if activation energy of reaction 3 were smaller than that of reaction 2 and specific rates of both reactions were comparable at low temperatures.

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Specific Interactions of Phenols with Water

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The extrapolated distribution coefficients P_1 at infinite dilution of phenol derivatives between cyclohexane and water and their transfer enthalpies were determined. The data are compared with those of other kinds of molecules. When the specific interactions with water do not exist or remain constant the influence of increasing the molar volume ϕ on the transfer free energy ΔG_1° is nearly the same for all substances, $\delta\Delta G_1^\circ/\delta\phi$ being of the order of 0.04 kcal mol^{-1} cm^3. It is then possible to compute the value $\Delta G_1^{\circ*}$ that a given substance would present if its molar volume would be equal to a given reference value. Differences in $\Delta G_1^{\circ*}$ are mainly due to the specific interactions of the dissolved monomolecules with water. The stabilization through "basic" hydrogen bonds with water increases $\Delta G_1^{\circ*}$ with respect to hydrocarbons without specific bonds of some 2.8 kcal mol^{-1} in anisole, while in diethyl ether this increase is of the order of 4.2 kcal mol^{-1}. For phenols the O–H bond forms "acidic" hydrogen bonds with water which increases the stabilization; the difference of $\Delta G_1^{\circ*}$ with respect to the hydrocarbons rises to the order of 5.8 kcal. In alcohols the supplementary effect of the acidic O–H bonds is weaker. Analogous estimations of the effects of the specific bonds on $\Delta G_1^{\circ*}$ were made for amines and anilines. For phenols without ortho substituents the value of ΔG_1° rises as the pK_a approaches that of water. Methyl groups in ortho position clearly lower the value of $\Delta G_1^{\circ*}$. A good approximation for the value of P_1 at 25° for the phenols can be computed from the relation log $P_1 = -1.06 + 0.03\phi - 0.25pK_a + 0.44n_{ortho}$. The transfer enthalpies ΔH_1 depend in an analogous manner on the molar volume, the pK_a, and the presence of ortho substituents.

Introduction

In a previous work[1] we showed from the distribution coefficients of anilines between cyclohexane and water that these substances not only engage in hydrogen bonds as proton acceptors but also that the N–H links act as proton donors in hydrogen bonds with the neighboring water mole-

cules. These deductions were based on the influence of methyl and chloro substituents on the distribution coefficient at high dilution P_1 and on the enthalpy of transfer ΔH_1 of the monomolecules from water to cyclohexane.

In the present paper we apply this method to phenol derivatives which are compared with compounds belonging to other groups.

TABLE I: Distribution Coefficients P_1 of the Monomolecules between Cyclohexane and Water at 25° and Transfer Enthalpy ΔH_1

Substances	P_1 (this work)	P_1(lit.)	ΔH_1, kcal mol^{-1} (Van't Hoff)	ΔH_1 (calorimetric)	P_1 (calcd, eq 7)
2-Methylphenol	1.00 ± 0.03	1.097,[a] 1.349,[b] 1.259,[c] 1.59[d]	4.1	4.2	1.13
3-Methylphenol	0.46 ± 0.03	0.502,[a] 0.708,[b] 0.631,[c] 0.794[d]	4.6	4.9	0.47
4-Methylphenol	0.45 ± 0.08	0.794,[b] 0.646[c]	4.7	4.8	0.42
2,5-Dimethylphenol	9.07 ± 0.25	19.0,[b] 8.51[c]	2.7	3.6	8.71
3,5-Dimethylphenol	1.64 ± 0.03	3.47,[b] 1.86[c]			1.46
Phenol	0.154 ± 0.08	0.100,[a] 0.191,[b] 0.170,[c] 0.154,[e] 0.117,[f] 0.100[g]	5.2	4.7	
4-Chlorophenol	0.50 ± 0.02	0.20,[a] 0.55[e]	4.7	4.4	0.52
3,5-Dichlorophenol	2.81 ± 0.16				2.61
Anisole	119.4 ± 0.8	199.6[h]		0.8	
Ethylbenzene	579 ± 20				
Diethyl ether	8.57 ± 0.25		4.3		

[a] Reference 2a. [b] Reference 2b. [c] Reference 2c. [d] Reference 2d. [e] Reference 2e. [f] Reference 2f. [g] Reference 2g. [h] Reference 2h.

Experimental Quantities

The distribution coefficient of the monomolecule P_1 can be obtained by extrapolation of the distribution coefficient P at infinite dilution:

$$P_1 = \lim P_{(F_0 \to 0)} \qquad (1)$$

As in the previous work the determination of P_1 was performed by extrapolation from some 20 experimental values of P in a range of concentration F_0 in the organic phase going from 0.015 to 2 M (if the solubility is high enough). The standard free energy of transfer $\Delta G_1°$ is related to P_1 by the classical expression

$$RT \ln P_1 = -\Delta G_1° \qquad (2)$$

The transfer enthalpy ΔH_1 can be computed from measurements of P_1 at different temperatures using the Van't Hoff equation but it can also be obtained from direct calorimetric measurements giving the dilution heat at zero concentration.

Experimental Results

The values of P_1 at 25° as well as those of ΔH_1 (determined by both methods) are given in Table I and a comparison is made with values in the literature. Data on similar systems can also be found in the extensive work of Hansch and his collaborators.[2e]

Discussion

In order to specify the nature of the factors which can influence the distribution coefficients of the molecules we have assembled in Table II the values of the free energy of transition $\Delta G_1°$ computed by eq 2 from values of P_1 listed in this paper and in the literature. We also present the pK_a of the acid and the pK_b of the bases as well as the molar volume ϕ. For solids this molar volume is not that of the pure compound which can be strongly influenced by the forces which are responsible for the establishment of the crystalline network, but is calculated starting from that of analogous liquid substances and using the following volume

increments for the substituents: $CH_3 = 16.7$ cm^3; $Cl = 12.6$ cm^3. In the case of alkanes the organic medium is not cyclohexane but the alkane itself and the values of $\Delta G_1°$ derive thus directly from the solubility of the alkane in water. The value for water was computed from its solubility in cyclohexane.

A. Influence of the Molar Volume on the Free Energy of Transfer. When one plots the value of $\Delta G_1°$ for saturated hydrocarbons which are not capable of forming specific bonds with water as a function of their molar volume (Figure 1), one observes that for the normal alkanes and for the cycloalkanes the points lie approximately on the same straight line. The slope of this line is −0.04 kcal mol^{-1} cm^3. The values for branched hydrocarbons lie slightly higher but the slope remains practically the same.

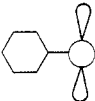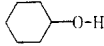On the other hand, in our previous work[1] we showed that the influence of the molar volume ϕ on the value of log P_1 of the anilines could be described by a value of 0.030 mol^{-1} cm^3 for the partial derivative $\delta \log P_1/\delta \phi$. From eq 3 in that paper one finds then a value 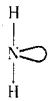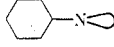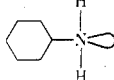of −0.041 kcal mol^{-1} cm^3 for the partial derivative $\delta \Delta G_1°/\delta \phi$. It appears thus that this partial derivative, obtained maintaining the specific interactions constant or zero, is nearly the same for all systems. $\Delta G_1°$ is related to the ratio of Henry's law constants k_{aq}/k_{org} of the solute in both solvents. In the organic phase k_{org} depends on the molar volume of the solute which influences among others the energy of the dispersion forces. The value of k_{org} can also be influenced by nonspecific effects of dipoles of the molecule of the solute on the surrounding solvent molecules. As a first approximation one can write

$$\log k_{org} = A_o \phi + f_{o,ns} \qquad (3)$$

where $f_{o,ns}$ is a factor which takes the nonspecific effects into account.

Log k_{aq} also depends on the molar volume of the solute but the corresponding term $A_w \phi$ involves the energy needed to destroy the hydrogen bonds between water molecules. On the other hand, k_{aq} can be strongly influenced by the hydrogen bonds between the solute and the surrounding water molecules. This leads to the expression

TABLE II: Free Energy of Transfer ΔG_1 at 25°

Family	Specific groups	Compound	Molar volume, cm^3 mol^{-1}	pK_a	pK_b	$\Delta G_1°$, kcal mol^{-1}	$\Delta G_1°*$ (at 110 cm^3)
Alkanes		Pentane	115.2			−5.73[a]	−5.50
		Hexane	130.5			−6.58[a]	−5.70
		Heptane	146.6			−7.30[a]	−5.75
Branched alkanes		Isopentane	116.4			−5.59[a]	−5.32
		2-Methylpentane	131.9			−6.36[a]	−5.43
		2,2-Dimethylbutane	132.9			−6.18[a]	−5.21
Cycloalkanes		Cyclopentane	94.1			−5.01[a]	−5.68
		Cyclohexane	108.8			−5.64[a]	−5.69
		Methylcyclopentane	112.4			−5.77[a]	−5.67
		Methylcyclohexane	127.6			−6.45[a]	−5.69
Aromatic hydro-carbons		Benzene	88.9			−3.07[b]	−3.96
		Ethylbenzene	122.5			−2.83[c]	−3.23
Ethers		Diethyl ether	103.8		17.6[g]	−1.27[c]	−1.53
Aromatic ethers		Anisole	109.3		20.5[g]	−2.83[c]	−2.85
Alcohols		1-Propanol	74.8			+2.11[d]	+0.62
		1-Butanol	91.3	16.8[h]		+1.17[d]	+0.38
		1-Pentanol	108.2			+0.25[d]	+0.18
		2-Propanol	76.5			+2.41[d]	+1.00
		2-Butanol	91.7	17.2[h]		+1.32[d]	+0.55
		2-Pentanol	108.8			+0.36[d]	+0.31
		tert-Butyl alcohol	94.0	17.6[h]		+1.59[d]	+0.91
		tert-Pentyl alcohol	109.4			+0.62[d]	+0.60
Water		Water	18	15.7	15.7	+5.82[c]	+1.93
Phenols		Phenol	88.2	9.99[i]		+1.11[c]	+0.19
		2-Methylphenol	105.0	10.33[j]		+0.00[c]	−0.21
		3-Methylphenol	105.0	10.10[i]		+0.46[c]	+0.25
		4-Methylphenol	105.0	10.28[j]		+0.47[c]	+0.26
		2,6-Dimethylphenol	121.7	10.62[j]		−1.30[c]	−0.80
		3,5-Dimethylphenol	121.7	10.20[i]		−0.29[c]	+0.21
		4-Chlorophenol	100.9	9.44[j]		+0.41[c]	+0.03
		3,5-Dichlorophenol	113.5	8.18[i]		−0.61[c]	−0.46
Tertiary amines		Trimethylamine	88.1		4.29[k]	+0.60[e]	−0.33
Primary amines		*n*-Butylamine	98.7		3.23[k]	+0.39[e]	−0.08
Anilines		N,N-Dimethyl-aniline	127.3		8.25[g]	−2.97[f]	−2.23
		Aniline	91.6		9.40[g]	−0.05[f]	−0.82

[a] Reference 3a. [b] Reference 3b. [c] Reference 3c. [d] Reference 3d. [e] Reference 3e. [f] Reference 3f. [g] Reference 3g. [h] Reference 3h. [i] Reference 3i. [j] Reference 3j. [k] Reference 3k.
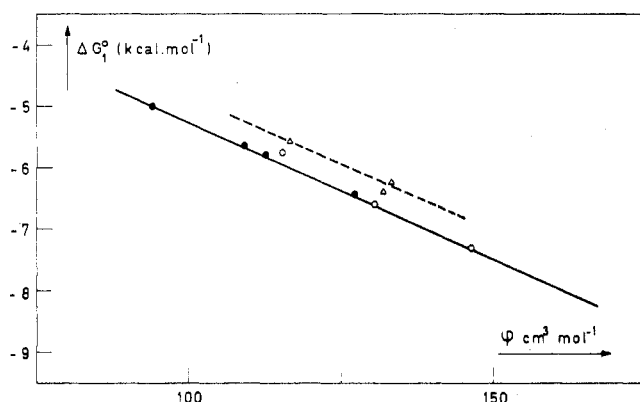
Figure 1. Standard free energy of transition $\Delta G_1{}^{\circ}$ between water and the organic phase of hydrocarbons: normal alkanes (O); cycloalkanes (●); branched alkanes (△).

$$\log k_{aq} = A_w\phi + f_{w,ns} + f_{w,hb} \qquad (4)$$

where $f_{w,ns}$ and $f_{w,hb}$ refer respectively to the nonspecific and to the specific effects of the solute on water.

It thus appears that the difference $A_o - A_w$ remains nearly constant for the systems studied here. This can be interpreted by admitting that this difference is mainly determined by the modifications of the autoassociation of water. An increase of the volume of the cavity corresponding to the addition of a CH_2 group would bring about modifications in the structure of water which are practically independent of the nature of the molecules.

Anyhow, the observed regularity permits the elimination of the effects of difference in the volume of the molecules on the values of $\Delta G_1{}^{\circ}$. Taking as reference the value of 110 cm³ (which corresponds approximately to the mean of the values of Table II) one can compute from the experimental value of $\Delta G_1{}^{\circ}$ *the value of* $\Delta G_1{}^{\circ}*$ *which would be observed if the molar volume of the compound was 110 cm³* by means of the equation

$$\Delta G_1{}^{\circ}* = \Delta G_1{}^{\circ} - 0.041(110 - \phi) \qquad (5)$$

These values are also reported in Table II.

B. Order of Magnitude of the Specific Effects on ΔG_1*. In $\Delta G_1{}^{\circ}*$ the effects of differences in molar volumes are eliminated. *Strong differences between the values of $\Delta G_1{}^{\circ}*$ for the various compounds are mainly due to the difference of the specific interactions of these compounds with water* (and thus to differences in the factor $f_{w,hb}$). Secondary effects may also result from the variation of the difference $f_{o,ns} - f_{w,ns}$ or from the differences in the shape of the molecules.

It appears from the data of Table II that for alkanes and cycloalkanes $\Delta G_1{}^{\circ}*$ has a mean value of -5.67 and -5.30 kcal mol⁻¹. We can thus take -5.67 and -5.30 kcal mol⁻¹ as reference values of $\Delta G_1{}^{\circ}*$ in absence of specific interactions. (The choice between these two values would be made taking the shape of the considered molecules into account.)

As a first approximation, neglecting changes in the difference $f_{o,ns} - f_{w,ns}$, the difference

$$\delta\Delta G_1{}^{\circ}* = \Delta G_1{}^{\circ}* - \Delta G_1{}^{\circ}*_{\text{hydrocarbons}} \qquad (6)$$

can be ascribed to the influence of the specific bonds between the solute and water and *gives an order of magnitude* of this stabilization effect.

(1) *Basic Sites.* In diethyl ether the basic sites of the oxygen atom form specific interactions with water that in-

TABLE III: Effects of the Specific Sites on the Free Energy of Transfer (Molar Volume 110 cm³ mol⁻¹) between Water and Cyclohexane at 25° (in kcal mol⁻¹)

Basic site	$\delta\Delta G_1{}^{\circ}*$	Basic sites + acidic sites	$\delta\Delta G_1{}^{\circ}*$	Diff.
⬡	2.0			
(O lone pairs)	4.1	(OH)	6.3	2.2
(cyclohexyl-O)	2.8	(cyclohexyl-OH)	5.9	3.1
(N)	5.3	(N–H)	5.6	0.3
(cyclohexyl-N)	3.4	(cyclohexyl-N–H)	4.9	1.4

crease $\Delta G_1{}^{\circ}*$ 4.10 kcal mol⁻¹ with respect to the hydrocarbons. On the other hand, the aromatic ring of benzene can also act as a basic site in the interactions with water. The increase of $\Delta G_1{}^{\circ}*$ is of the order of magnitude of 2 kcal mol⁻¹ (a discrepancy of some 0.7 kcal mol⁻¹ exists between the two data).

The conjugation of the basic sites of the oxygen atom and of the aromatic ring lowers to a great extent the proton-acceptor capacity in the hydrogen bonds with water. In fact anisole shows only an increase for $\Delta G_1{}^{\circ}*$ of 2.8 kcal mol⁻¹ with respect to the hydrocarbons.

The interactions of the electron pair of the nitrogen atom with water are very strong. In trimethylamine they bring about an increase in $\Delta G_1{}^{\circ}*$ of 5.3 kcal mol⁻¹.

Again, the conjugation of the aromatic ring has an unfavorable effect. In N,N'-dimethylaniline this stabilization falls to 3.4 kcal mol⁻¹.

(2) *Acidic Sites.* One can observe that all the molecules of Table II which have acidic sites also contain basic sites. Under these conditions one can only describe the global effect and note the difference between this effect and that which occurs when only the basic sites are present. This difference does not correspond exactly with the effect that would be observed if the acidic site would act alone, but nevertheless gives us an idea of its order of magnitude.

In the alcohols the O–H group causes an increase of $\Delta G_1{}^{\circ}*$ of 6.3 kcal mol⁻¹, the values however depend slightly on the nature of the alcohol. In phenol the stabilization effect is of the order of 5.9 kcal mol⁻¹.

In Table III we present additional data concerning the order of magnitude of the effects of the specific bonds on the stabilization of the molecules in water.

In the particular case of the phenols one observes that the basic site as well as the acidic site plays an important role in the stabilization of the molecule in water. Compared with aliphatic alcohols, the influence of the basic site is less while that of the acidic site (data from the last column) is greater.
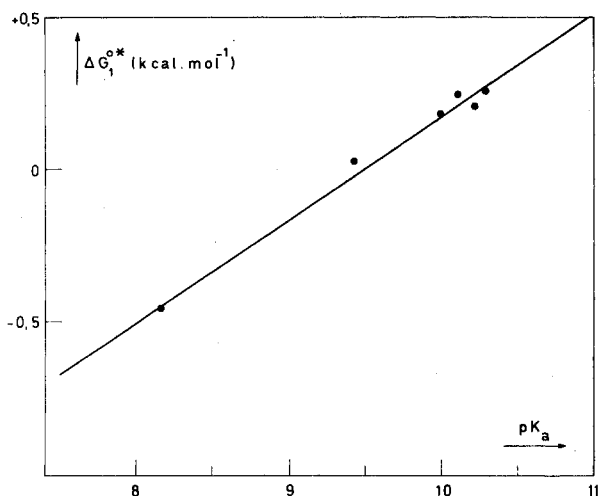
Figure 2. Standard free energy of transition $\Delta G_1^{\circ}{}^*$ (reduced to a molar volume of 110 cm³) of phenols vs. pK_a.

The situation appears to be different in the case of aliphatic amines where the basic site is particularly effective while the role of the acidic site fades. In the anilines the N–H groups intervene again to a greater extent to the detriment of the basic function.

C. Influence of the pK_a of Phenols on Specific Interactions with Water. When the values of $\Delta G_1^{\circ}{}^*$ of phenols without ortho substituents are plotted against their pK_a one observes an approximative linear correlation (Figure 2) whose slope is positive with a value of 0.34 kcal mol⁻¹.

Increasing the acidity of phenol thus has an unfavorable influence on its stabilization in water.

On the other hand, it may be supposed that in the case of the acidic bond O–H ··· O–H₂ a decrease of the pK_a, which enhances the proton donor character of the O–H group, would have a favorable influence on the stability of this hydrogen bond. The fact that the global effect takes place in the opposite sense must be ascribed to a more important influence of the variation of the pK_a on the "basic" bonds of the phenols with water.

In this connection we can notice that if the molecule does not bear acidic sites the effect of the pK_a is more important. When the values of Table II concerning *N,N*-dimethylaniline and trimethylamine are compared, one can compute a value of $\delta\Delta G_1^{\circ}{}^*/\delta$p$K_a$ of 0.42 kcal mol⁻¹. The comparison of anisole and of diethyl ether gives us a value of 0.48 kcal mol⁻¹. From data of previous work relative to anilines (where the acidic N–H groups still play a role) we arrive at a value of 0.38 kcal mol⁻¹.

The presence of acidic O–H groups reduces thus the influence of pK_a on $\Delta G_1^{\circ}{}^*$ but the preponderant effect remains that exerted on the basic sites. As a consequence, the value of $\Delta G_1^{\circ}{}^*$ of a phenol rises as its pK_a approaches that of water.

From a quantitative point of view it must be borne in mind that nonspecific effects on k_{aq} and on k_{org}, which could affect the difference $f_{o,ns} - f_{w,ns}$, can also play a role in the change of $\Delta G_1^{\circ}{}^*$ with the pK_a.

D. Influence of Steric Groups. The values of $\Delta G_1^{\circ}{}^*$ of the phenols with methyl groups in ortho position are systematically lower (0.6 kcal mol⁻¹ per group). One can conclude that this group disfavors the specific interactions with water.

Taking into account the various effects which have been discussed, the following relation can be proposed to compute the distribution coefficient P_1 of the phenols at 25°:

$$\log P_1 = -1.06 + 0.031\phi - 0.25\text{p}K_a + 0.44 n_{\text{ortho}} \quad (7)$$

where n_{ortho} is the number of methyl groups in ortho position.

The values of P_1 which are calculated in this way are reported in Table I.

E. Role of Water in the Organic Phase. From the extensive work of Christian and coworkers[4] it appears that the presence of water in the organic phase can affect the partition coefficient of a given compound. This effect cannot much alter the values of P_1 in the present case because at the low concentrations used for this determination the ratio between the number of water molecules and the number of the molecules of the compound in the organic phase remains fairly low. For instance, our determinations of the concentration of water in the organic phase, using the Karl Fisher method, show that for the phenols at concentrations lower than 0.2 M, this ratio is lower than 0.1 at 25°.

F. Factors Influencing the Transfer Enthalpy. The intervention of the acidic O–H group in the stabilization of these substances in water clearly appears in the difference between ΔH_1 of anisole and of phenols of similar volumes.

The precision of the determination of ΔH_1 does not permit obtaining quantitative relations as in the case of ΔG_1°.

From a qualitative point of view, one observes the influence of the same factors on ΔH_1 as on ΔG_1°.

Thus, comparison of the values of ΔH_1 for cresols clearly shows that this value decreases when there is a methyl substituent in ortho position. On the other hand, the mean value of ΔH_1 seems to increase with the molar volume and with the pK_a of phenols.

Experimental Section

The apparatus used in this work, the products, and their purification were described in the preceding papers.[1,5]

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