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Acid-Catalyzed Hydration of Dienes. 2. Changes in Activity Coefficient Ratios, Enthalpy, and Entropy as a Function of Sulfuric Acid Concentration

J. L. Jensen,* V. Uaprasert, and C. R. Fujii

Department of Chemistry, California State University, Long Beach, California 90840

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Acidity and temperature dependence of rates of hydration and equilibrium ratios for hydration of 1,3-cycloalkadienes are reported over the acidity range 0.5–10.3 M H_2SO_4. $\Delta H^\ddagger$ decreases by 9 kcal mol^{-1} and $\Delta S^\ddagger$ decreases by 12 eu over the acid range 0.5–5.6 M H_2SO_4. Above 5.6 M H_2SO_4 the decrease in $\Delta G^\ddagger$ is due almost solely to $\Delta S^\ddagger$ increasing by 20 eu. Plots of $\Delta H^\ddagger$ vs. $\Delta S^\ddagger$ are linear with slopes (β) of 670 and 80 over the respective acidity ranges. Changes are ascribed to a dielectric solvation effect in dilute acid being overcome by increasing solvent structure as availability of water decreases below 7:1 H_2O:H_2SO_4 mole ratio. Kinetic acidity dependence is consistent with significant but incomplete proton transfer in the transition state for hydration. Acidity dependence of the equilibrium ratio is not described by known combinations of acidity functions H_R, H_C, and/or H_{ROH}, suggesting that triaryl carbinols are poor models for 2-cycloalkenols regarding activity coefficient behavior. Evidence is presented indicative of alcohol protonation becoming significant in about 40% H_2SO_4, provided the quantity $a_{H^+}f_D/f_{ROH_2^+}$ is nearly independent of acidity—this requires that $f_D/f_{ROH_2^+}$ decrease be dramatic. ΔG is nearly independent of acidity; however, ΔH and ΔS change in exactly the same manner as $\bar{C}_p$ (solv) and all exhibit a minimum value at H_2O:$H_2SO_4 \simeq 7$:1.

An excellent recent review observes that sulfuric acid solutions as solvent for acid-catalyzed reactions demonstrate properties which are unparalleled in toto by any other single acid medium.[1] It is for this reason that more data exist for reactions in moderate to concentrated sulfuric acid than for any other mineral acid. However, in many ways H_2SO_4 solutions are far from the ideal acidic medium. In addition to the often noted tendency of concentrated H_2SO_4 solutions to sulfonate or oxidize solutes, the thermodynamic properties of the solvent change markedly with changing acid concentration. There exist several cases where, for example, pK_a data are obtained in H_2SO_4 (using an acidity function treatment) and only later is it observed that totally different results are obtained in $HClO_4$.[2] Often the cause of "anomalous" behavior in H_2SO_4 solutions has not been determined. For these reasons we wish to report on a thermodynamic study of a reaction previously investigated in $HClO_4$ solution.[3] That closely similar behavior in $HClO_4$ and H_2SO_4 solutions is found confirms the assumption that sulfonation or oxidation reactions do not compete with the reaction of interest.

Of particular relevance to our study are the changes in solvent molar energy terms with increasing H_2SO_4 concentration.[4] To our knowledge, no explanation has been proffered for these changes, in terms translatable to influencing an acid-catalyzed reaction rate. The method employed in this report is to establish whether changes in enthalpy and entropy as determined by kinetic and equilibria studies parallel changes in solvent enthalpy or entropy terms. The conclusion suggested is that although the nature of the solvent is changing markedly, measured changes in enthalpy and entropy of activation are explainable simply in terms of medium effects on a chemical reaction.

Previous discussions of the acidity dependence of reactions in acid media have been limited to the acidity function treatment, which allows discussion of changes in free energies as indicated by changes in activity coefficient ratios.[1,5] The present study discusses entropic and enthalpic contributions. The rather smooth overall changes in free energies observed arise from compensating changes in enthalpy and entropy terms.

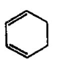
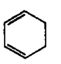
Experimental Section

Materials and Kinetic Method. Substrates were obtained from Aldrich Chemical Co. and were molecularly distilled. The procedure for 1,3-cyclohexadiene has been described previously.[3] 1,3-Cyclooctadiene was more conveniently handled as ca. 10^{-2} M solution in ethanol; concentrations of ethanol in final kinetic solutions of acid were ≤5% and did not affect the reaction rate significantly. The general kinetic method was that reported earlier.[3]

Product Analysis. The reaction being studied is eq 1. That the product is indeed 2-cycloalkenol rather than a diol was confirmed (as in an earlier study)[3] by noting that (a) products exhibited a strong short-wavelength absorbance and (b) corresponding cycloalkenes are not measurably hydrated nor are cycloalkanols dehydrated under conditions used in this study. k_{obsd} for 1,3-cyclohexadiene in 2.56 M H_2SO_4 at 80 °C is $>10^4$ that of cyclohexene.[7] Both observations support the rapid reversible hydration of 1,3-cycloalkadienes in acidic media to form 2-cycloalkenols (eq 1).

Attempts to extend conditions reported in Table I (higher acidities and temperatures) failed because of the incursion of other, as yet uncharacterized, reactions. For example, 1,3-cyclohexadiene and 1,3-cyclooctadiene upon standing for 15–20 half-lives in >6 M H_2SO_4 yielded pink and yellow solutions. These reactions are presumably

Table I. Values of k_{obsd} and Equilibrium Ratios ([Prod]/[Reactant])[a]

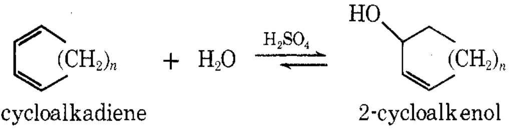
$M_{H_2SO_4}$	$10^4 k_{obsd}$		[2-cycloalkenol]/[1,3-cycloalkadiene]	
				
20 °C				
4.04	6.16		5.82	
5.64	54.9		12.6	
10.3		30.4		2.90
30 °C				
4.04	16.2		8.76	
5.64	148		13.7	
9.21		13.2		3.07
10.3		92.4		5.08
40 °C				
2.56	8.27		4.23	
4.04	50.6		6.31	
5.64	359		12.8	
7.02		1.29		2.88
8.00		5.49		3.59
9.21		43.2		4.87
10.3		262		7.51
50 °C				
1.05	2.34		3.43	
2.56	23.4		4.47	
4.04	114		7.28	
7.02		3.79		3.93
8.00		17.3		5.28
9.21		111		8.01
60 °C				
0.51	2.33			2.45
1.05	8.66		2.46	
2.56	59.8		4.24	
4.04	246		5.59	
5.64		1.22		3.55
7.02		9.99		4.74
8.00		45.8		5.61
9.21		255		11.1
70 °C				
0.51	8.46		1.92	
1.05	25.0		2.65	
2.56	157		4.45	
4.04	678		8.72	
5.64		2.90		4.29
7.02		27.8		5.62
8.00		116		8.35
9.21		492		16.4
80 °C				
0.51	23.0		1.99	
1.05	60.9		2.56	
2.56	311	.52	4.98	.68
4.04		1.59		1.53
5.64		6.15		4.77
7.02		41.6		5.96
8.00		195		13.6

[a] Mean values measured at λ_{max} of diene; average deviation of replicate measures ≤5%.

linked to the increasing concentration of cycloallylic ions as sulfuric acid concentration increases.[8-10] The uv-visible spectra of these solutions evidenced broad multiple absorption bands over the entire range 500–200 nm; further discussion of these kinetic results is deferred to a time when the reaction products can be characterized. *All* data within Table I reflect clear hydration–dehydration over 8–10 half-lives of reaction time; i.e., data reported in Table I are for eq 1.

Results

The reactions investigated are reversible and at equilibrium the product concentration is generally greater than that of reactant. Pseudo-first-order rate constants were obtained in



(1)

the traditional manner[3] by following decreasing absorbance at λ_{max} of cycloalkadiene; linear first-order kinetic plots were obtained for 3 half-lives (or longer) of reaction time. Since reactant (1,3-cycloalkadiene) is the only species absorbing light significantly at the wavelengths used to follow the reaction, calculation of the equilibrium ratio is considerably simplified.

$$\frac{[\text{2-cycloalkenol}]}{[\text{1,3-cycloalkadiene}]} = \frac{A_0 - A_e}{A_e} \qquad (2)$$

where A_0 = absorbance at time zero, A_e = absorbance at equilibrium (i.e., at time "infinity") and concentrations of species refer to the equilibrium state.

Normally $A_0 - A_e$ can be obtained most accurately by extrapolating the first-order rate plot back to zero time (i.e., time of mixing); however, for slower reactions particularly, the same value can be obtained by measuring A_0 immediately upon mixing.

Having measured the pseudo-first-order observed rate constant and the equilibrium ratio, the rate constant for hydration may be calculated using the following relationships.[11]

$$k_{obsd} = k_{hyd} + k_{dehyd} \qquad (3)$$

$$\frac{[\text{2-cycloalkenol}]}{[\text{1,3-cycloalkadiene}]} = \frac{k_{hyd}}{k_{dehyd}} \qquad (4)$$

where k_{hyd} = rate constant for the forward reaction in eq 1 and k_{dehyd} = rate constant for the reverse reaction in eq 1.

In most instances the equilibrium ratio is considerably greater than unity and therefore k_{hyd} is more precisely defined than k_{dehyd} (i.e., k_{dehyd} is the small difference between the two larger rate constants, k_{obsd} and k_{hyd}, in eq 3). As a consequence, this paper for the most part discusses effects of structure and solvent on rate constants for hydration.

Thermodynamic Parameters. Usual treatment of the dependence of k_{hyd} on temperature[3] yields enthalpies and entropies of activation. Table II displays values resulting from a least-squares analysis of the data. Values are in a range typical for alkene hydration.[3]

Since equilibrium ratios in Table I are of a size allowing precise measurement ($\leq \pm 5\%$ for $K \leq 10$), thermodynamic parameters for equilibrium 1 were calculated using eq 5.

$$\Delta H - T\Delta S = -RT \ln \frac{[\text{2-cycloalkenol}]}{[\text{1,3-cycloalkadiene}]} \qquad (5)$$

Of course, the same thermodynamic parameters are obtainable by treating k_{dehyd} (from eq 3 and 4) in the traditional way and comparing activation parameters for hydration and dehydration. Use of eq 5 is more direct since equilibrium 1 is discussed in a subsequent section; however, it must be remembered that a standard deviation of ±0.5 kcal/mol for $\Delta H^{\ddagger} \simeq 25$ kcal/mol is a different order of precision than ±1 kcal/mol for $\Delta H = 0.5$ kcal/mol. That is, although equilibrium ratios and rate constants can be measured with comparable precision, the former is *much* less sensitive to changes in temperature (i.e., $\Delta H < \Delta H^{\ddagger}$). This is just another way of stating that ΔH is the rather small difference between two much larger $\Delta H^{\ddagger}$ values, those for hydration and dehydration. In general, the same conclusions hold for ΔS as well.

For our discussion, use of ‡ denotes $\Delta H^{\ddagger}$ and/or $\Delta S^{\ddagger}$ cal-

Table II. Thermodynamic Parameters[a]

1,3-Cyclohexadiene					1,3-Cyclooctadiene				
$M_{H_2SO_4}$	ΔH^c	$\Delta H^{\ddagger b}$	ΔS^c	$\Delta S^{\ddagger b}$	$M_{H_2SO_4}$	ΔH^c	$\Delta H^{\ddagger b}$	ΔS^c	$\Delta S^{\ddagger b}$
0.51	−3.5	25.1	−9	−1.1	4.04		20.8		−17.4
1.05	−3.0	23.3	−7	−3.6	5.64	3.5	19.0	13	−20.6
2.56	1.0	19.8	6	−10.0	7.02	4.1	19.8	15	−13.8
4.04	0.4	18.0	5	−12.2	8.00	6.8	20.3	24	−9.1
5.64	0	16.5	5	−12.9	9.21	8.6	19.3	31	−8.5
					10.3	8.7	20.7	32	−0.2

[a] Calculated at 25 °C, standard deviation in enthalpies and entropies ≤ 0.5 kcal mol^{-1} and ≤ 2 eu, respectively. [b] Calculated from pseudo-first-order rate constants for hydration (eq 3 and 4 and ref 1). [c] Calculated from equilibrium ratios (eq 2 and 5), standard deviations in enthalpies and entropies ≤ 1 kcal mol^{-1} and ≤ 4 eu, respectively.

culated from rate data; *absence* of ‡ denotes ΔH and/or ΔS calculated from equilibrium data. Use of $\Delta H°$ and/or $\Delta S°$ is avoided, since none of our data can be related meaningfully to standard state.

Acidity Dependence. Earlier rigorous discussions of acidity dependence of olefin protonation and hydration[12–14] presumably applies to these reactions as well, and therefore extensive comment as to whether H_0 is an appropriate acidity function is unnecessary. Suffice it to say that plots are reasonably linear over the acidity ranges studied and that slopes, $d(\log k_{\rm hyd})/{-d(-H_0)}$, approximate unity.

Our data was also plotted against H_C, a recently defined acidity function based on protonation of carbon bases (mainly substituted azulenes).[15] While fairly linear, $d(\log k)/d(-H_C) \simeq 0.6$, and thus it appears that H_0 is still as good or better for describing the acidity dependence of rate-controlling proton transfer to olefins as any acidity function available. Use of H_0 has certain advantages, since it has been more widely studied and thus is the most closely defined acidity function. Of particular relevance to our study is the change in H_0 with increasing temperature. $d(-H_0)/d(T)$ has recently been defined:[16] using these values for H_0, $d(\log k)/d(-H_0) \simeq 1.3$ in moderately concentrated sulfuric acid solutions. Although plots of $-H_0$ vs. $\log k_{\rm hyd}$ are reasonably linear, there appears to be slight upward curvature with increasing acid concentration [i.e., $d(\log k)/d(-H_0) \simeq 1.1$ in dilute acid solution, 0.5–3 M]. While $d(-H_0)/dT$ is a significant quantity, it changes rather regularly with both increasing temperature and increasing acid concentration; thus using H_0 values at 25 °C[16–18] to correlate rate data obtained at 80 °C $d(\log k)/d(-H_0) = 1.05$; using H_0 values at 80 °C[16] the plot curvature is about the same and $d(\log k)/d(-H_0) = 1.15$. The conclusion is, then, that in a few marginal cases temperature effects on acidity dependence may lead to erroneous conclusions, but the approximate nature of $d(\log k)/d(-H_0)$ correlations precludes serious complications.

The cause of decreasing H_0 with increasing temperature is interesting. A significant amount of the change (20–40%) is attributable to changing concentration of H_2SO_4 as the temperature is increased; i.e., $\rho^{25}/\rho^{100} = 1.04$.[16] Since correlations of H_0 and/or $\log k$ with, say, $[H_2SO_4]$ always refer to $[H_2SO_4]$ as titrated at 25 °C, rate data obtained at 100 °C in x M H_2SO_4 *should*, for appropriate correlation, correlate with H_0 values at 25 °C for $0.96x$ M H_2SO_4. As mentioned above, however, such corrections are sufficiently minor as to be unwarranted. The rest of the change of H_0 with increasing temperature (the majority) must lie in the activity term of the definition. This is corroborated by the fact that $d(-H_0)/dT \neq d(-H_R)/dT$.[16,19] For example, 2% H_2SO_4 behaves 0.10 H_R units and 0.03 H_0 units *weaker* an acid at 45 °C, whereas 70% H_2SO_4 behaves 0.49 H_R units *stronger* and 0.35 H_0 units *weaker* an acid at 45 °C.[16,19] Clearly differences in temperature dependence of acidity functions become increasingly significant as acid concentration increases. The consequence of this result is clear: *differences* in acidity function behavior can only be discussed near 25 °C or for cases where the temperature dependence of the acidity function is known. For this reason, our later discussion of $H_R - H_C$ is in reference only to data at ≤40 °C.

One further point requires brief elaboration. Variation of H_0 with temperature may be expressed as $d(-H_0)/d(1/T)$ and is thus incorporated into the experimental $\Delta H^{\ddagger}$ value. Fortunately $d(-H_0)/d(1/T)$ values are known to be small.[16] The maximum effect in our study is in 10.3 M H_2SO_4 where $d(-H_0)/d(1/T) = 1.28 \times 10^{-3}$ deg^{-1} and $d(\log k)/d(-H_0) \simeq 1.4$; the corresponding maximum contribution to $\Delta H^{\ddagger}$ is 8×10^{-6} kcal mol^{-1}. Consequently, all such insignificant contributions to $\Delta H^{\ddagger}$ are ignored.

Discussion

The mechanism of hydration of 1,3-cycloalkadienes has been proposed as in Scheme I,[3,20] where . . . refers to partial bonding, D designates 1,3-cycloalkadiene, DH^+ designates cycloallylic carbonium ion intermediate, ROH_2^+ designates protonated 2-cycloalkenol, and ROH designates 2-cycloalkenol.

As developed elsewhere,[3,20] the extent of D–H bond formation in tr^+ is significant, but not complete. Thus in subsequent discussions relating to solvation of tr^+, the solvation energy of tr^+ is found to be closer to that for alcohols than to the very large solvation energy for protonated alcohols.

It is assumed throughout our discussion that medium dependence of hydration of 1,3-cyclohexadiene is essentially equal to that of 1,3-cyclooctadiene; i.e., the solvation energy of tr^+ is reasonably similar for these two compounds. This rational assumption is experimentally corroborated by data in Table II: heats and enthalpies of hydration, while not equal, change comparably over the range 4–6 M H_2SO_4.

Kinetic Acidity Function Treatment. The quantity $d(\log k_{\rm hyd})/d(M_{H_2SO_4})$ is greater than $d(-H_0)/d(M_{H_2SO_4})$ and less than $d(-H_R)/d(M_{H_2SO_4})$. Thus, as observed previously for other olefin hydrations, the activity ratio term f_D/f_{tr^+} increases relative to f_B/f_{BH^+} and decreases relative to f_{ROH}/f_{R^+} or f_C/f_{CH^+}.

$$k_{\rm hyd} = k_1 a_{H^+} f_D / f_{tr^+} \tag{6}$$

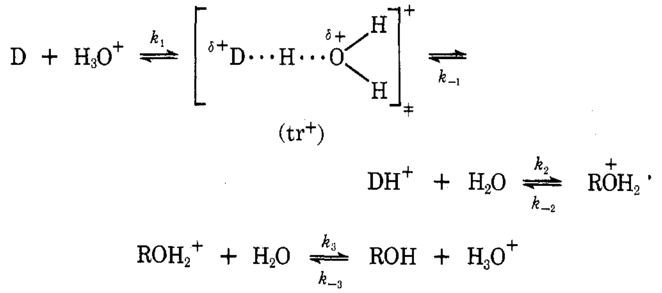
$$H_0 \equiv -\log a_{H^+} f_B / f_{BH^+} \tag{7}$$

$$H_R \equiv -\log (a_{H^+}/a_{H_2O})(f_{ROH}/f_{R^+}) \tag{8}$$

$$H_C \equiv -\log a_{H^+} f_C / f_{CH^+} \tag{9}$$

where $k_{\rm hyd}$ = experimental rate constant for hydration of 1,3-cycloalkadienes, k_1 = thermodynamic rate constant for rate-controlling proton transfer to 1,3-cycloalkadiene, a_{H^+} = activity of "proton", f_D = activity coefficient of 1,3-cycloalkadiene, f_{tr^+} = activity coefficient of the transition state for 1,3-cycloalkadiene hydration. H_0, H_R, and H_C are acidity functions based on anilinium ion (BH^+),[17] and aryl carbinol (ROH)[24] ionization and azulene (C) protonation,[15] respectively.

Scheme I



This is perhaps most easily understood in terms of a greater solvation requirement for tr^+ than for CH^+, but less than for BH^+ (although to be precise, this statement *must* be made relating f_{tr^+} to f_D, f_{CH^+} to f_C, and f_{BH^+} to f_B, since it is improbable that f_D changes with increasing acidity just as f_C or f_B).[25] The conclusion reached, then, is that tr^+ is solvated more than a carbonium ion but less than a primary anilinium ion, which is, of course, consistent with the structure of tr^+ given in Scheme I incorporating a H_3O^+/H_2O intermediate species partially bonded to the 1,3-cycloalkadiene. A further conclusion regarding extent of proton transfer is implied by noting that activity coefficient ratios change with increasing acidity according to the order $f_{ROH}/f_{R^+} > f_C/f_{CH^+} > f_D/f_{tr^+} > f_B/f_{BH^+} \gg f_{ROH}/f_{ROH_2^+}$, where the latter ratio refers to the recently defined acidity function for ethanol protonation, H_{ROH}.[21] This order is only consistent with tr^+ having significant proton transfer; i.e., tr^+ does *not* possess sites of such great solvation energy as ROH_2^+ possesses and thus a significant lessening of positive charge on oxygen is indicated in tr^+. This is in agreement with the solvent isotope effect $k_{H_2O}/k_{D_2O} = 2.3$[20] and the measured Bronsted α of 0.7–0.8 for hydration of isobutylene[23] and styrenes.[14,22]

Equilibrium Acidity Function Treatment. Dependence of the equilibrium ratio (4) on acidity is rather complex, but suggests that *if* alcohols are protonated in ≤10 M H_2SO_4 solution, the activity coefficient $f_{ROH_2^+}$ must be *dramatically* medium dependent. Under our experimental conditions, the equilibrium ratio measured using eq 4 and Scheme I is

$$\frac{[ROH] + [ROH_2^+]}{[D]} = \frac{k_1k_2k_3}{k_{-1}k_{-2}k_{-3}} a_W f_D/f_{ROH} + \frac{k_1k_2}{k_{-1}k_{-2}} a_{H^+} \frac{f_D}{f_{ROH_2^+}} \quad (10)$$

In very dilute acid, ROH_2^+ terms drop out and the equilibrium ratio should change as $a_W f_D/f_{ROH}$. Several measurements given in Table I show the equilibrium ratio in 0.5 and 1 M H_2SO_4 to be virtually equal (as eq 10 predicts, since $a_W f_D/f_{ROH}$ is nearly constant over that region). By comparing acidity functions, it is possible to see quantitatively how terms similar to those in eq 10 behave. Using definitions given by eq 8, 9, and 11

$$H_{ROH} \equiv -\log a_{H^+} f_{EtOH}/f_{EtOH_2^+} \quad (11)$$

$$H_R - H_C = \log (a_W f_C/f_{ROH}) \quad (12)$$

$$H_R - H_C - H_{ROH} - \log a_W = \log (a_{H^+} f_C/f_{EtOH_2^+}) \quad (13)$$

Equations 12 and 13 do not show log (f_{R^+}/f_{CH^+}) and log (f_{EtOH}/f_{ROH}) terms, since it is customary to assume that changes in these terms are minimal relative to changes in eq 12 and 13; i.e., medium dependence of protonated azulene CH^+ and triaryl carbonium ions is comparable, as is that of ethanol and triaryl carbinols. Table III lists these quantities along with log (equil ratio), eq 10. *Provided* that azulenes are good models for 1,3-cycloalkadienes, triaryl carbinols are good models for 2-cycloalkenols, and protonated ethanol is a good model for protonated 2-cycloalkenols, log (equil ratio) should decrease somewhat (according to $H_R - H_C$) until protonation of 2-cycloalkenol becomes significant, at which time a slight leveling off should be observed (according to $H_R - H_C - H_{ROH} - \log a_W$). Clearly log (equil ratio) does not behave as predicted by the H_R, H_C, and/or H_{ROH} functions; however, the behavior is as close as could be expected considering what is now known about the above "customary assumptions". Yates has recently compiled data demonstrating that even among solutes of similar charge or functional grouping, activity coefficient behavior is a complex function of dielectric, solvation, and bulk effects.[25] Therefore the data in Table III are suggestive of minimal changes in log $(a_W f_C/f_{ROH})$ and log $(a_{H^+} f_C/f_{ROH_2^+})$ terms, which is consistent with the observed changes in log (equil ratio). Qualitatively, it is surprising that log (f_C/f_{ROH}) decreases with increasing acidity; the data compiled by Yates shows the quantity $f_{benzene}/f_{benzyl\ alcohol}$ increasing with increasing acidity. Before any data of the type in Table III (excluding our experimental data) can be discussed semiquantitatively, more data similar to the compilation by Yates is required.

Table III. Activity Coefficient Behavior of Olefins, Alcohols, and Protonated Alcohols

$M_{H_2SO_4}$	Log $(a_W f_D/f_{ROH})^a$	Log $(a_{H^+} f_C/f_{EtOH_2^+})^b$	Log (equil ratio)^c
0.51	−0.10 (−0.09)		
1.05	−0.14 (−0.12)		
2.56	−0.49 (−0.42)		−0.14 (−0.07)^d
4.04	−0.81 (−0.66)	0.20	0.04 (0.18)^d
5.64	−1.01 (−0.73)	0.39	0.34 (0.62)^d
7.02	−1.02 (−0.58)	0.74	0.46 (0.89)
8.00	−1.34 (−0.76)	0.69	0.56 (1.14)
9.21	−1.65 (−0.85)	0.75	0.69 (1.49)
10.3	−2.01 (−0.96)	0.76	0.88 (1.92)

[a] $H_R - H_C$, eq 12 in text. Numbers in parentheses are $H_R - H_C - \log a_W = \log f_C/f_{ROH}$. [b] $H_R - H_C - H_{ROH} - \log a_W$, eq 13 in text. [c] Equation 10 of text. Values in parentheses are log (equil ratio) − log a_W. [d] Values normalized to fit on 1,3-cyclooctadiene scale; value of 2.2 for equilibrium ratio in 5.64 M H_2SO_4 was obtained by extrapolation of 1,3-cyclooctadiene values in Table I.

The conclusion from data in Table III is that no acidity function or combination of acidity functions adequately describes changes in the equilibrium ratio. *Qualitatively,* it appears that f_D/f_{ROH} increases somewhat with increasing acidity, but that the quantity $a_{H^+} f_D/f_{ROH_2^+}$ is rather insensitive to acidity (which requires the latter activity coefficient ratio to decrease dramatically as acidity is increased). This accounts for the difficulty encountered in actually observing protonation of alcohols by the several methods attempted:[26–32] protonation occurs over such a broad range of acidity that accompanying medium effects are truly massive. Data in Table III are consistent with protonation of 2-cycloalkenols becoming significant in 5.64 M (42%) H_2SO_4.

Enthalpy and Entropy Changes. Thermodynamic data have been reported for H_2SO_4 solutions as partial molal quantities; i.e., $\bar{C}_P$ (H_2SO_4) and $\bar{C}_P$ (H_2O) and $\bar{S}$ (H_2SO_4) and $\bar{S}$ (H_2O). However, quantities actually measured are, of course, those of the solvent. However, H_2SO_4 solutions are *not* merely mixtures of H_2SO_4 and H_2O molecules, but rather complex mixtures of H_2SO_4, HSO_4^-, H_3O^+, $H_9O_4^+$, H_2O, etc., and of a composite nature varying with acid concentration. Therefore we preferred to use quantities $\bar{C}_P$ (solv) and $\bar{S}$ (solv) which refer to experimental quantities obtained by others but reported differently by them. Figure 1 shows changes in solvent heat capacity and entropy. The complex change in $\bar{C}_P$ (solv) is truly remarkable and well outside experimental error. Simplistically, Figure 1 shows that *if* there were a mechanism

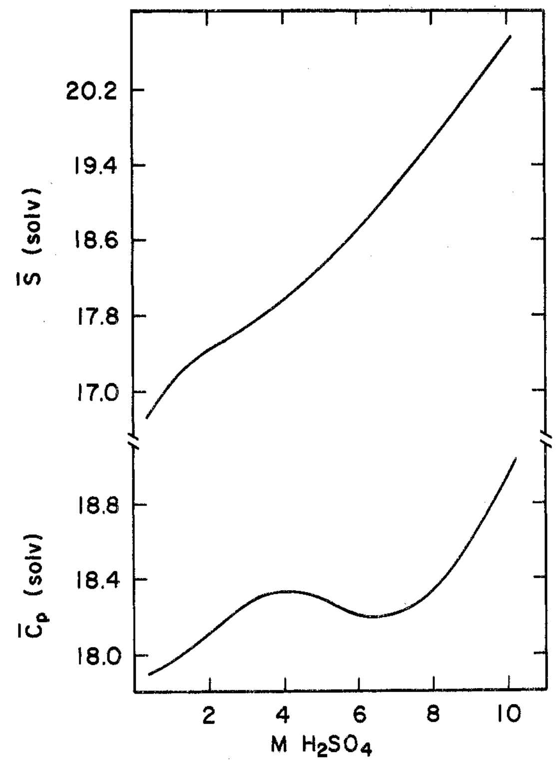


Figure 1. Plot of solvent entropy ($\bar{S}_{\text{solvent}}$, cal/deg mol solvent, top portion) and solvent heat capacity ($\bar{C}_P$ (solvent), cal/deg mol solvent, bottom portion) vs. molarity of sulfuric acid in water. Data calculated from ref 4, 1 mol of solvent ≡ (X mol H_2O + Y mol H_2SO_4)/($X + Y$).

for the solvent to transfer energy from the heat term directly toward progress on the enthalpy reaction coordinate, 4 M H_2SO_4 would have a lower $\Delta H^{\ddagger}$ than 1 M H_2SO_4 by an amount well within our experimental error (±500 cal mol^{-1}). Consequently this *direct* energy transfer process can be ignored. Secondly, *if* whatever changes in solvent that cause $\bar{C}_P$ (solv) to change also affect the enthalpies in the chemical reaction, changes in $\bar{C}_P$ (solv) may parallel changes in $\Delta H^{\ddagger}$ or ΔH. Similar logic holds for entropy terms. Figures 2 and 3 show changes in $\Delta H^{\ddagger}$, ΔH, $\Delta S^{\ddagger}$, and ΔS as a function of H_2SO_4 molarity. Clearly, changes in Figures 2 and 3 do not always parallel changes shown in Figure 1. The conclusion reached, then, is that changes in entropy and enthalpy of 1,3-cycloalkadiene hydration are explanable in terms of medium effects on enthalpy and entropy reaction coordinates. That is, the foregoing discussion justifies the assumption that changes in thermodynamic parameters observed do *not* reflect changes within the solvent alone. This allows discussion of not just the free energy changes, as is customary in acidity function treatments (activity coefficient ratio changes, etc.), but of the relative contribution of enthalpy and entropy to the overall smooth change in free energy (reflected as a smooth increase in f_D/f_{tr^+} and f_D/f_{ROH} terms).

Activation Parameters. Clearly, the medium dependence of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ does not parallel changes in comparable solvent thermodynamic properties (cf. Figures 1 and 2). Both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ *decrease* up to 6 M H_2SO_4. A plot of $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ is linear through 5.6 M H_2SO_4 with a slope (β)[33] of 670, indicating that changes in $\Delta H^{\ddagger}$ predominate over compensating changes in $\Delta S^{\ddagger}$. Beyond 5.6 M H_2SO_4 the data show some scatter but a new line appears to be established of slope 80, indicating that changes in $\Delta S^{\ddagger}$ predominate over compensating changes in $\Delta H^{\ddagger}$. Thus the rather smooth change in free energy observed (as reflected in continuously increasing f_D/f_{tr^+} ratios, for example) is attributed to enthalpy decrease up to 5.6 M H_2SO_4 and entropy increase beyond 5.6 M H_2SO_4. Further, the linear relationship of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ suggests a common source of medium dependence. In moderately concentrated acid solution (5.6–10.3 M) the increasing entropy of activation is qualitatively consistent with Scheme I: an H_3O^+ species is formally bonded to the substrate in the transition state, the increasing entropy arises from the less strongly solvated tr^+ relative to H_3O^+ (the H_2O:H_2SO_4 molar ratio changes from 7.5:1 to 2.9:1 over this region).[4] The slight increase in $\Delta H^{\ddagger}$ is scarcely outside experimental error over this range.

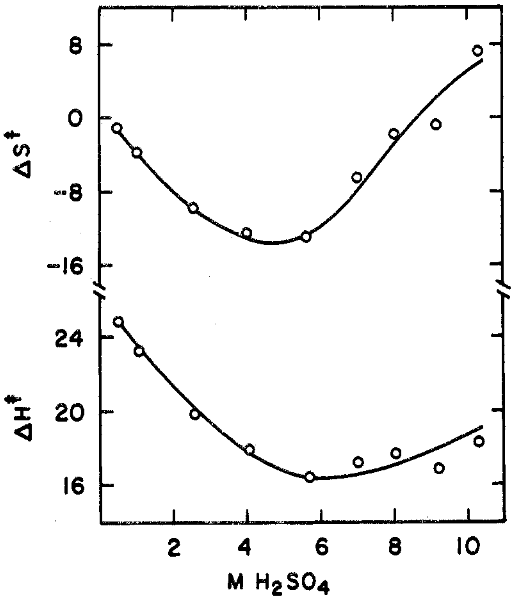


Figure 2. Plot of entropy of activation ($\Delta S^{\ddagger}$, cal/deg mol, top portion) and enthalpy of activation ($\Delta H^{\ddagger}$, kcal/mol, bottom portion) vs. molarity of sulfuric acid in water. Smooth curve represents data in Table II, considering error limits and normalizing $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for 1,3-cyclooctadiene to scale for 1,3-cyclohexadiene (e.g., $\Delta H^{\ddagger}$ plotted ≥5.6 M H_2SO_4 = $\Delta H^{\ddagger}$ (1,3-cyclooctadiene) − 2.5 kcal mol^{-1}. The amount 2.5 kcal mol^{-1} is the difference between the $\Delta H^{\ddagger}$ values for the two compounds at the common acid molarity 5.64 M).

Rationalization of changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in dilute acid (0.5–5.6 M) is more complex, but still consistent with Scheme I. The increase in f_D/f_{tr^+} ratio was explained in terms of solvation requirement for tr^+ being intermediate to that of triaryl carbinols and anilinium ions: that is reflected in an overall *decrease* in $\Delta G^{\ddagger}$ over this acid range. Water is present in excess over this range of acidity ([H_2O]:[H_2SO_4] changes from 55:1 to 7.5:1):[4] decreasing $\Delta S^{\ddagger}$ reflects incorporation of the solvent aggregates in the transition state, an effect which appears to be rather dramatically overcome by increasing solvent structure above 5.6 M H_2SO_4. The 9 kcal/mol decrease in $\Delta H^{\ddagger}$ over the dilute acid range is consistent with a dielectric effect (a greater "salting-in" of tr^+ than reactants). However as water becomes less capable of solvating tr^+, the dielectric effect is compensated for by loss of solvating ability and $\Delta H^{\ddagger}$ appears nearly medium independent beyond 5.6 M H_2SO_4. The common source of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ changes, then, is capability of water to solvate ions in solution. In this regard it is striking that the minima in the curves of Figure 2 occur at H_2O:H_2SO_4 molar ratio of 7:1. Assuming that three water molecules are needed to solvate the three partially negative oxygens of HSO_4^- and four water molecules are needed to solvate the three partially positive protons of H_3O^+, the total requirement is 7:1 = [H_2O]:[H_2SO_4].

Medium dependence of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ suggest that the availability of water as solvating agent controls changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Further, these quantities do not change continuously over normal acidity ranges studied but seem to be quite sensitive to solvent structure, as determined by existence of "free water" (water molecules not specifically solvating a δ^+ H–O or a δ^- O–S).

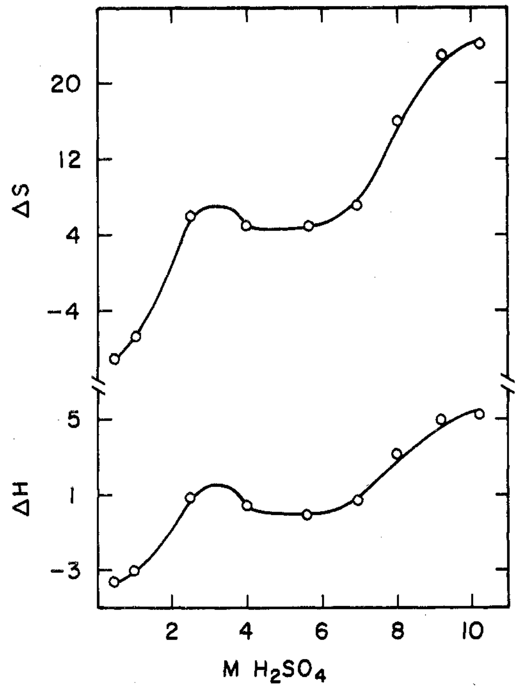


Figure 3. Plot of entropy (ΔS, cal/deg mol, top portion) and enthalpy (ΔH, kcal/mol, bottom portion) calculated from the equilibrium ratio vs. molarity of sulfuric acid in water. Smooth curve represents data in Table II, considering error limits and normalizing ΔH and ΔS for 1,3-cyclooctadiene to scale for 1,3-cyclohexadiene (e.g., ΔH plotted ≥5.6 M H_2SO_4 = ΔH (1,3-cyclooctadiene) − 3.5 kcal mol^{-1}. The amount 3.5 kcal mol^{-1} is the difference between the ΔH values for the two compounds at the common acid molarity 5.64 M H_2SO_4).

Equilibrium Thermodynamic Parameters. Medium dependence of ΔH and ΔS parallels changes in $\bar{C}_P$ (solv), as evident from Figures 1 and 3. A plot of ΔH vs. ΔS is linear and the slope is 265; that is, changes in ΔH are almost compensated for by changes in ΔS and the overall ΔG is nearly constant (which is reflected by the very small change in log (equil ratio) in Table III). It is striking that the curves in Figures 1–3 exhibit minima at about 6 M H_2SO_4 ($[H_2O]:[H_2SO_4] \simeq 7:1$). Further, the linearity of ΔH and ΔS over the entire acidity range suggests that changes in ΔH, ΔS, and $\bar{C}_P$ (solv) with acidity have a common source over the range. It is possible, of course, that the changes in ΔH and ΔS are fortuitously similar to changes in $\bar{C}_P$ (solv): the former may change because of significant protonation of 2-cycloalkenols above 4–5 M H_2SO_4. We prefer to link ΔH, ΔS, and $\bar{C}_P$ (solv), but available data do not justify any conclusions. In other words, there are sufficient open parameters to explain *any* medium dependence in Figure 3. Therefore we merely report the above observations with the comment that sulfuric acid solutions, based on these thermodynamic properties, seem to undergo a definite sort of solvent change at ~6 M H_2SO_4.

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Registry No.—H_2SO_4, 7664-93-9; 1,3-cyclohexadiene, 592-57-4; 1,3-cyclooctadiene, 1700-10-3.

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