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Equilibrium Constants for Dehydration of Water Adducts of Aromatic Carbon−Carbon Double Bonds

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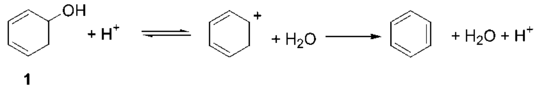
Abstract: Equilibrium constants (K_{de}) are reported for the dehydration of hydrates of benzene, naphthalene, phenanthrene, and anthracene. Free energies of formation of the hydrates (ΔG°_f(aq)) are derived by combining free energies of formation of the parent (dihydroaromatic) hydrocarbon with estimates of the increment in free energy (ΔG^{OH}) accompanying replacement of a hydrogen atom of the hydrocarbon by a hydroxyl group. Combining these in turn with free energies of formation of H_2O and of the aromatic hydrocarbon products furnishes the desired equilibrium constants. The method depends on the availability of thermodynamic data (i) for the hydrocarbons from which the hydrates are derived by hydroxyl substitution and (ii) for a sufficient range of alcohols to assess the structural dependence of ΔG^{OH}. The data comprise chiefly heats of formation and standard entropies in the gas phase and free energies of transfer from the gas phase to aqueous solution (the latter being derived from vapor pressures and solubilities). They also include experimental measurements of equilibrium constants for dehydration of alcohols, especially cyclic, allylic, and benzylic alcohols. In general ΔG^{OH} depends on whether the alcohol is (a) primary, secondary, or tertiary; (b) allylic or benzylic; and (c) open chain or cyclic. Differences in geminal interactions of the hydroxyl group of the alcohol with α-alkyl and vinyl or phenyl groups account for variations in ΔG^{OH} of 5 kcal mol^{-1}. Weaker variations which arise from β-vinyl/OH or β-phenyl/OH interactions present in the aromatic hydrates but not in experimentally studied analogues are estimated as 1.0 kcal mol^{-1}. Equilibrium constants for dehydration may be expressed as their negative logs (pK_{de}). Reactions yielding the following aliphatic, aromatic, and antiaromatic unsaturated products then have pK_{de} values: +4.8, ethene; +15.0, ethyne; +22.1, cyclopropene; +28.4 cyclobutadiene; −22.2, benzene; −14.6, naphthalene; −9.2, phenanthrene; −7.4, anthracene. Large positive values are associated with formation of strained or antiaromatic double bonds and large negative values with aromatic double bonds. Trends in pK_{de} parallel those of heats of hydrogenation. The results illustrate the usefulness of a substituent treatment for extending the range of currently available free energies of formation. In addition to hydroxyl substituent effects, ΔG^{OH}, values of ΔG^{π} for substitution of a π-bond in a hydrocarbon are reported.

Introduction

The aim of this paper is to derive equilibrium constants for the dehydration of water adducts (hydrates) of aromatic molecules. Experimentally, dehydration occurs readily in the presence of an acid catalyst to yield the aromatic product.[1,3] The reaction is illustrated by the aromatization of benzene hydrate (**1**) shown in Scheme 1 and is closely related to the acid-catalyzed dehydration of alcohols to form alkenes.[2] Rate constants for dehydration have been measured for hydrates of benzene, naphthalene, phenanthrene, and anthracene[1] and also benzofuran and benzothiophene.[4] However, because the reaction lies strongly in favor of the aromatic product, direct measurements of equilibrium constants have not been possible.

Scheme 1



The equilibrium constant for the dehydration reaction K_{de} may be expressed as a difference in free energies of formation of reactants and products, as shown in eq 1. Insofar as the free energies of formation of water and benzene (and other aromatic molecules) are known,[5,6] evaluation of K_{de} reduces to measurement or estimation of a free energy of formation of the aromatic hydrate. Measurements of unknown free energies are not easily undertaken, and the approach of this paper is to estimate ΔG°_f for the hydrates from existing thermodynamic data or measurements of equilibrium constants of related reactions.

$$-RT \ln K = \Delta G^\circ_f(C_6H_6) + \Delta G^\circ_f(H_2O) - \Delta G^\circ_f(\text{hydrate}) \quad (1)$$

The free energies of formation required refer to aqueous solution at 25°. Hitherto, thermodynamic data have been more

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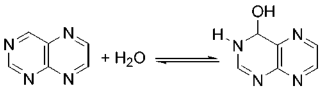
readily available for the gas phase than solution. However, Hine[7] and Guthrie[5] have used vapor pressures and aqueous solubilities of organic compounds to evaluate free energies of transfer from gas to solution. By this means Guthrie has calculated a wide range of free energies of formation and has developed a scheme of additive group contributions,[5] similar to those of Benson and others for heats of formation in the gas phase,[8] which allow estimation of values of $\Delta G°_f$(aq) for compounds for which measurements are lacking.

In principle, Guthrie's group contributions may be used to estimate values of $\Delta G°_f$(aq) for aromatic hydrates. However, as emphasized by Benson,[8] the generality of the group method makes some sacrifice of precision. Thus, for prediction of equilibrium constants, which are commonly measured with a higher precision than thermodynamic data, a more precise method is desirable.

For not too large molecules it is possible to calculate heats of formation for the gas phase by molecular mechanics or by semiempirical or ab initio quantum methods[9−11] and to combine these with measured, computed, or estimated entropies, vapor pressures, and solubilities to obtain $\Delta G°_f$(aq). Such methods have been applied to calculations of equilibrium constants for the addition of water to carbon−oxygen[10] and carbon−nitrogen[11] double bonds, including hydration of polyazanaphthalenes (eq 2) and nucleotide bases.[12]



(2)

In this paper, however, we adopt an approach used by Guthrie for extrapolating the free energy of formation of an unknown compound from that of a known related structure. Guthrie estimated equilibrium constants for addition of water or alcohols to the carbonyl groups of esters and amides to form tetrahedral adducts by taking as models for the adducts corresponding ortho esters or orthoamides in which a proacyl hydroxyl group had been replaced by methoxyl and for which a free energy of formation was available or could be measured. He evaluated the effect of replacing the methoxyl by hydroxyl (e.g. as in eq 3) from differences in experimentally measured free energies of formation of alcohols and methyl ethers and of acetals and hemiacetals.[13]

$$\mathrm{RCH(OMe)_2 + H_2O \rightleftharpoons RCH(OMe)OH + MeOH} \qquad (3)$$

To estimate free energies of formation of aromatic hydrates, we have used a similar approach. A substantially larger body of thermodynamic data exists for hydrocarbons than alcohols. This means that an unmeasured value of $\Delta G°_f$(aq) for an alcohol may be estimated from the effect of replacing a hydrogen atom of the hydrocarbon by a hydroxyl group. This replacement is shown in eq 4, where R−H and R−OH represent the hydrocarbon and alcohol and ΔG^{OH} is a difference in their free energies of formation.

$$\mathrm{R{-}H} \xrightarrow{\Delta G^{\mathrm{OH}}} \mathrm{R{-}OH} \qquad (4)$$

The unknown $\Delta G°_f$(aq) is derived by examining values of ΔG^{OH} for alcohols and hydrocarbons for which $\Delta G°_f$(aq) is known. Data are available from thermodynamic measurements and from measurements of equilibrium constants for the hydration of alkenes[14−16] (if $\Delta G°_f$(aq) for the alkene is known). The structure of the target alcohol is matched to that of alcohols in this database and ΔG^{OH} assigned accordingly.

The plan of this paper reflects this objective. First, equilibrium constants for dehydration of simple alcohols and their dependence on the structure of the alcohol and alkene are examined. Then values of $\Delta G°_f$(aq) for alcohols, from conventional thermodynamic measurements and from the hydration equilibria, are converted to free energies for hydroxyl replacement [$\Delta G^{OH} = \Delta G°_f(\mathrm{R{-}OH}) - \Delta G°_f(\mathrm{R{-}H})$], and their dependence on the structure of R is evaluated. Finally, appropriate values of ΔG^{OH} are combined with measured or estimated values of $\Delta G°_f$(aq) for dihydroaromatic molecules to obtain $\Delta G°_f$(aq) for the arene hydrates. We can then derive equilibrium constants for dehydration from eq 1 provided $\Delta G°_f$(aq) for the corresponding aromatic molecules are known.

Results

Free Energies of Formation. Free energies of formation in aqueous solution of a number of the alcohols and corresponding hydrocarbons used in this paper have been compiled by Guthrie.[5] They include straight chain primary alcohols and secondary and tertiary alcohols containing one or two α-methyl substituents, respectively. They also include secondary cycloalkanols, allyl alcohol, benzyl alcohol, and vinyl alcohols (enols). Free energies of formation of further alcohols, including acyclic and cyclic allylic or benzylic alcohols, have been evaluated from experimental measurements of equilibrium constants for dehydration[14−17] combined with a knowledge a of $\Delta G°_f$(aq) for the unsaturated product.

Free energies of formation of the products of dehydration, and of the hydrocarbons from which $\Delta G°_f$(aq) for alcohols were derived by hydroxyl substitution, were generally available for the gas phase from the TRC compilation "Thermodynamics of Organic Compounds in the Gas State".[6] This compilation provides a source of experimental and calculated entropies which allows conversion of heats of formation compiled by Pedley[18] into free energies of formation for the gas phase and updates the previously collected source of such data by Stull et al.[19] Many of the values of interest here are for cycloalkyl rings for

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which values were critically reviewed and new calculations of $S°$ undertaken by Dorofeeva et al.[20] In a few instances experimental values of $\Delta H°_f(g)$ for these compounds were not available. Thus for cyclobutadiene $\Delta H°_f(g)$ was a calculated value.[21] For 1,2-dihydronaphthalene $\Delta H°_f(liq)$ was available[22] and was combined with $\Delta H_v = 13.6$ kcal mol^{-1} estimated from the bp (as described below) to give $\Delta H°_f(g)$, which could be combined with a calculated value[20] of $S°$ to obtain $\Delta G°_f(g) = 55.1$ kcal mol^{-1} from eq 5. For 1,4-dihydronaphthalene $\Delta G°_f(g) = 59.3$ kcal mol^{-1} was similarly derived from[21] $\Delta H°_f(l) = 20.1$ kcal mol^{-1} using the same value for ΔH_v as that used for its isomer; again $S°$ was a calculated value.[6]

$$\Delta G°_f(g) = \Delta H°_f(liq) + \Delta H_v - 298.16\Delta S°_f(g) \qquad (5)$$

For cyclobutanol, a value of $\Delta H°_f(g) = -34.6$ kcal mol^{-1} is available and $S°$ can be estimated from the value for cyclobutane plus an average of the increment in entropy for replacement of H by OH in cyclopentane and cyclohexane. This led to $\Delta G°_f(g) = -10.4$ kcal mol^{-1}.[23]

For the unsaturated cyclic hydrocarbons, in most instances, values of free energies of transfer ΔG_t were required to convert gas-phase data into free energies of formation for aqueous solution. These were obtained from the vapor pressure and aqueous solubility at 25 °C following the procedure of Hine and Guthrie summarized in eqs 6−8. In these equations γ is Hine's activity coefficient referring to transfer of a mole of gas from an ideal 1 M concentration in the gas phase to aqueous solution at 25 °C, p is the vapor pressure of the gas in millimeters of mercury at 25 °C, c_g is the corresponding molar concentration of the gas, and c_w is the (molar) solubility in water (assuming that this is low enough for an ideal solution to prevail).

$$\log c_g = \log p - 4.269 \qquad (6)$$

$$\gamma = c_w/c_g \qquad (7)$$

$$\Delta G_t = -1.364\{\log \gamma - 1.39\} \qquad (8)$$

The data required therefore are vapor pressures and aqueous solubilities at 25 °C.[7] Solubilities of a number of cyclic and acyclic hydrocarbons have been measured by McAuliffe,[24] who has shown that linear correlations exist between solubility and molar volume for different ring sizes or with the degree of unsaturation at constant ring size. Where the molar volume (molecular weight/density) is not available, as for example for cyclobutadiene, similar correlations of molar volume with ring size or number of double bonds exist. These correlations allow solubilities of all cyclic hydrocarbons of ring sizes from 3 to 8 to be inferred if measurements are lacking. Also inferred was the solubility of *trans*-2-butene. Further solubility data have been reported by Deno and Berkheimer.[25]

There are a number of compilations of vapor pressures[26−29] from which vapor pressures at 25 °C may be obtained either as a direct measurement, by extrapolation of a plot of log p against T, or from coefficients of the Antoine equation calculated from the temperature dependence of the vapor pressure in a temperature range removed from 25 °C.[26] For cyclopropane and butadiene, for which vapor pressure data are lacking, the required value was derived from the (estimated) boiling point and the heat of vaporization of the liquid (ΔH_v) by making use of eq 9.[30] In this equation, p is the vapor pressure at 25 °C and T_b is the boiling point of the liquid (K). In the absence of satisfactory models for estimating ΔC_{vap}[31] for the hydrocarbons concerned, the values were taken as −12.[30]

$$\ln p = \ln 760 - \frac{\Delta H_v}{\mathrm{R}}\left\{\frac{1}{298} - \frac{1}{T_b}\right\} + \frac{\Delta C_{vap}}{R}\left\{1 - \frac{298}{T_b} - \frac{\ln 298}{T_b}\right\} \qquad (9)$$

Evaluation of the vapor pressure requires a knowledge of ΔH_v, which itself will normally be unavailable in the absence of vapor pressure measurements as a function of temperature. Fortunately, accurate estimates of ΔH_v can be obtained from correlations of ΔH_v with bp[32] or by group contributions,[33] which have been well-developed for cyclic hydrocarbons.[33]

Even where the bp of a compound is lacking, as for cyclobutadiene, a value may be inferred from a correlation of boiling points with the molecular connectivity parameter χ used by Kier and Hall.[34] White has used such a correlation to predict bps for polycyclic aromatic hydrocarbons.[35] For small and medium ring hydrocarbons, the correlation is not linear and there are separate correlation lines for cycloalkanes, cycloalkenes, and cycloalkadienes, etc. However, these correlations are nearly parallel, and it is possible to infer a bp ∼ −15 °C for cyclobutadiene (if it is assumed that there is no difference in bp between singlet and triplet structures).

Values of vapor pressure p and corresponding values of c_g for these compounds are listed in Table 1 together with values of γ and ΔG_t obtained from their combination with c_w according to eqs 6−8. For a few bi- or tricyclic hydrocarbons, notably 1,2-dihydronaphthalene, indene, indane, 9,10-dihydronaphthalene, and 9,10-dihydroanthracene, solubility measurements are lacking. Our own attempts at spectrophotometric measurements of the solubility of the lower molecular weight bicyclic molecules were poorly reproducible, partly because the compounds are liquids and less easily handled than solids. Although dihydroanthracene and dihydrophenanthrene are solids, they were too insoluble to allow straightforward measurements. In these cases therefore values of log γ were again interpolated, from comparisons within a matrix of similar structures, as shown in Charts 1 and 2, in which values of log γ are displayed below the structures and the interpolated values are shown in brackets.

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Table 1. Solubilities, Free Energies of Transfer and ΔG°_f(aq) (kcal mol^{-1}) for Cyclic Hydrocarbons

	log c_w	p^a	log c_g	log γ	ΔG_t	ΔG°_f(g)	ΔG°_f(aq)
cyclobutane^{b,c}	−2.20	1175	−1.2	−1.00	3.26	26.80	30.06
cyclopropene^{b,d}	−1.15	5320	−0.54	−0.62	2.74	68.50	71.2
cyclobutene^{b,c}	−1.60	1695	−1.04	−0.56	2.66	48.33	51.0
cyclobutadiene^{b,d,f,g}	−1.12	2030	−0.96	−0.14	2.09	103.3	105.4
cyclopentadiene^{b,e}	−1.62	437	−1.63	0.01	1.88	42.55	44.43
1,3-cyclohexadiene^{b,e}	−2.10	98	−2.27	0.17	1.66	43.5	45.2
1,4-cyclohexadiene^{b,h}	−2.06	67.5	−2.44	0.38	1.38	44.60	46.0
trans-2-butene	−2.26^j	760^k	−1.39	−2.26	3.09	15.13	18.22
1,2,3,4-tetrahydronaphthalene	−3.49	0.233	−0.03	1.41	−0.03	40.07	40.04
indene				1.45^p	−0.08	56.2	56.1
indane				1.25^p	0.19	40.04	40.2
1,2-dihydronaphthalene				1.65^p	−0.35	55.10	54.75
1,4-dihydronaphthalene				1.75^p	−0.49	59.1	58.6
9,10-dihydrophenanthrene				2.70^p	−1.79	69.15	67.36
9,10-dihydroanthracene				3.10^p	−2.33	70.76	68.43
trans-1,3-pentadiene				−0.46^q	2.52	34.90	37.42

[a] Vapor pressure (mmHg) measurements at 25 °C. [b] Solubility from correlation of c_w with molecular volume.[24] [c] Vapor pressure from the Antoine equation. [d] Vapor pressure at 25 °C from bp and a value of ΔH_v estimated from a correlation of ΔH_v and bp for cyclic and noncyclic hydrocarbons, or as otherwise indicated. [e] The vapor pressure at 25 °C from Smith and Srivatsava.[27] [f] Molecular volume predicted from correlation with ring size and degree of unsaturation. [g] Bp from a plot of bp versus χ for cycloalkenes, alkenes, and alkadienes.[35] [h] Solubility from McAuliffe.[24] [j] Solubility estimated from value for 1-butene multiplied by the ratio of values for *trans*-2-pentene and 1-pentene.[24] [k] Gas solubility measured at 1 atm pressure. [m] Solubility from ref 25; vapor pressure from ref 29. [p] log γ interpolated as described in text. [q] log γ estimated as the value for 1,4-pentadiene corrected for the difference between 1-pentene and 2-pentene (values from ref 5).

Chart 1

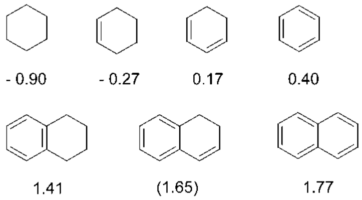
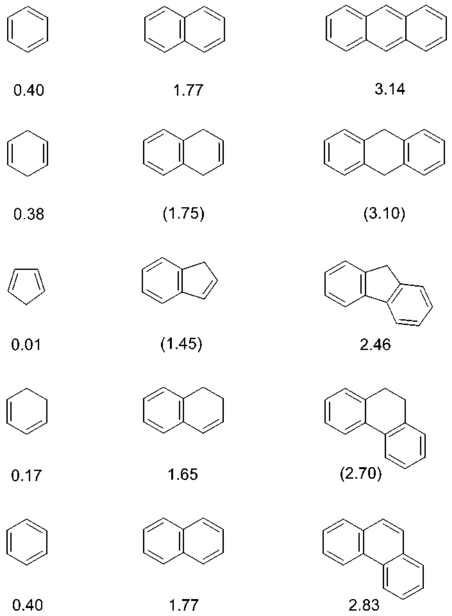


Chart 2



In Chart 1 the value for dihydronaphthalene comes from allowance for the combined effects of (a) the degree of unsaturation and (b) benzoannelation. Thus, the ratio of increments between compounds in the second row of the chart is taken to be the same as that for the last three compounds of the first.

In Chart 2 other values of log γ are interpolated from consideration of the effects of benzoannelation and unsaturation on five- and six-membered rings. These interpolations make use of the value for dihydronaphthalene from Chart 1 and recognize that the more compact structure of two isomeric molecules (e.g. phenanthrene compared with anthracene) is characterized by a smaller value of log γ.

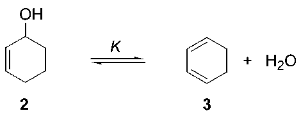
More specifically the increments in log γ between adjacent compounds in row two were assumed to be the same as in row one (with interpolated values rounded to 0.05 log units). For rows three and four it was assumed that the ratio of increments between the first and the second and the second and the third compounds was the same in the two rows. This ratio is similar to but not quite the same as the corresponding ratio in row 5.

The remaining value to be assigned in Chart 2 is log γ for indane which is taken as 1.25 by assuming that the difference from indene is the same as the difference between 1,2-dihydronaphthalene and 1,2,3,4-tetrahydronaphthalene. Despite the arbitrary nature of these interpolations the error in log γ should not be greater than 0.05 which amounts to a 10% change in equilibrium constant.

For cyclobutanol a value of log γ was inferred from inspection of the difference in log γ between alcohols and the corresponding hydrocarbons. For primary, secondary and tertiary alcohols with 2−5 carbons and cyclopentanol and cyclohexanol this difference falls between 4.90 and 5.06: for cyclobutanol a value of 4.9 was assigned, equal to that for the cyclic alcohols.

Experimental Measurements of Equilibrium Constants. Direct measurements of equilibrium constants for dehydration are often made only with difficulty because of the slow rate at which equilibrium is achieved and the small amount of alkene present at equilibrium with the dominant alcohol. For allylic and benzylic alcohols, however, the rate of dehydration is faster than for aliphatic alcohols, and there is a substantial fraction of alkene formed at equilibrium. Moreover a strong chromophore for the alkene allows the equilibrium constant to be conveniently measured using UV−vis spectrophotometry. Equilibrium constants for reactions relevant to this paper have been measured by Schubert and Keeffe,[14] Jensen and co-workers,[15] Gold and Gruen,[16] and ourselves. Earlier measurements are cited in ref 17.

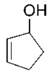
These measurements are important in offering access to cyclic allylic or benzylic alcohols, which are close analogues of arene hydrates. No thermodynamic measurements are available for such alcohols, but the combination of a measurement of an equilibrium constant, for example for dehydration of cyclohexenol (**2**) to cyclohexadiene (**3**, eq 10), with a value of $\Delta G°_f$(aq) for the diene product allows us to derive $\Delta G°_f$(aq) for the alcohol, as illustrated in eq 11.



(10)

$$\Delta G°_f(C_6H_9OH)(aq) = -RT \ln K + \Delta G°_f(C_6H_8)(aq) + \Delta G°_f(H_2O) \quad (11)$$

The alcohols for which equilibrium measurements were carried out were 2-cyclohexenol (**2**), 2-cyclopentenol (**4**), 1-phenylpropan-1-ol (**5**), and *trans*-3-penten-2-ol (**6**); measurements for tetralol (**7**) and indanol (**8**) were available from a previous study.[1] Values of $\Delta G°_f$(aq) for the products of dehydration, namely, cyclohexadiene, cyclopentadiene, *trans*-1,3-pentadiene, 1,2-dihydronaphthalene, and indene are listed in Table 1.



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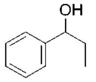

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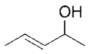

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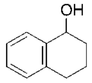

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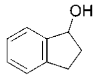


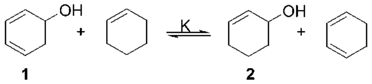
8

There are experimental difficulties even with these measurements, however. At 25 °C the acid-catalyzed approach to equilibrium still occurs rather slowly. Equilibrium constants have to be extrapolated from measurements in fairly concentrated solutions of strong acids therefore, and, as the value appears to be sensitive to the amount of acid in the medium, this extrapolation is subject to some uncertainty. This difficulty is compounded by the low solubility of the alkenes, their tendency to polymerize, and in some cases their volatility or high concentration relative to the alcohol at equilibrium. The equilibrium constants are thus subject to a significant experimental error (e.g. 20%). Nevertheless, the uncertainty is generally small compared with the variations in magnitude of equilibrium constants with changes of structures of the alkenes or alcohols under examination.

The measurements were based on spectrophotometric monitoring of the reactions and are described in the Experimental Section of the paper. By combining the equilibrium constants found with values of $\Delta G°_f$(aq) for the appropriate dienes or styrenes the following values of $\Delta G°_f$(aq) were calculated for the alcohols (kcal mol^{-1}) using eq 11: 2-cyclohexenol (**2**), −12.85; 2-cyclopentenol (**4**), −11.2; tetralol (**7**), −0.1; indanol (**8**), 0.8; 1-phenylpropan-1-ol (**5**), −7.1; *trans*-3-penten-2-ol (**6**), −20.3. In addition, values of $\Delta G°_f$(aq) were derived for 1-penten-3-ol (−17.8) and 1-buten-3-ol (−19.8), by assuming that the substituent effect of replacing H by OH in 2-pentene to give 3-penten-2-ol was the same as the corresponding replacement in 1-pentene and 1-butene to give 1-penten-3-ol and 1-buten-3-ol, respectively.

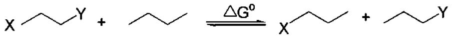
Rate constants were also measured for the acid-catalyzed hydration or dehydration reactions. Values for aqueous solution were extrapolated from measurements in concentrated acid solutions based on plots of logs of second-order rate constants against the medium acidity parameter X. The measurements refer to 25° and gave 4.5×10^{-4} (cyclopentenol), 1.6×10^{-4} (1-phenyl-1-propanol), 5.3×10^{-6} (cyclohexenol), and 1.7×10^{-5} (3-penten-2-ol) with units $M^{-1}\ s^{-1}$. The measurements could be made by taking either the alcohol or alkene as reactant, and the rate constants represent a sum of values for the hydration and dehydration reactions. In the case of 3-penten-2-ol the rate constant (and equilibrium constant) measured refers to formation of the *trans*-1,3-pentadiene (piperylene), as equilibrium is established much more rapidly with the *trans*- than *cis*-pentadiene product. An approximate rate constant for conversion of *cis*-pentadiene to an equilibrium mixture of *trans*-3-penten-2-ol and *cis*- and *trans*-pentadienes was measured as 3.0×10^{-6} $M^{-1}\ s^{-1}$.

1,2-Substituent Interactions. The main structural difference between the alcohols for which equilibrium studies have been carried out and the arene hydrates for which equilibrium constants are to be estimated is illustrated by comparison of benzene hydrate (cyclohexadienol) **1** and cyclohexenol **2**. There is an additional double bond in the hydrate not present in cyclohexenol. If we consider the difference in free energy changes accompanying introduction of a hydroxyl substituent into cyclohexene and cyclohexadiene, respectively, it is apparent that this corresponds to the energy of what is formally a 1,2-interaction between the hydroxyl group and the remote (4, 5) double bond of cyclohexadienol, as expressed by the isodesmic reaction of eq 12. If the measurable free energy change between cyclohexene and cyclohexenol is to be transformed into that between cyclohexadiene and the hydrate, therefore account must be taken of this interaction.



(12)

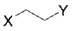
It appears that no thermodynamic data or equilibrium measurements exist for 3,4-unsaturated alcohols, i.e., alchohols which include the structural feature of interest. The magnitude of the interaction must be inferred therefore by considering other 1,2-interactions. In general, for substituents X and Y this may be expressed by the isodesmic equilibrium of eq 13. If the equilibrium constant for the reaction is unity ($\Delta G° = 0$ kcal mol^{-1}), there is no net stabilization or destabilization. If the equilibrium constant is <1 ($\Delta G°$ positive), the interaction is stabilizing, and if the equilibrium constant is >1 ($\Delta G°$ negative), the interaction is destabilizing.



(13)

Available measurements based on eq 13 are listed in Table 2. The table includes values of $\Delta H°$ based on data for the gas phase[18,19] in addition to values of $\Delta G°$ for the gas phase[6,19] and aqueous solution.[5] For X = Y = Cl it is found that $\Delta H°(g) = -3.2$ kcal mol^{-1}, $\Delta G°(g) = -3.4$ kcal mol^{-1}, and $\Delta G°(aq) = -4.6$ kcal mol^{-1}; i.e., the 1,2-interaction of two chlorine atoms is quite strongly repulsive. The same is true to a lesser degree of two bromine atoms or two iodine atoms. On the other hand, a chlorine atom and a methyl group are attractive ($\Delta G°(aq) =$

Table 2. 1,2-Interaction Energies (kcal mol^{-1}) between X and Y Based on Equation 13[a]

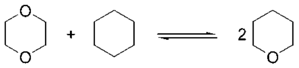


X	Y	$\Delta H°$ (g)	$\Delta G°$(g)	$\Delta G°$(aq)
CN	CN	−5.9		
Cl	Cl	−3.2	−3.4	−4.6
Br	Br	−0.6	−2.4	−3.5
F	F	0.6	0.2	
NH_2	NH_2	1.6		
HO	HO	1.0	−2.7	−1.0
$CH_2{=}CH$	$CH_2{=}CH$	0.2	−0.75	−0.65
Ph	Ph	0.2		
CH_3	CH_3	0	0.6	0
CN	CH_3	−0.7	−0.7	
Cl	CH_3	2.0	4.3	3.8
Cl	CH_2Cl	−0.2	1.0	
F	CH_3	−0.4	−0.5	
NH_2	CH_3	0.4		
HO	CH_3	−0.2	0.1	1.2
$CH_2{=}CH$	CH_3	0.4	−0.1	0.05
Ph	CH_3	0.7	−0.25	−0.1

[a] Data from refs 5, 6, and 18: positive values indicate favorable interactions.

3.8 kcal mol^{-1}). In general, the interactions seem to show a dependence on the electronegativity (and possibly polarizability) of X and Y.

The behavior of two OH (or NH_2) groups is a little different from that of the halogens insofar as $\Delta H°$ in the gas phase is positive; i.e., the interaction is attractive. This is presumably because $HOCH_2CH_2OH$ and $NH_2CH_2CH_2NH_2$ are stabilized by hydrogen bonding. For two ether oxygen atoms, for example in dioxan, for which no hydrogen bonding is possible, the interaction is again repulsive. Thus, for the equilibrium of eq 14, $\Delta H° = -2$ kcal mol^{-1}.

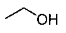
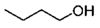
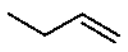
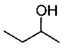
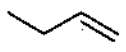
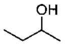
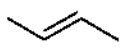
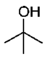
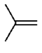
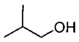

(14)

On the other hand $\Delta G°$ for $HOCH_2CH_2OH$, in the gas phase is −2.7 kcal mol^{-1}, despite the positive value of $\Delta H°$. Presumably this reflects hindering of rotation about the C−C bond by the hydrogen bonding. $\Delta G°$ remains negative in aqueous solution ($\Delta G°(aq) = -1.0$ kcal mol^{-1}), and in the absence of intramolecular hydrogen bonding apparently the mutual repulsion of the electronegative oxygen atoms reasserts itself.

However, the repulsion between two oxygen atoms is noticeably less than between two chlorine atoms. Similarly, the interaction between OH and CH_3 ($\Delta G°(aq) = 1.2$ kcal mol^{-1}) is less favorable than between Cl and CH_3 ($\Delta G°(aq) = 3.8$ kcal mol^{-1}). In this connection, it is noteworthy that the fluorine−fluorine interaction in FCH_2CH_2F is positive rather than negative ($\Delta G°(g) = +0.6$ kcal mol^{-1}) and the interaction between F and CH_3 is negative rather than positive ($\Delta G°(g) = -0.4$ kcal mol^{-1}). Thus, the oxygen atoms appear to be intermediate in behavior between Cl and F.

Our interest is in the interaction between OH and a double bond or phenyl group. Two vinyl groups (in 1,5-hexadiene) are mildly repulsive in aqueous solution ($\Delta G°(aq) = -0.65$ kcal mol^{-1}), and if this is an electronegativity effect, it seems likely that the same is true of vinyl and OH, especially if this interaction is compared with the interaction of OH and an alkyl group (as it is when a 3,4 double bond is introduced into a cycloalkanol, e.g. in transforming **2** to **1**). It is difficult to judge the magnitude of this interaction, but it seems likely that it is less than that between two oxygen atoms. We have chosen −1.0 kcal mol^{-1} for both vinyl and phenyl groups, therefore. Although this is an arbitrary choice, it seems clear that the free energy of interaction between hydroxyl and vinyl or phenyl must be small and negative so the uncertainty in the assignment should also be small.

Table 3. Equilibrium Constants (K_{de}) for Dehydration of Aliphatic Alcohols in Aqueous Solution at 25 °C

Alcohol	K_{de}[a]	Alkene	pK_{de} (log K_{H2O})
	1.6×10^{-5}		4.80
	0.011		1.96
	5.9×10^{-5}		4.23
	0.011		1.94
	1.6×10^{-5}		4.79
	1.0×10^{-3}		2.98
	1.1×10^{-4}		3.94[d]
	0.83		0.08

[a] K_{de} is the equilibrium constant for *de*hydration: [alkene]/[alcohol]. [b] pK_{de} is the negative log of K_{de}. [c] K_{H_2O} is the equilibrium constant for *hydration*; values are calculated from values of $\Delta G°_f$(aq) (especially from ref 5). [d] Measured experimentally.[16]

Discussion

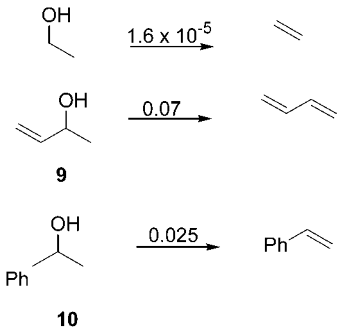
Dehydration of Aliphatic Alcohols. Equilibrium constants for dehydration (K_{de}) of a series of aliphatic alcohols to form alkenes are shown in Table 3. The equilibrium constants refer to the reaction in the dehydration direction, although it is often useful to consider values for the reverse hydration (K_{H2O}). The constants are expressed as p*K*s, i.e., the negative logarithms of the dehydration constants (which correspond to log K_{H_2O} for hydration). To emphasize the direction to which K_{de} and pK_{de} refer, the normal double arrows for the equilibria are replaced by single arrows. It should be noted that because water is the solvent, its concentration is not included in the equilibrium and K_{de} and K_{H_2O} are expressed as in eqs 15 and 16.

$$K_{de} = [\text{alkene}]/[\text{alcohol}] \tag{15}$$

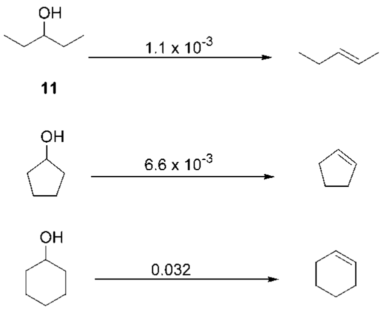
$$K_{H_2O} = 1/K_{de} \tag{16}$$

Examination of the structural dependence of the equilibrium constants shows that, as is well-known, for simple aliphatic alcohols the alcohol is favored over the alkene, but that the equilibrium is shifted to the right by methyl substitution of the double bond. Thus, the equilibrium constants for dehydration

Scheme 2



Scheme 3



of ethanol, *n*-propanol, and isobutanol to give ethene, propene, and isobutene are 1.6×10^{-5}, 0.011, and 0.83, respectively.

Perhaps less well appreciated is that a methyl substituent on the double bond of the alkene which is α rather than β to the hydroxyl group of the alcohol does not have the same effect and that the equilibrium constant for dehydration of 2-propanol is hardly more favorable than that for ethanol (5.9×10^{-5} compared with 1.6×10^{-5}). This is a manifestation of the stabilizing effect of a "geminal" interaction between the methyl group and hydroxyl group in the alcohol reactant. The magnitude of this interaction is expressed by $\Delta G°(\text{aq}) = 5.5$ kcal mol^{-1} and equilibrium constant $K = 10^{-4}$ for the "bond separation" reaction of eq 17. It arises from the favorable interaction between carbon−oxygen and carbon−carbon σ-bonds and has been discussed in detail in the literature, especially for the stronger mutual interaction of carbon−oxygen bonds in acetals which forms the basis of the anomeric effect.[36,37]

$$CH_3CH_2OH + CH_4 \rightleftharpoons CH_3OH + CH_3CH_3 \qquad (17)$$

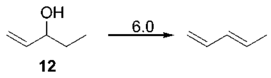
It is worth noting that the equilibria are also influenced by statistical factors. Thus, dehydration of 2-propanol is favored by a factor of 6 corresponding to the six equivalent hydrogen atoms in the alcohol. There are three equivalent hydrogens in ethanol, but the influence of these is compensated by a factor of 2 in the hydration direction arising from the equivalence of the two carbon atoms in the ethene product. In the absence of statistical factors there would be practically no difference in equilibrium constant for the two alcohols. Coincidentally, when corrected for the presence of nine equivalent hydrogen atoms in the alcohol,[17] the equilibrium constant for dehydration of *tert*-butyl alcohol also becomes the same as that for ethanol and 2-propanol.

Allylic, Benzylic, and Cyclic Alcohols. If the range of equilibrium constants is extended to allylic and benzylic alcohols, we find, again as expected, that the alkene product is stabilized and its concentration at equilibrium is increased. This is illustrated by the three reactions of Scheme 2, which lead to formation of ethylene, butadiene, and styrene, respectively. It can be seen that the vinyl and phenyl substituents in 3-buten-2-ol (**9**) and α-phenylethanol (**10**) favor dehydration by factors of 4400 and 1500, respectively. This arises from the expected stabilization of the alkene. In contrast to alkyl substitution, there is practically no influence of α-vinyl or α-phenyl substitution upon the stability of the alcohol.

The effect of constraining double bond formation within a five- or six-membered ring is shown in Scheme 3. It can be seen that reaction is more favorable within the ring than in the open-chain alcohol by a factor of 6 for cyclopentanol and 30 for cyclohexanol.

It may seem surprising that dehydration occurs more easily in the six- than in the five-membered ring, but this reflects not the respective stabilities of the double bonds but the relative stabilities of the hydroxyl groups in the five- and six-membered rings. Thus introduction of a double bond into cyclohexane is energetically less favorable than into cyclopentane, but this is more than compensated by the corresponding difference for the hydroxyl group. The relative stabilities of the open-chain compound and five- and six-membered rings containing a double bond compared with the corresponding saturated hydrocarbons are 1:6:2.5.

However, of principal interest in this paper are equilibrium constants for dehydration of unsaturated and benzoannelated cyclic alcohols rather than simple alicycles. When considering the combined effect of double bond and ring structure, therefore, it should be noted that Scheme 2 shows the effect of a double bond (or phenyl group) replacing a hydrogen atom in ethanol as reactant and ethylene as product. In Scheme 3 by comparison ethanol has been replaced by 3-pentanol (**11**) as the reference open-chain alcohol, in recognition of the fact that the cyclic alcohols are secondary alcohols yielding alkenes with alkyl substituents at each carbon atom of the double bond. Introduction of a double bond into the alcohols in Scheme 3 therefore means that it replaces an alkyl group rather than a hydrogen atom in both the alcohol and alkene, as may be seen by comparing **11** (in Scheme 3) with 1-penten-3-ol (**12**) in eq 18 (cf. also footnote *c* in Table 5).



(18)

In practice, both the open-chain alkene and alcohol are stabilized by alkyl substitution. This means that replacing an alkyl group rather than hydrogen by a double bond or phenyl group is *less* stabilizing for both the alkene and the alcohol. The effects on the equilibrium constant for dehydration are compensating, therefore, and in practice the double bond in 1-penten-3-ol increases the equilibrium constant for dehydration (eq 18) by 5450-fold which differs little from the 4400-fold difference between **9** and ethanol in Scheme 2.

We are now in a position to examine the effect of ring formation upon dehydration of saturated, unsaturated, and phenyl

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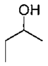
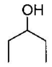
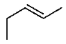
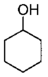
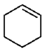
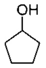
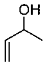
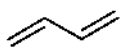
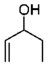
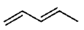
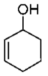
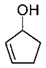
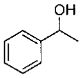
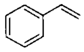
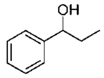
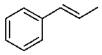
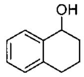
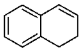
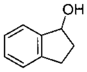
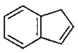
(36) Chang, Y.-P.; Su, T.-M. *J. Phys Chem. A* **1999**, *103*, 8706, and references cited therein.

(37) Harcourt, M. P.; More O'Ferrall, R. A. *Bull. Soc. Chim. Fr.* **1988**, *407*; Richard, J. P.; Aymes, T. L.; Rice, D. J. *J. Am. Chem. Soc.* **1993**, *115*, 2523.

Table 4. Equilibrium Constants (pK_{de}) for Dehydration of Allylic, Benzylic, and Cyclic Alcohols in Aqueous Solution at 25 °C

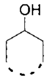
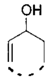
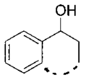
Alcohol	K_{de}[a]	Alkene	pK_{de}[b] (log K_{H2O})[c]
	1.6×10^{-5}		4.80[d]
	1.1×10^{-3}		2.95[d]
	0.032		1.50[d]
	6.6×10^{-3}		2.18[d]
	0.07		1.16[d,e]
	6.0		-0.78[d,e]
	0.1		1.0[f,g]
	3.5		-0.54[f]
	0.025		1.60[h]
	2.3		-0.36[f]
	22		-1.34[f]
	10		-1.0[f]

[a] Equilibrium constant for dehydration. [b] pK_{de} is the negative log of K_{de}. [c] K_{H_2O} is the equilibrium constant for hydration. [d] Calculated from $\Delta G°_f$ (aq) for alcohol and alkene. [e] $\Delta G°_f$(aq) for alcohol estimated by assuming ΔG^{OH} (eq 21) is the same as that for 3-penten-2-ol. [f] This work. [g] See also ref 15. [h] Reference 14.

substituted alcohols. Absolute and relative equilibrium constants for dehydration of open-chain and five- and six-membered ring alcohols are shown in Table 4 and Table 5, respectively. In Table 5 the unsaturated cyclic alcohols are **4** and **2**, and their phenyl substituted counterparts are the benzoannelated derivatives, **8** and **7**. The equilibrium constants in the table are measured relative to the dehydration of **11** (the second reaction in Table 4).

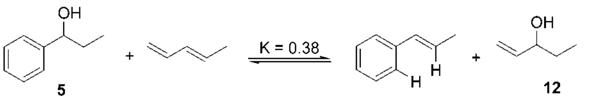
For the cyclic as for the acyclic alcohols the presence of the double bond increases the extent of dehydration. This can be seen in Table 5 by reading from left to right. On the other hand, reading down the table it can be seen (by comparing the first two columns) that the transformation from open-chain to cyclic structure has a different effect upon saturated and unsaturated alcohols. Thus, while reaction within a ring favors dehydration of saturated alcohols, the corresponding reaction of cycloalkenols to form cycloalkadienes is strongly disfavored. Thus, reaction of cyclohexenol (**2**) is 60 times less favorable than that of its open-chain analogue 1-penten-3-ol (**12**) in eq 18.

Table 5. Relative Equilibrium Constants (K_{de}) for Dehydration of Open-Chain and Cyclic Saturated, Unsaturated, and Benzoannelated Alcohols

			
Open chain[a]	1[b]	5,450[c]	2,090
5-membered ring	6.0	3,180[d]	9,090[e]
6-membered ring	29	91[f]	20,000[g]

[a] Reaction of open-chain alcohol to form *trans*-alkene. [b] Equilbrium constant, 3-pentanol → 2-pentene, $K_{de} = 1.1 \times 10^{-3}$ (Scheme 3). [c] 1-Penten-3-ol → 1,3-pentadiene. Note that replacement of 1-penten-3-ol by 2-hexen-4-ol increases this factor of 5450 to 20 000 (if the influence of the extra methyl group is modeled by the difference in the effect of a methyl group on the double bond of propene and butadiene). The larger value should provide a better comparison with the cyclic alcohols. [d] 3-Cyclopentenol → cyclopentadiene, $K_{de} = 3.5$. [e] Indanol → indene, $K_{de} = 10.0$. [f] 3-Cyclohexenol → 1,3-cyclohexadiene, $K = 0.1$. [g] Tetralol → 1,2-dihydronaphthalene, $K_{de} = 22$.

This difference is presumably a result of ring strain in the cycloalkadiene. However, as can be seen by comparing columns one and three in Table 5, surprisingly, the influence of ring formation in benzoannelated cycloalkenols reverts to the pattern of the saturated alcohols, with ring formation weakly favoring dehydration! This effect of benzoannelation is reflected in a difference in equilibrium constants for isodesmic reactions comparing the effect of replacing a double bond by a benzene ring in open-chain reactions (eq 19) and cyclic reactions (eq 20), which amounts to a factor of nearly 600-fold.



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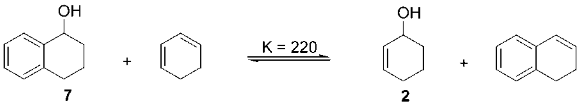

(20)

The surprisingly large value of the equilibrium constant for eq 20 was previously interpreted as partly reflecting a significant difference in geminal interactions between the hydroxyl group and a double bond and a hydroxyl group and a phenyl ring.[1] As discussed below, it now seems likely that the contribution from this source amounts only to a factor of 3 and that the main contribution to the difference is a greater stabilization of a conjugated annular double bond by a phenyl ring than a second double bond.

It is remarkable that contrary behavior is seen for the open-chain equilibrium (eq 19). In this case the conjugated π-bond is *more* stabilizing than the phenyl group. It seems best to ascribe this difference to a greater steric hindrance to achieving a planar configuration favoring conjugation between a double bond and a phenyl ring than between two double bonds in the open-chain structures.

In the five-membered ring, benzoannelation displays a smaller advantage over the π-bond (i.e. in comparing indanol and cyclopentenol), and the behavior here is intermediate between that of the open-chain and six-membered ring structures.

Hydroxyl and π-Bond Replacements. This detailed discussion of dehydration equilibria introduces an attempt to estimate the effect of exchanging a hydroxyl group for a hydrogen atom upon the free energy of formation of different hydrocarbons. This effect may be denoted ΔG^{OH} and is expressed by eq 21. Our objective is to evaluate (and then predict) the influence of alkyl and aryl substituents R upon this free energy change.

$$\Delta G^{\mathrm{OH}} = \Delta G^{\circ}_{\mathrm{f}}(\mathrm{R{-}OH}) - \Delta G^{\circ}_{\mathrm{f}}(\mathrm{R{-}H}) \qquad (21)$$

In practice, it is more convenient to consider the effect of a *change* in the alkyl group than absolute values of ΔG^{OH}. Adopting Grunwald's notation[38] this may be represented as $\delta_{\mathrm{R}}\Delta G^{\mathrm{OH}}$ and corresponds to a substituent effect on the process of hydroxyl substitution. It is also convenient to choose a reference structure (or substituent) with which different R groups can be compared. If the reference is taken as a hydrogen atom ($\mathrm{R} = \mathrm{H}$), $\delta_{\mathrm{R}}\Delta G^{\mathrm{OH}}$ corresponds to the reaction $\mathrm{R{-}H} + \mathrm{H_2O} \rightarrow \mathrm{R{-}OH} + \mathrm{H_2}$ and the analysis of structural changes achieves most of the elements of a free energy relationship.

In practice, use of H as a reference is less useful here than in other free energy relationships. This is because the reaction then includes a bond between two hydrogen atoms, whereas we will be concerned solely with C−H (and C−OH) bonds. A methyl group might seem a suitable alternative choice, but in the context of dehydration reactions ethyl is to be preferred, because ethyl alcohol is the simplest alcohol that can undergo dehydration. As shown in eq 22, with ethyl as reference $\delta_{\mathrm{R}}\Delta G^{\mathrm{OH}}$ corresponds to the free energy change for the reaction shown in eq 23 with equilibrium constant K_{S}. At the risk of abusing Grunwald's notation,[38] $\delta_{\mathrm{R}}\Delta G^{\mathrm{OH}}$ in eq 22 is abbreviated as δ^{OH} (or $\delta_{\mathrm{R}}\mathrm{OH}$). The relationship between δ^{OH} and ΔG^{OH} is then given by eq 24 in which −39.5 (kcal mol^{-1}) is the value of ΔG^{OH} for ethyl alcohol.

$$\delta^{\mathrm{OH}} = \delta_{\mathrm{R}}\Delta G^{\mathrm{OH}} = -RT \ln K_{\mathrm{S}} \qquad (22)$$

$$\mathrm{R{-}H} + \mathrm{CH_3CH_2OH} \overset{K_{\mathrm{S}}}{\rightleftharpoons} \mathrm{R{-}OH} + \mathrm{CH_3CH_3} \qquad (23)$$

$$\delta^{\mathrm{OH}} = \Delta G^{\mathrm{OH}} + 39.5 \qquad (24)$$

An advantage of choosing the ethyl group as reference is that it can be used not only for introducing an OH group into a hydrocarbon but also for introducing a *double bond*. The influence of alkyl structure upon the stability of a π-bond can then be considered analogously to that of a hydroxyl group. This is shown by defining δ^{π} in analogy with δ^{OH} as the free energy for replacing two hydrogen atoms on adjacent carbon atoms by a π-bond, as is summarized in eqs 25−27. In eq 27, the free energy change 23.4 (kcal mol^{-1}) is ΔG^{π} for ethylene, i.e., the counterpart of ΔG^{OH} for ethanol (−39.5 kcal mol^{-1}) in eq 24.

$$\delta^{\pi} = -RT \ln K_{\mathrm{S}} \qquad (25)$$

$$\mathrm{R{-}CH_2CH_3} + \mathrm{CH_2{=}CH_2} \overset{K_{\mathrm{S}}}{\rightleftharpoons} \mathrm{R{-}CH{=}CH_2} + \mathrm{CH_3CH_3} \qquad (26)$$

$$\delta^{\pi} = \Delta G^{\pi} - 23.4 \qquad (27)$$

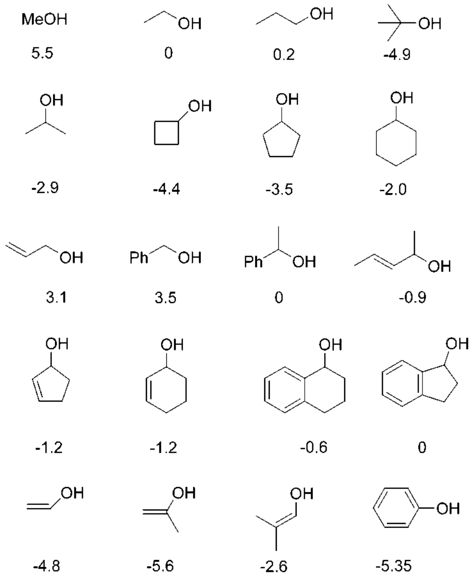

Figure 1. Values of δ^{OH} (kcal mol^{-1}) (eqs 22 and 24) for replacement of H by OH in an alkane (relative to ethane and ethanol, $\Delta G^{\mathrm{OH}} = -39.5$ kcal mol^{-1}).

Although alkenes are not the principal concern of this paper, eq 27 in combination with eq 24 provides a convenient framework for factoring structural effects upon dehydration equilibria into contributions from the alcohol reactant and alkene product, as was shown above to be necessary for interpreting substituent effects on these equilibria. The difference in substituent effects upon introduction of a hydroxyl group and a double bond ($\delta^{\mathrm{OH}} - \delta^{\pi}$) corresponds to the difference in (the log of) the equilibrium constants for dehydration of ROH and ethanol. For this reason, and to provide a comparison with the treatment of alcohols, a brief summary of alkyl and aryl substituent effects upon the stabilities of double bonds as well as of alcohols is presented.

At the outset, it should be recognized that these substituent effects cannot be represented in the normal graphical form of a free energy relationship. Although δ^{π} and δ^{OH} correspond to clearly defined reactions (eqs 23 and 26) and substituent effects, no reference reaction has been defined. In principle the process corresponding to δ^{OH} (e.g.) could be defined as a reference "reaction" and then used to correlate substitution of hydrogen by other groups or atoms such as chlorine (δ^{Cl}). However, for unknown values of δ^{OH} (or δ^{π}) themselves we rely on inspection of structural analogies.

Representative substituent effects δ^{OH} and δ^{π} are shown in Figures 1 and 2, respectively. Considering first the values for alcohols, it can be seen in the top row of Figure 1 that methanol has a positive value of $\delta^{\mathrm{OH}} = 5.5$ kcal mol^{-1}. This implies that the free energy change for the reaction shown in eq 28 is unfavorable by this amount. The positive value of δ^{OH} is a consequence of the geminal interaction between methyl and hydroxyl groups attached to the same carbon atoms present in ethanol but not in methanol, as noted above. Moving from left to right in the first row of the figure, and to 2-propanol in the second row, it can be seen that extension of the alkyl chain length in a primary alcohol has little influence on this geminal effect, but that secondary (second row) and tertiary alcohols

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[38] Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*, McGraw-Hill: New York, 1963.

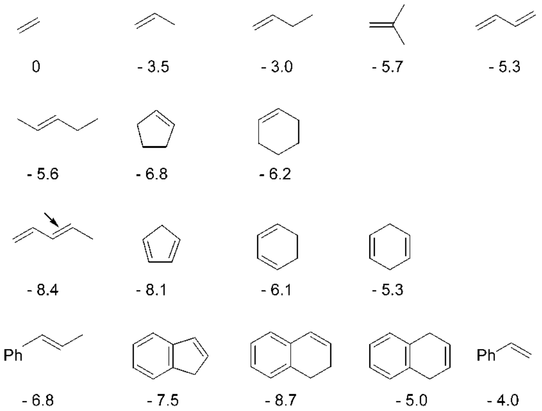


Figure 2. Values of δ^{π} (kcal mol^{-1}) for replacement of two hydrogens by a double bond in an alkane (relative to ethane and ethylene, $\Delta G^{\pi} = 23.4$ kcal mol^{-1}).

introduce additional, although attenuated, stabilizing interactions, as is apparent from the magnitude and sign of their δ^{OH} values (e.g. -2.9 kcal mol^{-1} for 2-propanol). In row two, the smaller differences of open-chain from cyclic alcohols can also be seen, although it should be recognized that cyclopentanol and cyclohexanol are favored over their open-chain counterparts by statistical factors of 5/2 and 6/2, respectively.

$$CH_3CH_2OH + CH_4 \xrightleftharpoons{\Delta G°(aq)} CH_3OH + CH_2CH_3 \quad (28)$$

So far, the values of δ^{OH} considered have been based on values of $\Delta G°_f$ (aq) for alcohols and alkanes from Guthrie's compilation of free energies of formation for organic molecules.[5] The same is true for the allyl and benzyl alcohols in row three: these alcohols show positive values of δ^{OH} reflecting the less favorable geminal interaction of a hydroxyl group with a vinyl or phenyl substituent than an alkyl group. Row four shows values of δ^{OH} for cyclic allylic and benzylic alcohols for which values of $\Delta G°_f$(aq) are not available in the literature and which have been derived, as described above, by combining measurements of equilibrium constants for dehydration with known or estimated values of $\Delta G°_f$ (aq) for the alkene products.

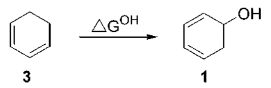
From comparison of rows two and four it can be seen that, as for the open-chain alcohols, a double bond or phenyl group α to the hydroxyl group reduces δ^{OH} relative to the cycloalkanol. However, there are significant deviations from additivity of the effects of cyclization and incorporation of double bonds or phenyl groups for five- and six-membered ring alcohols. These were considered in detail in the discussion of dehydration equilibria, and Figure 1 summarizes the contribution to the equilibria from changes in the stability of the alcohol: thus hydroxyl substitution at an allylic carbon is consistently more favorable than at a benzylic carbon atom by between 0.4 and 1.3 kcal mol^{-1}. Finally, in rows five and six the corresponding influence of structure upon δ^{OH} for enolic (and phenolic) hydroxyl groups is shown. Apparently the stabilizing effect of an α-(geminal) substituent on the double bond is much smaller than for alphatic alcohols. One and especially two β-alkyl groups are destabilizing, probably because of a steric effect.

Figure 2 likewise summarizes the contribution of changes in the stability of the alkene to structural effects on equilibrium constants for dehydration. The stabilizing effect of alkyl substitution and of conjugation upon a double bond as well as the more subtle effects of cyclic structures are shown in rows one and two. Consistent with the discussion of equilibria, the opposite effects of passing from an open-chain structure to five- or six-membered rings upon the stabilizing effect of conjugation of two double bonds on the one hand and upon conjugation of a double bond and a phenyl group on the other are evident from comparing rows three and four.

The general conclusion to be drawn from Figures 1 and 2 is that although there is considerable variation in the effects of incorporating a hydroxyl group or double bond into a hydrocarbon molecule, these variations can be interpreted in a fairly straightforward manner. For the alcohols, which are of principal concern in this study, the effects arise from geminal interactions of alkyl, vinyl, and phenyl groups and a smaller influence of cyclization. The results are sufficiently systematic to give some confidence in the prediction of $\Delta G°_f$ (aq) for alcohols which are not structurally too far removed from the examples of Figure 1.

Free Energies of Formation of Aromatic Hydrates. If we turn now to aromatic hydrates, such as benzene hydrate (cyclohexadienol) **1** and naphthalene hydrate **14**, it is clear that their free energies of formation can be estimated if $\Delta G°_f$(aq) for the corresponding hydrocarbon is known and the value of δ^{OH} (or ΔG^{OH}) for replacement of hydrogen by a hydroxyl group can be estimated, on the basis of a satisfactory structural model.

For benzene hydrate and naphthalene hydrate the relevant hydrocarbons are 1,3-cyclohexadiene **3** and 1,2-dihydronaphthalene **13**. Evaluation of $\Delta G°_f$ (aq) for these structures has been described above, and the transformation to their hydrates is shown in eqs 29 and 30. Inspection of Figure 1 suggests that the closest models for estimating ΔG^{OH} for these transformations are provided by the conversion of cyclohexene to 3-cyclohexenol (**2**) and 1,2,3,4-tetrahydronaphthalene to tetralol (**7**).



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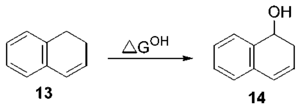

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The single structural difference of the models from the desired hydrocarbons and alcohols is the presence of an extra double bond with a 1,2-relationship to the hydroxyl group. Unfortunately, as noted above, no thermodynamic measurements appear to have been made for molecules possessing this structural feature. A correction for the interaction of a hydroxyl group and double bond has been crudely estimated therefore on the basis of inspection of available measured 1,2-interactions of substituents (Table 2). As already described, although interactions between electronegative atoms can introduce a correction as large as 3−4 kcal mol^{-1}, the best approximation for hydroxyl and vinyl (or phenyl) substituents at present appears to be approximately 1 kcal mol^{-1}. Thus, $\Delta G°_f$(aq) for benzene and naphthalene hydrates may be based directly on values of ΔG^{OH} for cyclohexenol and tetralol, respectively, with a correction of $+1.0$ kcal mol^{-1}. The only further correction to be made is a statistical factor of 2 arising from the fact that there are four equivalent H atoms that may be substituted by hydroxyl in

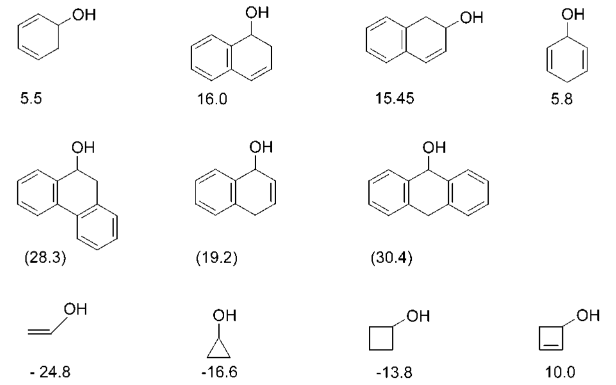
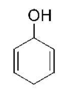


Figure 3. Free energies of formation ΔG°_f(aq) for cycloalkanols and arene hydrates. Values in brackets are based on estimated values of ΔG_t (free energy of transfer from gas to aqueous solution for the parent hydrocarbon).

tetrahydronaphthalene and only two in dihydronaphthalene. The resulting values of ΔG°_f(aq) are shown in Figure 3.

Other aromatic hydrates for which it was possible to estimate ΔG°_f(aq) in a similar manner include the isomeric hydrates of benzene and naphthalene, **15**−**17** and the 9,10-water adducts of phenanthrene **18** and anthracene **19**. For the naphthalene hydrate **16** a model for ΔG^{OH} is now provided by cyclohexenol corrected for a statistical factor of 2 and a 1,2-interaction between a hydroxyl group and phenyl group, again taken as +1.0 kcal mol^{-1}. A similar estimate can be made for the 9,10-hydrate of phenanthrene using the value of ΔG^{OH} for tetralol together with a correction for an OH/phenyl 1,2-interaction again equal to +1.0 kcal mol^{-1}. The derived value of ΔG°_f(aq) and that for **15** are also shown in Figure 3.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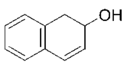
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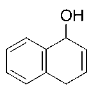
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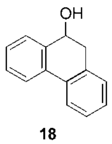
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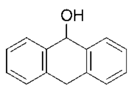
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A different estimate is required for the 1,4-hydrates of benzene **15** and naphthalene **17** and the 9,10-hydrate of anthracene **19**. These molecules have two phenyl groups or double bonds, or a phenyl group and a double bond, α to the position of hydroxyl substitution. The hydroxyl group is subject to geminal interactions with the phenyl or vinyl groups, and these interactions are modified by incorporation in the cyclohexyl ring. Insofar as geminal effects are not additive, and ineraction of OH with the saturated cycloalkane is more favorable than with annular vinyl or phenyl groups, we have assumed that the second alkyl group (in cyclohexanol) has 60% of the effect of the first (in cyclohexenol or 1-hydroxy-1,4-dihydronaphthalene). This is quite a crude assumption but is based on the observation that accumulation of other geminal substituents including alkyl leads to a fall off in their effects relative to hydrogen and probably also to vinyl and phenyl. On the basis of Figure 1 the presence of a double bond and a phenyl ring in cyclohexanol increases ΔG^{OH} by 0.2 and 0.8 kcal mol^{-1}, respectively (allowing for the fact that there are 12 equivalent hydrogens in cyclohexane compared with four in cyclohexene or 1,2,3,4-tetrahydronaphthalene). Values of ΔG°_f(aq) for the 1,4-hydrates of benzene and naphthalene and 9,10-hydrate of anthracene are based on values of ΔG^{OH}, reflecting an increase of 0.3 and 1.5 kcal mol^{-1} for their additional double bond or phenyl ring, respectively. These are also included in Figure 3.

Before values of ΔG°_f(aq) in Figure 3 are used to estimate equilibrium constants, it is of interest to derive values of ΔG°_f(aq) for a further group of alcohols which on dehydration yield the antiaromatic product cyclobutadiene or the nonaromatic but highly strained small-ring alkenes cyclopropene and cyclobutene. Estimates of δ^{OH} for these molecules are cruder than for the aromatic hydrates. However, the gas-phase free energies of formation of saturated and unsaturated cycloalkanes, from cyclopropane to cyclooctane, have been compiled and critically evaluated by Dorofeeva et al.[20] These provide data both for the products of dehydration and for the hydrocarbons from which ΔG°_f(aq) for the alcohol can be derived, provided that free energies of transfer from the gas phase to solution and values of δ^{OH} have been measured or can be estimated. In the case of cyclobutadiene the value of ΔH°_f for the gas phase is based on a mean of recently calculated values.[21]

As described above, evaluation of ΔG_t can be satisfactorily carried out by estimating solubility data and vapor pressures, the latter based if necessary on bps of liquid hydrocarbons. Even for cyclobutadiene, a bp can be predicted from a correlation of bps of cyclic hydrocarbons with the molecular connectivity parameter χ [35] (although this does not take account of the fact that the ground state of cyclobutadiene is a triplet rather than a singlet, i.e., that correlation of the bp with singlet cycloalkadienes may be oversimplified).

For cyclobutanol ΔG°_f(aq) was based on an experimental value of ΔH°_f(g) and interpolated values of $S^\circ(g) = 75.8$ cal deg^{-1} mol^{-1} and log γ. More speculatively $\delta_{OH} = -4.7$ kcal mol^{-1} for cyclopranol was assigned by assuming a smooth variation of statistically corrected values of δ_{OH} for cyclic alcohols upon ring size, with the value for acetaldehyde enol taken as that for a two-membered ring. This may be compared with an STO31G calculation which showed that ΔH for replacement of H by OH in cyclopropane in the gas phase to be 2.8 kcal mol^{-1} more favorable than for the 2-position of propane.[39] Taking $\delta^{OH} = -2.9$ kcal mol^{-1} for cyclopropanol from Figure 1 our value for this difference (free energy in aqueous solution) is 1.8 kcal mol^{-1}. For 3-hydroxycyclobutene δ^{OH} was taken as −1.5 kcal mol^{-1} on the basis of $\delta^{OH} = -4.4$ kcal mol^{-1} for cyclobutanol and the effect upon δ^{OH} of introducing a 2,3-double into cyclopentanol and cyclohexanol (Figure 1).

The free energies of formation estimated for these alcohols are included in Figure 3. To obtain equilibrium constants for the dehydration reactions, it remains only to combine these with the known or already estimated values of ΔG°_f(aq) for the unsaturated reaction products.

Dehydration of Aromatic, Antiaromatic, and Ring-Strained Hydrates or Alcohols. Negative logs of equilibrium constants (pK_{de}) for the dehydration reactions of alcohols for which ΔG°_f(aq) has been estimated are shown in Table 6. For comparison the dehydration equilibria for ethanol, 2-propanol, cyclohexenol, and vinyl alcohol (ethenol) are included in the table.

The dehydration of vinyl alcohol to form acetylene is also included for comparison with the dehydration of the three-, four-,

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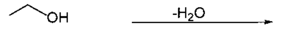
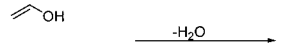
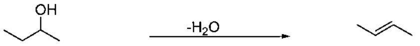
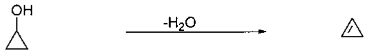
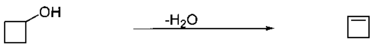
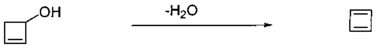
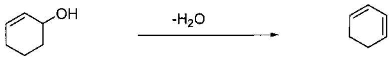
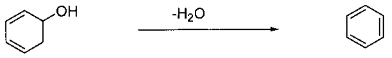
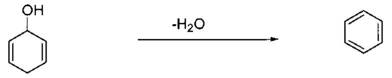
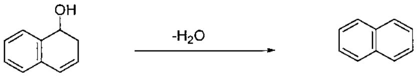
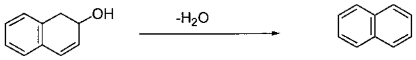
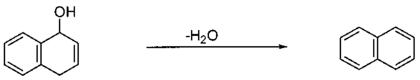
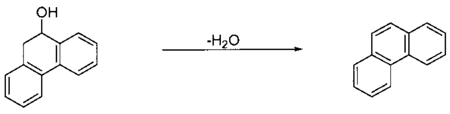
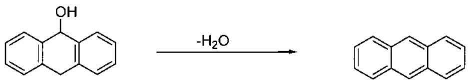
(39) Clark, T.; Spitznagel, G. W.; Klose, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 4412.

Table 6. Equilibrium Constants for Dehydration of Alcohols Yielding Aromatic, Antiaromatic, or Strained Cyclic Products

Dehydration Reaction	pK_{de} ($\log K_{H2O}$)
	4.80
	15.0[a]
	3.3
	22.1
	5.95
	28.4
	1.0
	-22.2
	- 22.2
	- 14.6
	- 14.2
	-16.9
	-9.2
	- 7.4

[a] Calculated from free energies of formation. That for vinyl alcohol is based on the value for acetaldehyde and a tautomeric constant $K_T = 5.89 \times 10^{-7}$ (Chiang, Y.; Hojatti, M.; Keeffe, J. R.; Kresge, A. J.; Schepp, N. P.; Wirz, J.: *J. Am. Chem. Soc.* **1987**, *109*, 4000.

five-, and six-membered rings. Again we consider the double bond as a limiting case within a comparison of ring sizes as if it were a two-membered ring. In fact, both vinyl alcohol and cyclopropanol show a much greater resistance to dehydration than does ethanol, consistent with the large ring strain present in a small ring. The magnitude of the ring strain accompanying formation of cyclopropene from cyclopropanol is revealed by an equilibrium constant that is 18 orders of magnitude less favorable than for the formation of propene from 2-propanol. Interestingly, the reaction of vinyl alcohol to form acetylene is *more* favorable than formation of cyclopropene from cyclopropanol by 5 orders of magnitude. This implies that there is less strain in the "two-membered" than three-membered unsaturated ring. A fanciful interpretation of this is that the extra two π-electrons of the unsaturated two-membered ring render it aromatic!

The elimination within the four-membered ring is not very much less favorable than within structurally similar open-chain molecules. The relatively high stability of a double bond in a four-membered ring is also evident from heats of hydrogenation and has been attributed to compensation between an increase in angle strain and decrease in torsional strain between cyclobutane and cyclobutene.[40]

The moderately unfavorable equilibrium constant for cyclobutene formation contrasts with the most energetically unfavorable equilibrium in the table represented by dehydration of cyclobutenol to form the antiaromatic cyclobutadiene ($pK_{de} = 28.4$), which is believed to exist in a ground-state triplet electronic configuration. Although $\Delta H°_f$ for this product is a calculated rather than experimental value, much effort has been expended in establishing a reliable energy for this small molecule.[21]

Moving down Table 6 brings us to dehydration of the aromatic hydrates. As expected these reactions are all highly favorable with the ease of dehydration reflecting the stability of the aromatic product, i.e., benzene > naphthalene > phenanthrene > anthracene. The calculation of these values provided the main motivation for this paper. Although none have been directly evaluated experimentally, in the following paper it is shown that values for the 9,10-anthracene hydrate and the naphthalene hydrate **16** can be derived from thermodynamic cycles based on experimental data and provide surprisingly good agreement with the calculated values (+7.5 compared with a calculated value of +7.4 for anthracene and −13.7 compared with −14.2 for naphthalene).[41]

The equilibrium constants in Table 6 vary over 40 orders of magnitude between the extremes of aromatic and strained antiaromatic molecules represented by benzene and cyclobutadiene, respectively. Since there is relatively little variation in the energy of replacing hydrogen by hydroxyl in generating the alcohol products, this variation reflects mainly the energy of hydrogenation of the double bonds, which is usually used to represent π-bond stability especially in aromatic molecules. The principal differences between energies of hydration and hydrogenation as measures of stability are the use of free energies of hydration compared with heats of hydrogenation and that the hydration reactions refer to aqueous solution and hydrogenation to the gas phase. Neither factor is likely to have a great influence on relative values.

Relative free energies of hydrogenation may be represented by the free energies of introduction of a double bond into a hydrocarbon molecule (in place of vicinal hydrogen atoms) as shown in Figure 2. The relative stabilities of the double bonds in the products of elimination in Table 6 are shown in the same way in Figure 4. Again the measurements are reported relative to the free energy of double bond formation in ethane (or hydrogenation of ethene) denoted δ^{π} above. The range of free energies is numerically a little greater than that of values of $\log K_{de}$ as a consequence of the relationship $\Delta G = 1.364 \log K_{de}$, where the factor 1.364 corresponds to $2.303RT$ at 25°.

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(40) Wiberg, K. B.; Fenoglio, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 3395.

(41) MacCormack, A. C.; McDonnell, C. M.; More O'Ferrall, R. A.; O'Donoghue, A. C.; Rao, S. N. *J. Am. Chem. Soc.* **2002**, *124*, 8575 (following paper in this issue).

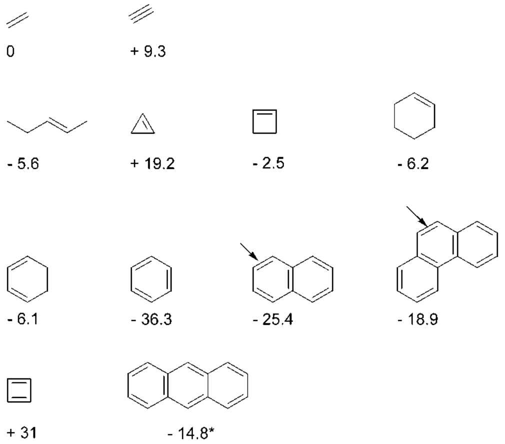

Figure 4. Additional values of δ^{π} (kcal mol^{-1}) for replacement of two hydrogen atoms of a hydrocarbon by a double bond (relative to ethane and ethylene, $\Delta G^{\pi} = 23.4$ kcal mol^{-1}). *Parent hydrocarbon, 9,10-dihydroanthracene.

The value of $\delta^{\pi} = -34.7$ kcal mol^{-1} for benzene (compared with ethylene) is close to the traditional value of 36 kcal mol^{-1} for the resonance energy of benzene. The large positive energies of δ^{π} for cyclopropene and cyclobutadiene again emphasize the high level of strain (and in the latter case presumably avoided antiaromaticity) inherent in these molecules. The contrasting stability of the double bond in cyclobutene (3 kcal mol^{-1} less stable than in an open-chain structure) is again noteworthy.

In conclusion, we note that in principle any organic functional group can be submitted to the same treatment as the vinyl and hydroxyl groups described in this paper and summarized in Figures 1, 2, and 4. This is a potentially valuable tool for extending the range of available thermodynamic data and of equilibrium constants for organic reactions in aqueous solution. Molecular mechanics and ab initio calculations are now well-established as methods for accessing unmeasured thermodynamic data. In this paper we hope to have demonstrated that extrapolation from existing measurements based on substituent effects may offer a complementary means for achieving the same end. As emphasized in the Introduction to the paper a substituent treatment offers a significantly more precise method of estimation than one based on group contributions. In principle there is no limitation to the scope of the method provided that a sufficient body of data exist for related structures incorporating the functional group of interest, as is the case for alcohols and alkenes.

Experimental Section

Experimental measurements were confined to measurements of rate constants and equilibrium constants for hydration of alkadienes and arylalkenes to alkenols and aryl alcohols, respectively. Most of the compounds studied were purchased (usually from Aldrich) and used without further purification. Cyclopentadiene was freshly prepared from distillation of its dimer. Normally identity and purity were checked by NMR.

Kinetic and equilibrium measurements were made spectophotometrically using a Phillips PU8600 or Perkin-Elmer Hitachi Model 124 spectrophotometer equipped with a thermostated cell compartment. Measurements were normally initiated by injection of 20−25 μL of a 10^{-2} M solution of diene or alkenol substrate in acetonitrile or methanol into 2 mL of aqueous $HClO_4$ in a spectrophotometric cell prethermostated at 25 °C. Reactions were monitored for at least three half-lives (more for equilibrium measurements) and rate constants and limiting absorbances determined from a best fit of the dependence of absorbance upon time to an exponential increase or decay using a weighted least squares computer program.

Equilibrium Constants for Hydration. For a solution of cyclohexadiene in 2.51 M $HClO_4$ at 40 °C Jensen and Le Carré[15] reported that the absorbance at $\lambda_{max} = 257$ nm falls to 15% of its value after eight half-lives of reaction. In a subsequent paper Jensen et al. reported K_{H_2O} = [cyclohexenol]/[cyclohexadiene] = 8.8 and 13.7 at 4.0 and 5.6 M H_2SO_4, respectively (at 30 °C). We found erratic kinetic behavior of cyclohexadiene at low acid concentrations, but a satisfactory reaction of a solution of cyclohexenol (10.3 mg/10 mL CH_3CN diluted by 0.1−2.1 mL with $HClO_4$). This gave limiting absorbances 0.16 at 2.39 M, 0.165 at 4.0 M, and 0.16 at 5.22 M $HClO_4$. Based on $\epsilon = 3000$ for cyclohexadiene an average value of $K = 0.1$ was evaluated.

For *trans*-2-methylstyrene the equilibrium for hydration to 1-phenylpropan-1-ol (**5**) lies further in favor of the alkene than for cyclohexadiene, and equilibrium constants were based on initial and final absorbances for the reaction. Measured changes in absorbances in concentrated solutions of $HClO_4$ were 1.01 → 0.69 (6.97 M); 0.99 → 0.71 (6.77 M), and 0.99 → 0.68 (5.98 M). Taking 0.006 as the absorbance of the 1-phenylpropan-1-ol gives an average $K_{de} = 2.3$ (K_{H_2O} = 0.43). The limiting absorbances at completion of reaction were extrapolated from absorbance measurements over 2.5−3.5 half-lives of the first-order reactions: no correction was made for isomerization of *trans*- to cis-α-methylstyrene.

Cyclopentadiene reacted fairly rapidly in more dilute acid solutions and multiple determinations of initial and final absorbances at different acid concentrations were easily made: 0.46−0.386, 0.466−0.365, 0.467−0.355 (1.0 M); 0.480−0.367, 0.497−0.383, 0.489−0.391 (1.5 M); 0.634−0.502, 0.495−0.354, 0.486−0.387 (2.0 M); 0.646−0.499, 0.536−0.420; 0.494−0.392 (2.5 M). These gave an average value of K_{de} = [cyclopentadiene]/[cyclopentenol] = 3.5.

An equilibrium constant was also measured for the hydration of *trans*-piperylene (*trans*-1,3-pentadiene) to 3-penten-2-ol (**6**). The identity of the product was confirmed by the observation that the rate of approach to equilibrium was the same starting with the 3-penten-2-ol as starting with the diene. Reaction of the isomeric 1-penten-3-ol (eq 18) was shown to be too slow for this isomer to be implicated in the equilibrium. Hydration of *cis*-piperylene was also shown to be approximately five times slower than the reaction of its trans-isomer. This is probably because the cis configuration inhibits achievement of a planar conformation for the incipient allylic carbocation in the transition state. The difference in stabilities of *cis*- and *trans*-piperylenes in the gas phase corresponds to an equilibrium constant of 7.2 favoring the trans-isomer. If this is also true in solution, then it is easy to show that the trans-isomer is equilibrated with 3-penten-2-ol 36 times (5 × 7.2) more rapidly than with its cis-isomer provided that, as must be true,[2,42] reaction of the carbocation intermediate to form the alcohol is faster than to form either diene. It follows that the equilibrium observed is that between 3-penten-2-ol and *trans*-piperylene only.

Equilibrium measurements were carried out for reactions in which the reactant was either the diene or the alkenol. Starting with the diene a satisfactorily stable dependence of absorbance upon time was observed only above 2.5−3 M concentration of $HClO_4$, while at concentrations above 6 M anomalous product absorbances suggested that the diene was undergoing a further reaction, probably polymerization.

A series of measurements for reactions of aqueous solutions of *trans*-piperylene with an initial absorbance of 1.4 gave the following final absorbances (A) at $\lambda_{max} = 222$ nm at the concentrations of perchloric acid indicated in brackets ($T = 25$ °C): 0.21 (2.15 M); 0.20 (3.15 M); 0.135 (4.2 M); 0.165 (5.52 M). Based on the relationship $K_{de} = A/(1.4 - A)$ an average equilibrium constant for dehydration K_{de} =([diene]/[alkenol]) = 0.14 was obtained.

Corresponding reactions of 3-penten-2-ol gave the following limiting absorbances at $\lambda = 222$ nm for a 1.72×10^{-4} M aqueous solution of

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(42) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1373.

alkenol and concentrations of perchloric acid indicated in brackets: 0.182 (1.05 M); 0.230 (2.1 M); 0.200 (3.15 M); 0.229 (4.20 M); 0.220 (5.25 M); 0.193 (6.30 M). Based on an extinction coefficient of 1.0 × 10^4 for *trans*-piperylene these values again gave an average value of $K_{de} = 0.14$.

We assumed that the equilibrium constant for hydration of *trans*-piperylene ($1/K_{de}$) corresponds to an equilibrium between *trans*-piperylene and an equilibrated mixture of *cis*- and *trans*-3-penten-2-ol. Formation of a carbocation intermediate can be expected to occur considerably more rapidly from the alcohol than the diene because conversion of the carbocation to alkene is normally rate-determining in dehydration reactions.[2,39] Since the equilibrium constant between *cis*- and *trans*-3-penten-2-ol appears not to have been measured it was assumed to have a value $K = [\text{trans}]/[\text{cis}] = 3.5$, which is intermediate between the gas-phase values of 3.2 and 4.0 for *cis*- and *trans*-2-pentene and *cis*- and *trans*-4-methyl-2-pentene, respectively, which could be calculated from known values of $\Delta G\,°_f$ in the gas phase. Correcting for this equilibration the experimental equilibrium constant $K_{de} = 0.14$ becomes $K_{de} = 0.18$ for the ratio of *trans*-1,3-pentadiene to *trans*-3-penten-2-ol.

Kinetic Measurements. In addition to the equilibrium measurements rate constants for the approach to equilibrium were measured for the hydration or dehydration reactions studied. First-order rate constants (k_{obs}) measured at 25 °C for different concentrations of aqueous $HClO_4$ are listed in Table S1 of the Supporting Information. The measurements were made spectrophotometrically as described above. Since most of the measurements refer to concentrated acid solutions values for dilute aqueous solution were obtained from plots of second-order rate constants against the medium acidity parameter X.[43] The desired rate constants were obtained as extrapolated values at $X = 0$ and are recorded in the results section of the paper.

In addition to rate constants for the reactions for which equilibrium measurements have already been described rate constants are reported for hydration of *cis*-piperylene. These are not as precise as the other measurements because hydration is followed by a more rapid but still kinetically significant conversion of the alcohol to *trans*-piperylene so that the reaction is not strictly first order. The measurements demonstrate, however, that reaction of the *cis*-piperylene is indeed slower than that of its trans-isomer, and since the second reaction is five or six times faster than the first, the error in identifying the measured rate constant with hydration of the cis-isomer is small.

Acknowledgment. This research was supported by the National Science Council for Ireland EOLAS (Grant No. SC/91/204). We thank the reviewers for helpful criticisms and suggestions.

Supporting Information Available: Table S1, listing first-order rate constants for hydration or dehydration of various substrates in concentrated $HClO_4$ (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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(43) Cox, R. A.; Yates, K. *J. Chem. Soc.* **1978**, *100*, 3861. Kresge, A. J.; Chen, J. J.; Capen, G. L.; Powell, M. F. *Can. J. Chem.* **1983**, *61*, 249. Bagno, A.; Scorrano, G.; More O'Ferrall, R. A. *Rev. Chem. Intermed.* **1987**, *7*, 313. Cox, R. A. *Adv. Phys. Org. Chem.* **2000**, *34*, 1.