SOLVATION OF PRIMARY AMINES: SHORT-RANGE SOLVATION OF PROTON TRANSFER COMPLEXES OF 2,4-DINITROPHENOL AND *n*-BUTYLAMINE*

SHUQIONG GUO and RONALD M. SCOTT**

Department of Chemistry, Eastern Michigan University, Ypsilanti, MI (U.S.A.) (Received 11 September 1989; in final form 27 November 1989)

ABSTRACT

The short-range solvation of the proton transfer complex formed between 2,4-dinitrophenol and *n*-butylamine was studied in benzene solution containing small amounts of three ethers: *n*propyl ether, tetrahydropyran, and dioxane. In all cases a pattern is observed in which solvation by the ether causes an increase in the equilibrium constant for the formation of the proton transfer complex until a plateau value is reached. This is followed on further increase of the ether concentration by a second rise followed by a second plateau. The equilibrium constants for each of the solvation events and the number of solvent molecules reacting per amine molecule were calculated. The first step involves two solvent molecules per amine, and the second step involves a larger number.

INTRODUCTION

Solvation effects can be divided into two groups, short-range and long-range effects. Short-range effects result from direct interaction, generally by hydrogen bonding, between the solute and a solvent, thereby changing the characteristics of the solute. Long-range effects relate to charge separation in the solute, and are a property of polar solvents. Since our solvent systems are composed of benzene with small amounts of a series of non-polar ethers added, long-range effects are not a significant factor in this study.

Short-range effects have been studied extensively in this laboratory. The first observation related to the relatively high reactivity of *n*-butylamine, a primary amine, in forming proton transfer complexes with *p*-nitrophenol in dimethylsulfoxide (DMSO) when compared with that of triethylamine [1]. The existence of hydrogen bonds between the DMSO and the amine protons of the primary and secondary amines was confirmed by NMR studies [2]. The

0022-2860/90/\$03.50 © 1990 — Elsevier Science Publishers B.V.

^{*}Presented at the IXth Workshop on Horizons in Hydrogen Bond Research held at Zeist (Utrecht), The Netherlands, 10–15 September 1989.

^{**}To whom inquiries should be addressed.

p-nitrophenol was replaced by the more acidic 2,4-dinitrophenol (DNP), which allowed the effect of the solvent on the formation of the proton transfer complex to be observed at much lower concentrations of DMSO [3]. The studies then focused on secondary amines, especially diethylamine, and were extended to a number of other electron-donating solvents [4]. It was determined that the amine proton was bound by what must be a bifurcated hydrogen bond to two solvent molecules in the case of every solvent studied [5]. Equilibrium constants were determined for the formation of the solute-solvent hydrogen

TABLE 1

Ether (wt.%)	$K_{ m eq}$			
	<i>n</i> -Propyl ether	Dioxane	Tetrahydropyran	
0	65	65	65	
0.1	76			
0.2	106	110		
0.3	101			
0.4	115	133	236	
0.6	140	135	118	
0.8	133	168	140	
1.0	133	205	175	
1.5			213	
2.0	115		247	
2.5	125			
3.0	128	218	428	
3.4	128			
4.0		233	420	
4.4	121			
4.8	121			
5.0	140	215	420	
5.2	130	258		
5.5	152	268		
5.7	132	305		
5.8	140			
5.9	152			
6.0	200	361	535	
6.5		508	805	
7.0		345	997	
7.5			1260	
8.0	203		1370	
9.0	190		1225	
10.0		360	1267	
12.0			1256	

Equilibrium constants for the formation of the proton transfer complex between 2,4-DNP and nBA at 25 °C in mixed benzene-ether solvents

bond. It was further determined that the solvation structure is a crowded structure, such that small increases in the steric demand of the solvent and/or amine blocked the solvation reaction [6]. To this time a detailed study of the more complex primary amine model was avoided because in preliminary studies in polar electron-donating solvents, measurements of the equilibrium constants for the solvation reaction or estimations of the number of solvent molecules associating with each amine proton were not possible [3,4]. We have now undertaken to make that study using DNP as the acid and *n*-butylamine (nBA) as the base in forming the proton transfer complex, and mixed solvent systems of benzene with small amounts of three ethers, *n*-propyl ether, tetrahydropyran, and dioxane as the experimental system.

MATERIALS AND METHODS

2,4-Dinitrophenol was Aldrich reagent grade. It was dried over magnesium sulfate, then recrystallized twice from benzene. The Aldrich reagent grade *n*-butylamine was purified by fractional distillation, then stored in a dark bottle under nitrogen until used. *n*-Propyl ether and tetrahydropyran were fractionally distilled before use. Benzene and dioxane were Aldrich spectral grade, and were used without further purification.

Methods of analysis and calculation were as described in previous papers [4-6].



Fig. 1. Equilibrium constants for the formation of the proton transfer complex between DNP and nBA in mixed benzene-*n*-propyl ether solvents versus wt.% *n*-propyl ether.



Fig. 2. Equilibrium constants for the formation of the proton transfer complex between DNP and nBA in mixed benzene-tetrahydropyran solvents versus wt.% tetrahydropyran.



Fig. 3. Equilibrium constants for the formation of the proton transfer complex between DNP and nBA in mixed benzene-dioxane solvents versus wt.% dioxane.

TABLE 2

Solvation parameters of nBA with various ethers

Solvent	K _{sr1} ^a	$n(1)^{\mathrm{b}}$	$K_{ m sr2}{}^{ m a}$	n(2) ^b
<i>n</i> -Propyl ether	1875	1.88	Large	Large
Dioxane	290	1.77	13 200	15
Tetrahydropyran	12.5	1.51	2 691	17

 ${}^{a}K_{sr1}$ and K_{sr2} are the equilibrium constants for the first and second solvation reactions, respectively. ${}^{b}n(1)$ and n(2) are the numbers of solvent molecules per amine for the first and second solvation steps, respectively.

RESULTS

Equilibrium constants were obtained for the formation of the proton transfer complex $(K_{\rm PT})$ between DNP and *n*BA in pure benzene and benzene–ether mixtures (Table 1). The result for *n*-propyl ether is shown in Fig. 1, for tetrahydropyran in Fig. 2, and for dioxane in Fig. 3. The results of calculations on the data are presented in Table 2.

DISCUSSION

The short-range solvation of nBA has been studied previously [3,4], but the added solvents were very polar (dimethylsulfoxide and dimethylformamide) so that long-range solvation was an important part of the solvation pattern. In those results, the $K_{\rm PT}$ values displayed a steep and continuous climb, devoid of other features, to values for $K_{\rm PT}$ that were sharply higher than are obtained with less polar solvents. We suspect that at higher concentrations of electron-donating solvent in both those studies the proton transfer complex is dissociating into dinitrophenolate and butylammonium ions [4]. The ethers used in the present study are sufficiently non-polar that little or no long-range solvation was evidenced in studies with secondary amines [4,5].

For all three of the solvents studied the most obvious and interesting feature of the results is the two-plateau pattern obtained for the rise in $K_{\rm PT}$ accompanying the short-range solvation of the amine. The primary amine has two amine protons available for short-range solvation. Since the first addition of a solvent molecule to one of these protons raises the electron density on the amine nitrogen, the formation of a solute-solvent hydrogen bond to the other proton should be more difficult. These facts support the interpretation that each rise represents the individual solvation of one proton. The obvious parallel is the titration of a diprotic acid. As in the case of the diprotic acid the second position does not react as readily as the first, so the first position solvates completely (arrival at the first plateau) before the second begins to solvate.

In every study of solvation of a secondary amine, two solvent molecules associated with the amine proton [4,5]. Applying these same methods of calculation to the first rise in the data for all three ethers, once again the involvement of two solvent molecules is indicated. This infers that the first stage of solvation is the exact parallel of the solvation of secondary amines.

Further examination of the results raises doubt about these assumptions. For all three ethers, calculations based on the second rise leads to a very high value for the number of solvent molecules involved in that step. Extending our "diprotic acid" model, we would expect to see exactly the same solvation pattern occurring at the second proton as at the first, that is the addition of two more solvent molecules to the solvation structure. Furthermore, since the increase in electron density on the amine nitrogen caused by solvation of the second proton should be very similar to that for the first solvation, one would expect that the second rise in the value of the equilibrium constant should display an increase that is comparable with the first rise. In fact, the results do not support either assumption. In the second stage of solvation a large number of solvent molecules is involved rather than two. The second rise is very similar in magnitude to the first in the case of dioxane, slightly larger than the first in the case of *n*-propyl ether, and considerably larger than the first in the case of tetrahydropyran.

A second model is therefore proposed to explain the results. The first rise represents the stepwise hydrogen bonding of one solvent molecule to each proton of the amine. The difference between the equilibrium constants for these two steps is perhaps too small to produce an intermediate plateau, so the result appears to be a single smooth curve. Further solvation is not easily accomplished, perhaps for steric reasons. Then, when the concentration of ether is sufficiently high, a structured but not hydrogen-bonded solvation shell of ether molecules surrounds the amine group, leading to the second rise in $K_{\rm PT}$. The number of ether molecules involved in this shell and its effectiveness at influencing the formation of the proton transfer complex varies with the structure of the ether, as seen in the variable nature of the second rise from one ether to the next. Tetrahydropyran, with the alkyl groups tied back in a ring, is more compact than *n*-propyl ether, allowing close approach of a larger number of ethers to the amine in the solvation shell. Dioxane is equally compact, but the second electronegative oxygen may be disruptive in the assembly of the solvation shell.

In studies with secondary amines, dioxane proved to be a bulky electrondonating solvent which displayed a very high value for $K_{\rm sr}$, the equilibrium constant for formation of the solute-solvent hydrogen bond. Clearly the situation is different in the solvation of primary amines. Bonding by dioxane is of intermediate strength. This can be construed as further evidence that the mechanism of the bonding is different in the cases of secondary versus primary amines.

SUMMARY

The short-range solvation of n-butylamine, a primary amine, by three ethers has been studied using the equilibrium constant for the formation of a proton transfer complex with 2,4-dinitrophenol as a probe. The solvation proceeds in two stages in each case. In the first stage, approximately two solvent molecules per n-butylamine are involved. The effect on the equilibrium constant for the proton transfer complex formation is least for n-propyl ether and greatest for tetrahydropyran, while the equilibrium constants for the binding of the solvent to the solute are in the opposite order. The second stage of solvation involves an indefinite but large number of solvent molecules, with the constants arranged in the same order as for the first stage. Two models for the process are presented. In one, the diprotic acid model, the solvent molecules attach only to one proton in the first stage, then to the other in the second. In the other model, one solvent molecule attaches to each proton in the first stage, and a structured, but not hydrogen-bonded, solvation shell forms in the second stage.

REFERENCES

- 1 R.M. Scott and S.N. Vinogradov, J. Phys. Chem., 72 (1968) 3192.
- 2 A. Reyes and R.M. Scott, J. Phys. Chem., 84 (1980) 3600.
- 3 E.D. Berman, R. Thomas, P. Stahl and R.M. Scott, Can. J. Chem., 65 (1987) 1594.
- 4 Z. Ye, S. Yazdani, R. Thomas, G. Walker, D. White and R.M. Scott, J. Mol. Struct., 177 (1988) 513.
- 5 M. Abduljabar and R.M. Scott, J. Mol. Struct., 237 (1990) 285.
- 6 J.A. Tayh and R.M. Scott, J. Mol. Struct., 237 (1990) 297.