

Journal of Molecular Structure 448 (1998) 143-148



Short-range solvation patterns of pentachlorophenol, triethylamine, and their reaction products by cyclic ethers in cyclohexane

Sister Mary Josepha Van Camp, Shawn Morris, Annmarie Mudge, Richard Points, Jodi B. Knight, Stephen E. Schullery*, Ronald M. Scott¹

Department of Chemistry, Eastern Michigan University, Ypsilanti, MI 48197, USA

Received 22 September 1997; revised 9 February 1998; accepted 9 February 1998

Abstract

The proton-transfer indicator reaction method is applied to the pentachlorophenol-triethylamine proton-transfer equilibrium K_{PT} undergoing solvation by tetrahydropyran, 1,3-dioxane, and 1,4-dioxane in bulk cyclohexane. A predicted decrease in K_{PT} occurs owing to hydrogen bonding solvation of the free phenol upon increasing ether concentration. However, the data unexpectedly suggest that hydrogen bonding solvation by the ethers to the proton of the proton-transfer adduct also occurs. © 1998 Elsevier Science B.V. All rights reserved

Keywords: Solvation; Pentachlorophenol; Triethylamine; Hydrogen bond; Proton-transfer

1. Introduction

Short-range solvation is the direct interaction of solute and solvent molecules, generally by means of hydrogen bonds. Such interactions alter the reactivity of the solutes in ways that can be measured readily in the laboratory. We use these changes in reactivity to provide insights into the binding constants and stoichiometry of the solute-solvent interaction.

Phenols (P) and amines (A) interact in solution such that the phenolic hydrogen and the unshared amine

electrons form a phenol-amine hydrogen-bonded adduct (PA). The phenolic hydrogen may then shift along the hydrogen bond axis toward the amine electrons, resulting in a phenolate ion and an ammonium ion joined by a hydrogen bond, a proton-transfer adduct (P^-A^+). K_{HB} and K_t are equilibrium constants for formation of hydrogen-bonded adduct and the conversion of hydrogen bonded adduct to proton-transfer adduct, respectively.

$$P + A \stackrel{K_{HB}}{\Leftrightarrow} PA \stackrel{K_{L}}{\Leftrightarrow} P^{-}A^{+}$$

Formation of the proton-transfer adduct is favored by involvement of more acidic phenols, more basic amines, and a more polar solvent system. The conversion of the phenol to a phenolate ion is readily observed in the UV-visible optical spectrum of the phenol. Our studies do not differentiate $K_{\rm HB}$ and $K_{\rm t}$,

^{*} Corresponding author. Tel: 001 313 487 0106; Fax: 001 313 487 1496.

¹ Professor Ronald M. Scott died unexpectedly on November 5, 1997, less than 3 months after presenting this paper at the XIIth Conference-Workshop on Horizons in Hydrogen Bond Research held in Styria, Austria. He was an exceptional person and will be greatly missed by his many students and colleagues.

providing rather the product of these constants, $K_{\rm PT}$.

$(K_{\rm HB})(K_{\rm t}) = K_{\rm PT}$

Studies in this laboratory first focused on the effect of varied solvent polarity-so-called long-range solvation—on K_{PT} [1]. Later, given evidence that the $K_{\rm PT}$ shifts were owing to hydrogen bonding by Lewis base solvents to the amine protons of primary and secondary amines involved in a proton-transfer adduct, extensive studies of such short range solvation were undertaken using formation of the 2,4-dinitrophenol (DNP) and diethylainine (DEA) proton-transfer adduct, and a variety of interactive solvents presented as the minor component in a mixed benzene-solvent system [2-5]. Experimental and computational methods were devised using the $K_{\rm PT}$ equilibrium as an indicator reaction reporting on the solvation state of both reactant and product species. Solvation stoichiometries and binding constants are evaluated as adjustable parameters in a binding isotherm that is fitted to experimental K_{PT} versus solvent concentration data [6]. For example, the binding isotherm for singlestage solvation of the adduct and one of the reactant species is

$$K_{PT} = K_{PT}^{o} \{ (1 + (K_s[S])^n) / (1 + (K_s'[S])^{n'})$$
(1)

where K_{PT}^{o} is the proton-transfer constant in the noninteractive bulk solvent, K_s and K_s' are the binding constants of *n* and *n'* solvent molecules to the adduct and reactant, respectively, and [*S*] is the molarity of the interactive solvent component. For solvation numbers *n* or *n'* greater than one, single-molecule binding constants K_s and K_s' are determined as the geometricaverage, *n*th or *n'*th root of the total solvation constants K_s and K_s' , respectively.

Several important findings resulted. First, the most common stoichiometry is two solvent molecules per proton hydrogen bonding site—bifurcated hydrogen bonds—at both the secondary amine proton of the DEA–DNP adduct and the phenolic hydrogen of free DNP, for aprotic Lewis base solvents including linear and cyclic ethers, esters, a urea, a nitrile, and even weakly basic thioethers [7]. Also, larger than normal binding constants for the six-membered-ring cyclic ethers (but not five-membered-ring ethers) having more than one ring oxygen (1,3-dioxane, 1,4dioxane and trioxane), implied that more than one of the ring oxygens are involved in a hydrogen bond [6,8]. Finally, application of the method to protonic solvation by alcohols yielded stoichiometries and binding constants for primary and secondary stages of solvation [9]. A review of both the aprotic and protic solvation has been published [10].

Although the binding constants determined by this method are of reasonable magnitude, there is little literature data available for direct comparison, and virtually none against which to judge either the aprotic bifurcation stolchiometries or the protic multistage stoichiometries. For example, although bifurcated hydrogen bonding is well known in the solid state [11], there are relatively few reports of such in the liquid state [12–16]. Thus, we are motivated to further test our model by applying it to systems for which it predicts significantly novel behavior.

All of the proton-transfer equilibria studied to date are shifted toward adduct (K_{PT} increases) upon addition of the interactive (and generally more polar) solvent component, whether protic or aprotic. This invited the criticism (discussed in Ref. [9]) that the K_{PT} increase might be owing to long-range, nonspecific dielectric stabilization of the zwitterionic adduct as the polarity of the mixed solvent system is raised. However, a decrease in K_{PT} is predicted for any proton-transfer system in which the solvent interacts more strongly with a reactant than with the adduct. The expected functional dependence is seen by setting $K_s = 0$ in Eq. (1), leading to Eq. (2):

$$K_{\rm PT} = \frac{K_{\rm PT}^{0}}{(1 + (K_{\rm s}'[S])^{n'})}$$
(2)

For the simplest case, n' = 1, this predicts a hyperbolic decline to a plateau for a plot of K_{PT} versus [S]. Any decrease in K_{PT} would clearly refute the dielectric stabilization hypothesis. We now present results for three systems designed to test this prediction.

This study reports the effect on the proton-transfer equilibrium of pentachlorophenol (PCP) and triethylamine (TEA) upon solvation by tetrahydropyran, 1,3-dioxane, and 1,4-dioxane in bulk cyclohexane solvent. In contrast to the diethylammonium moiety of the DNP-DEA adduct, the PCP-TEA adduct contains no exposed polar hydrogen inviting solvation. Therefore, the aprotic Lewis base solvents are expected to significantly interact only with the free PCP, and thereby produce a decrease in KPT upon increasing base concentration. The predicted decrease in K_{PT} is

Table 1 Experimental K_{PT} values in ether-cyclohexane mixed solvents at 25°C

Concentration	K _{PT}					
()	Tetra- hydropyran	1,3 -Dioxane	1,4 -Dioxane			
0	1150	1300	1300			
0.1	1050					
0.3	_	744	948			
0.4	_	695				
0.5	455	695	785			
0.75	<u> </u>	683	785			
0.9	_	607	—			
1.0	555	625	628			
1.05	_	—	596			
1.1		608	585			
1.2			665			
1.5	263	683	555			
1.7			528			
1.8	_		553			
1.9	_		430			
2.0	285	650	486			
2.5	200		563			
3.0	215					
4.0	180	—	_			
8.0	125	—	_			

observed, adding further support to the validity of the model, and ruling out non-specific dielectric stabilization as the dominant solvation mechanism in these systems. However, acceptable fits to the data cannot be obtained unless some unexpected, albeit weaker, solvation of the proton-transfer adduct also is invoked. Apparent solvation stoichiometries and binding constants are discussed.

2. Materials and methods

PCP was recrystallized from benzene and stored in a desiccator over calcium sulfate until use. Triethylamine was distilled, then stored in a dark bottle under dry nitrogen gas until use. Cyclohexane was either spectrograde, and used without further treatment, or was reagent grade and was distilled before use. 1,4-Dioxane was spectrograde and was used without further purification. Tetrahydropyran and 1,3-dioxane were distilled before use. All cyclic ethers were stored tightly stoppered until use to avoid contamination with water. Mixtures of PCP and TEA were prepared in a solvent of cyclohexane to which known concentrations of a cyclic ether were added. All solutions were prepared by weight. UV-visible spectra of these solutions were taken using a Perkin-Elmer Lambda 20 spectrophotometer with a temperature control set at 25.0°C.

Values for K_{PT} were determined by methods described earlier [2–5]. The resulting K_{PT} versus [S] data were subjected to non-linear least-squares curve fitting to Eqs. (1) and (2), assuming two and one solvation sites, respectively. The solvation binding constants K_s and K_s' were determined as adjustable parameters for a variety of assumed solvation stoichiometries *n* and *n'*. The computational method and justification of the assumptions are discussed in Ref. [9].

3. Results

The K_{PT} values for the PCP–TEA adduct at various molarities of cyclic ether in cyclohexane bulk solvent at 25°C are presented in Table 1, and are plotted in Figs. 1–3, along with all possible curves fitted to Eqs. (1) and (2) with *n* and *n'* values of 0, 1 and 2. The corresponding best-fit K_s and $K_{s'}$ solvation binding constants are presented in Table 2 in order of decreasing fit quality, along with the sums of squares of deviations of the data points from the values predicted by the best-fit equation.

4. Discussion

The predicted decrease in K_{PT} upon increasing [*S*] is observed for all three systems. This is consistent with the weaker solvation of the adduct, as expected owing to the absence of an exposed polar hydrogen. This equilibrium shift away from the adduct clearly rules out non-specific dielectric stabilization as the dominant solvation mechanism in these systems. However, in fitting the data to Eqs. (1) and (2), two unexpected findings emerge: (1) there does seem to be some significant solvation of the 'buried' adduct proton; and (2) the bifurcated hydrogen bonding to the free phenol seen in the earlier studies, although not ruled out, is not as clearly indicated for these systems.





The three acceptable fits for solvation by tetrahydropyran correspond to adduct: free phenol solvation numbers of 0:1, 1:1 and 2:1. None of these correspond to the bifurcated solvation of the free phenol, as seen in the earlier studies. However, the 2:2 solvation scenario provided a fit that could be considered marginally acceptable, and, if so, would be supportive of the bifurcated solvation of the free phenol. By contrast, solvation numbers of 0, 1, or 2 all are possibilities for the adduct proton. Note that, taking into account the phenol–amine hydrogen bond, the solvation number of 2 would represent trifurcated hydrogen bonding to the adduct proton. The binding constants generated by fitting to any of the six solvation patterns are of expected magnitudes and vary by



Fig. 2. Plot of K_{PT} versus 1,3-dioxane molarity in cyclohexane bulk solvent at 25°C. The best-fit curves for the four different n:n' solvation patterns, as labeled, are superimposed on the experimental data shown as solid circles.



Fig. 3. Plot of K_{PT} versus 1,4-dioxane molarity in cyclohexane bulk solvent at 25°C. The best-fit curves for the four different n:n' solvation patterns, as labeled, are superimposed on the experimental data shown as solid circles.

only a factor of two for K_s' and a factor of 10 for K_s (Table 2).

For solvation by 1,3-dioxane there are two acceptable fits, corresponding to adduct: free phenol solvation numbers of 1:1 and 2:2, and one marginally acceptable fit for the 2:1 solvation pattern. There is no doubt that solvation of the adduct occurs in this system. Either normal or bifurcated solvation of the free phenol are supported, but if the latter is accepted, then too must mixed trifurcated hydrogen bonding to the adduct proton be accepted. More puzzling is the fact that the solvation binding constants for both of the two best fits seem to be unreasonably large (Table 2), in comparison either to those obtained with the other two solvents in this study or to the same solvent in the earlier DNP-DEA study [6]. The graphical origin of these large binding constants can be seen in Fig. 2 as an exceptionally steep initial decline followed by an abrupt bend to a plateau, in contrast with the more gradually varying data of Figs. 1, and 3 (note different x-axis scale in Fig. 1).

There are three acceptable fits for solvation by 1,4dioxane, corresponding to adduct: free phenol solvation numbers of 1:1, 2:1, and 2:2. In addition, the 0:1 solvation pattern could be considered marginally acceptable. These data also strongly support solvation of the adduct, which, counting the adduct's internal hydrogen bond, would be either bifurcated or trifurcated. Again, the 2:2 solvation scenario is the only one supportive of the bifurcated solvation of the free phenol seen in the earlier studies. The binding constants are

 Table 2

 Least-squares fitting data for the six simplest solvation scenarios

Reactive solvent	Sum of squares	Model and parameters ^a				DNP $K_{s}^{\prime h}$
		n	n'	K _s	<i>K</i> _s '	
Tetrahydropyran	5.1 E4	1	1	1.59	26.8	
	5.3 E4	2	1	1.40	22.4	_
	5.6 E4	_	1	_	20.9	
	8.3 E4	2	2	13.9	32.7	11
	2.3 E5	1	2	10.0	26.6	
	2.6 E5		2		16.0	
1,3-Dìoxane	7 1 E3	2	2	60.5	86.4	
	8.1.E3	-	-	86.3	184	
	2.0 E4	2	1	8.2	25.9	
	1.9 E5		1		10.4	
	6.2 E5		2		10.6	_
	7.8 E5	1	2	7E-6	12.2	
14 Disusas	2754	2	,	2.50	14.0	
1,4-Dioxane	2.7 E4 2.0 E4	2	1	5.50	14.0	—
	3.0 E4	1	1	5.2	22.0	 50
	3.9 E4	2	2	17.9	28.7	55
	6.0 E4	—	1		8.84	
	3.2 E5	_	2		8.65	
	4.2 E5	1	2	1E-6	9.76	—

"Equilibrium constants are apparent binding constants in units of molarity. For solvation stoichiometries of n greater than one, single-molecule binding constants are determined as the geometric-average, nth root of the total solvation constant.

^bData from Ref. [6] for solvation of the free DNP in equilibrium with the DNP–DEA adduct in benzene bulk solvent.

of expected magnitudes and vary by less than a factor of three (Table 2).

In summary, of the six solvation number combinations presented, only the two that we most expected to observe-0:2 and 1:2-can be confidently excluded. Three of the remaining four solvation patterns require n' = 1 single salvation of the free phenol—0:1, 1:1 and 2:1-and, so, are contrary to DNP/DEA studies, where, for most aprotic solvents, two solvent molecules associate with each available phenolic proton [6]. In rationalizing this possible violation of that pattern, we recognize that the present study differs from the DNP/DEA studies in three ways. First, comparing DNP and PCP, the 6 position of DNP is unsubstituted, so when the phenolic hydrogen rotates toward that side of the ring there is more room for solvent molecules than is the case with PCP, where both the 2 and 6 positions are substituted. Second, the different acidity of PCP may result in a proton-transfer adduct less conducive to bifurcation. Finally, the prior studies were done in benzene bulk solvent, which can interact with a phenol by π -bonds, whereas cyclohexane, used in the present study, has no such interaction. On the other hand, the only acceptable solvation pattern that provides the expected bifurcation to the free phenol is 2:2, which also requires attachment of two solvents to the proton-transfer adduct. No specific solvation of the proton-transfer adduct was expected, so the possibility of n = 2 solvation, corresponding to mixed trifurcated hydrogen bonding, is doubly surprising. The proton of the proton-transfer bond is expected to be rather occluded by the pentachlorophenolate and triethylammonium ions. Further, hydrogen bonds as strong as specific solvation of the protontransfer adduct are normally too insistent on linear geometry to accommodate second and third participants [11].

In previous studies it was usually clear which set of stoichiometries was the best choice, but in this study it is less obvious. The origin of the overlapping and non-unique fits seen in the present study can be attributed to two factors. First, in the decreasing $K_{\rm PT}$ regime, even the simplest solvation pattern (single site, n' = 1) predicts a hyperbolic isotherm. In contrast, in the prior, increasing $K_{\rm PT}$ studies, the simplest solvation pattern (single site, n = 1) predicts a linear isotherm, distinctly different than any two-site solvation pattern. Second, in the decreasing $K_{\rm PT}$ regime, the $K_{\rm PT} = 0$ lower bound forces all single-stage solvation patterns to yield an isotherm that is at least approximately hyperbolic. Thus, the present decreasing- $K_{\rm PT}$ experiment permits unambiguous discrimination between possible short-range and long-range solvation mechanisms, but at the expense of discrimination among the possible short-range mechanisms.

References

- S.N. Vinogradov, R.A. Hudson, R.M. Scott, Biochim. Biophys. Acta 214 (1970) 6–27. and references therein.
- [2] E.D. Berman, R. Thomas, P. Stahl, R.M. Scott, Can. J. Chem. 65 (1987) 1594.

- [3] Z. Ye, S. Yazdani, R. Thomas, G. Walker, D. White, R.M. Scott, J. Mol. Struct. 177 (1988) 513–522.
- [4] M. Abduljaber, R.M. Scott, J. Mol. Struct. 237 (1989) 285– 295.
- [5] N. Hemati, R. Khan, R.M. Scott, J. Mol. Struct. 322 (1994) 312.
- [6] S.E. Schullery, R.M. Scott, J. Mol. Struct. 322 (1994) 287– 296. and references therein.
- [7] C.Q. Zhu, N.Z. Zhou, S.E. Schullery, R.M. Scott, J. Mol. Struct. 381 (1996) 101–105. and references therein.
- [8] A. Chen, S.E. Schullery, R.M. Scott, J. Mol. Struct. 322 (1994) 321–327.
- [9] S.E. Schullery, N. Hemati, R.M. Scott, J. Soln Chem. 24 (1995) 771–793.
- [10] S.E. Schullery, S.M. Wojdyla, R.A. Ostroski, R.M. Scott, J. Mol. Struct. 416 (1997) 167–178.
- [11] G.A. Jeffries, An Introduction to Hydrogen Bonding, Oxford University Press, New York, 1997.
- [12] C.L. Perrin, R.K. Gipe, Science 238 (1987) 1393.
- [13] F. Sciortino, A. Geiger, H.E. Stanley, J. Chem. Phys. 96 (1992) 3857–3865.
- [14] M.D. Newton, J. Phys. Chem. 87 (1983) 4288-4292.
- [15] S.F. Bureiko, N.S. Golubev, J. Mattinen, K. Pihlaja, J. Molec. Liq. 45 (1990) 139–145.
- [16] S.F. Bureiko, V.P. Oktiabr'sky, J. Mol. Struct. 349 (1995) 53-56.