculated from the differences between the observed Δ and that for the unprotonated alcohol (Δ_{ROH}) or the fully protonated alcohol ($\Delta_{ROH_2^+}$);
i.e., $I = \{ROH_2^+\}/\{ROH\} = (\Delta - \Delta_{ROH})/(\Delta_{ROH_2^+} - \Delta)$.

Because of the aforementioned tendency of alcohols to undergo chemical reactions in highly acidic media the least reliable datum used in these calculations is that for $\Delta_{ROH_2^+}$, the difference between the chemical shifts of α- and β-hydrogens in the fully protonated alcohol. However our value (181 cps) is consistent with the value of approximately 180 cps reported by Olah, et al.,[31] for fully protonated ethanol in fluorosulfuric acid solutions at $-60°$.

As Figures 1 and 2 illustrate, a sigmoidal curve is obtained when Δ is plotted against H_0 and a plot of log

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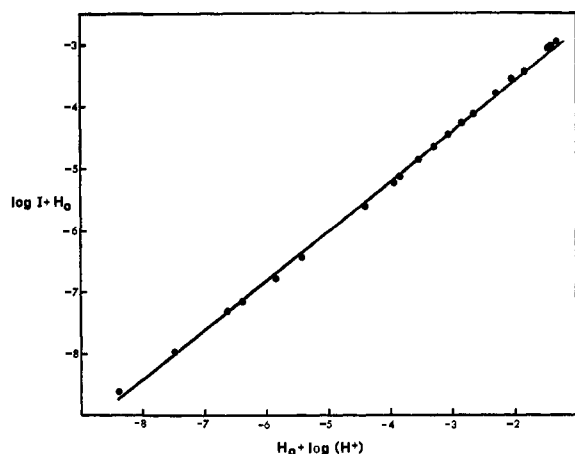
Figure 3. Bunnett–Olsen plot for ethanol, slope = 0.81; intercept = -1.94 ± 0.05; correlation coefficient = 0.999.

Figure 4. Acidity functions: H_R [N. C. Deno, J. J. Jaruzelski, and A. Schriescheim, *J. Amer. Chem. Soc.*, **77**, 3044 (1955); H_0 (ref 10); H_A (ref 11); H_{ROH} (this work).

I against H_0 is linear (slope = -0.25, intercept = -5.88 ± 0.14, and correlation coefficient = 0.997). The values for the slope and intercept are in good agreement with those obtained for methanol and 2-propanol by use of Raman spectroscopy.[1]

tion is linear in H_0. This we feel, in light of the previous discussion, is not an unrealistic assumption in the 20–90% H_2SO_4 region and it is also supported by the observation that the plots all showed a random scatter with no tendency to curvature.

Table I. Differences (Δ) between the Chemical Shifts for the α and β Hydrogens of Ethanol

H_2SO_4, %	Cps	Log I
0	149.2	
8.5	149.4	
19.2	150.4	
19.4	150.5	
32.8	151.8	-1.05
34.6	152.3	-0.97
35.8	152.4	-0.95
41.8	153.1	-0.85
44.6	154.1	-0.74
47.6	154.8	-0.67
51.7	155.9	-0.57
53.3	156.5	-0.53
55.9	157.4	-0.45
57.9	158.1	-0.41
60.1	159.0	-0.35
63.1	160.2	-0.28
64.4	160.5	-0.26
67.6	162.3	-0.15
74.6	167.0	0.10
77.7	168.9	0.21
81.2	171.9	0.40
83.0	173.3	0.50
88.9	176.3	0.76
93.7	178.2	1.02
97.0	180.4	
98.5	181.0	
100.1	181.2	

Table II. Correlation Coefficients for Log I vs. H_0 Plots Using Variable Values of $\Delta_{ROH_2}{}^+$

$\Delta_{ROH_2}{}^+$, cps	Correlation coefficient	Intercept
179	0.976	-5.5 ± 0.4
180	0.992	-5.7 ± 0.2
181	0.997	-5.9 ± 0.1
182	0.998	-6.1 ± 0.1
183	0.998	-6.2 ± 0.1
184	0.997	-6.4 ± 0.1
185	0.996	-6.5 ± 0.2
186	0.995	-6.7 ± 0.2
187	0.994	-6.8 ± 0.2
188	0.993	-6.9 ± 0.2
189	0.991	-7.0 ± 0.2
190	0.990	-7.2 ± 0.2
192	0.988	-7.4 ± 0.3
195	0.985	-7.7 ± 0.3
200	0.981	-8.2 ± 0.3

Table III. The Alcohol Acidity Function

H_2SO_4, %	H_{ROH}
33	-0.89
35	-0.95
40	-1.07
45	-1.20
50	-1.33
55	-1.46
60	-1.59
65	-1.72
70	-1.87
75	-2.05
80	-2.28
85	-2.51
90	-2.78
93	-2.95

As a further test of our data (and particularly the value of 181 cps for $\Delta_{ROH_2}{}^+$) we have attempted a form of curve fitting in which we allowed $\Delta_{ROH_2}{}^+$ to vary in increments of 1 cps from 179 to 200 cps and calculated the correlation coefficient for the log I vs. H_0 plots. As the results assembled in Table II indicate, the correlation coefficients pass through a shallow maximum at 182–183 cps, thus suggesting that the best calculated value of $\Delta_{ROH_2}{}^+$ is close to the experimental value of 181 cps. The validity of this test rests on the assumption that the acidity function which defines alcohol protona-
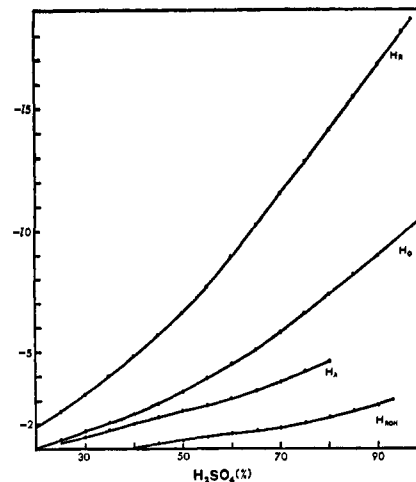
Following the procedure of Bunnett and Olsen we then plotted log I + H_0 against log $\{H^+\}$ + H_0 and obtained a straight line (slope = 0.81, intercept =

-1.94 ± 0.05, and correlation coefficient $= 0.999$) (see Figure 3). If the value for the intercept is accepted as a reliable estimate of the pK_{BH^+} of ethanol one is then able to calculate an acidity function for alcohols using eq 1. Since the protonation of ethanol spans a substantial range of acid concentrations it is possible to obtain H_{ROH} values from 33 to 94% H_2SO_4 using but a single indicator. Unfortunately the function is not defined for the very important region from the end of the pH scale to 33% H_2SO_4.

The values of H_{ROH} obtained by plotting $-(\log I + 1.94)$ against per cent H_2SO_4 and drawing a smooth curve through the experimental points are summarized in Table III and the function is compared with several other known acidity functions in Figure 4. As can be seen the alcohol acidity function increases much less rapidly with increasing acid concentration than for any other known acidity functions, thus suggesting that the protonation of alcohols (in analogy with most other oxygen bases) proceeds with a large demand for water of solvation.

Further work designed to bridge the low acid region and to correlate the rates of certain reactions of alcohols with this function are currently under way in our laboratories.

Mechanisms of β-Elimination Reactions in Which the Proton Is Activated by an Electron-Withdrawing Group

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Abstract: Leaving group effects for both syn and anti base-initiated eliminations from cyclohexane systems wherein the β proton is activated by an $ArSO_2$ group have been found to be small. From arguments based on the similarity of leaving group effects, activation parameters, and ρ values, it is concluded that both syn and anti eliminations in such activated systems (acyclic as well as C_5 and C_6 cyclic) are occurring by the *same* mechanism. Retardation of proton abstraction due to chair deformation in cyclohexane systems bearing 1,2-diequatorial substituents is pointed out as a hitherto unrecognized factor retarding syn elimination and contributing to high anti:syn rate ratios. The small leaving group effects are interpreted in terms of a carbanion mechanism. The faster rate of elimination reactions relative to deuterium exchange reactions in analogous systems, as well as the high degree of stereoselectivity shown in eliminations from acyclic systems, can be accommodated by the carbanion mechanism if internal return is assumed to play an important role.

The favorable geometry provided by a diaxial coplanar arrangement of leaving groups in base-initiated 1,2-elimination reactions was first pointed out by Hückel, Tappe, and Legutke in their dehydrochlorinations of menthyl and neomenthyl chlorides.[2] The importance of the geometric factor was emphasized by the 10^3–10^4 rate ratios for anti:syn eliminations in the benzene hexachloride system.[3] Cristol suggested a duality of mechanism to explain these results, a concerted mechanism for anti eliminations and a carbanion mechanism for syn eliminations.[3] A carbanion mechanism was also used to account for syn eliminations in systems where the favored anti coplanarity could not be readily attained.[4] A duality of mechanism, concerted anti for the erythro isomer and carbanion anti for the threo isomer, was also suggested for lyate ion initiated eliminations in ethanolic sodium hydroxide with 2-p-toluenesulfonyl-1,2-diphenylchloroethanes, which are stereoconvergent.[5]

When a β-hydrogen is activated by the strongly electron-withdrawing $ArSO_2$ group the geometric preference is overcome by an electronic factor, and activated syn elimination occurs to the exclusion of nonactivated anti elimination in the cyclohexane system.[6] Even the mildly electron-withdrawing phenyl group is able to activate the β-proton sufficiently to make activated syn elimination preferred to nonactivated anti elimination for the Hofmann degradation in the cyclohexane system.[7]

Reversible carbanion formation for $ArSO_2$-activated syn eliminations in the cyclohexane and cyclopentane series was ruled out by the observation of general base rather than specific hydroxide catalysis.[8] (This result has been augmented by more recent studies showing the absence of deuterium exchange in systems of this type.[9]) Rate-limiting "irreversible" carbanion formation[10] was

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