Thermochimica Acta, 137 (1988) 87–93
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CALORIMETRIC STUDY OF HYDROGEN-BOND FORMATION IN ACETONITRILE FOR SOME HYDROGEN-BIS-PHENOLATES AND HYDROGEN-TRIMETHYL-N-OXIDE-PHENOLATES AT 298.15 K

Z. PAWLAK* and G. URBANCZYK

Technology Department of Industrial Production, University of Gdansk, 81-824 Sopot (Poland)

(Received in final revised form September 7, 1988)

ABSTRACT

The enthalpy changes for the formation of hydrogen-bonded complexes of the types $(ArOHOAr_1)^-$ or $(CH_3)_3NOH^+OAr^-$ by the interaction of acids 2,6-Br_2-4-NO_2ArOH, C_6Cl_5OH, 2,4,6-Cl_3ArOH or $(CH_3)_3NOH^+$ with 12 quaternary substituted phenolates, $Bu_4N^+Ar_1O^-$ have been determined at 298.15 K in acetonitrile as a solvent by a calorimetric procedure. The formation process has been regarded as an acid-base interaction. The hydrogen bond enthalpy of heterocomplexes increases nearly linearly with the increase in basicity of the proton acceptor. The enthalpies of reaction are greater if Ar_1O^- is a stronger base than $Ar O^-$.

INTRODUCTION

Several experimental methods have supplied evidence for the existence in acetonitrile and propylene carbonate of strongly hydrogen-bonded complexes of the type hydrogen-bis-phenolates (a) or hydrogen trimethyl-N-oxide-phenolates (b) [1,2].

$Ar_1O^-....HOAr$ (a) $(CH_3)_3NOH^+....^-OAr_1$ (b)

---

* Present address: Department of Chemistry, Brigham Young University, Provo, Utah 84602, USA.

0040-6031/88/$03.50

The ΔpK_a^{AN} [= pK_a^{AN} (protonated form of acceptor) - pK_a^{AN} (donor)] values, from negative to positive indicated the formation of weak hydrogen-bonded heterocomplexes $\Delta pK_a^{AN} < 0$; strong hydrogen-bonded heterocomplexes $\Delta pK_a^{AN} > 0$; and homocomplexes $\Delta pK_a^{AN} = 0$. In a typical case, where Ar_1O^- is a stronger base than ArO^-, the complex $ArOHOAr_1^-$ can be formed in two different ways:

(i) reaction of ArOH with Ar_1O^-, $\Delta pK_a^{AN} > 0$

(ii) reaction of Ar_1OH^- with ArO^-, $\Delta pK_a^{AN} < 0$

These two processes will involve different energetics. Since in (i), a strong shift of the proton in the hydrogen bridge releases the main part of the total enthalpy in this process. This difference in energetics is illustrated by comparison of the two systems in propylene carbonate [2], each of which results in the formation of the same hydrogen-bis-carboxylate complex:

phenyloacetate + dichloroacetic acid, $\Delta_{HB}H = 25.02$ kJ mol^{-1} $\Delta pK_a^{PC} > 0$

phenyloacetic acid + dichloroacetate, $\Delta_{HB}H = 13.08$ kJ mol^{-1} $\Delta pK_a^{PC} < 0$

Agreement with the rule that the strength of hydrogen bonding increases both with the acidity of the proton donor and with the basicity of the proton acceptor has been observed [1-3].

The present article is a full report on our determination of enthalpies of hydrogen bond formation ($\Delta_{HB}H$) for 2,6-dibromo-4-nitro-, pentachloro-, and 2,4,6-trichlorophenol and protonated trimethyl-N-oxide in acetonitrile at 298.15 K with 12 quaternary substituted phenolates.

EXPERIMENTAL

Acetonitrile was purified and dried by a previously described method [4].

All solid acids were recrystallized two or three times from methanol or (methanol+water) and dried in vacuum over P_2O_5. The tetraalkylammonium salts were prepared as described elsewhere [5].

The enthalpies of reaction were measured with a TRONAC 450 titration calorimeter. The reaction vessel contained 30 cm^3 of 0.0150 mol dm^{-3} phenolate and the titration solution of 0.30 mol dm^{-3} acid was added from a syringe buret of 2.00 cm^3 capacity with a delivery rate of 0.00226 cm^3 sec^{-1}.

Both solutions were at the same temperature, namely 298.15 K. The enthalpy of dilution $\Delta_{dil}H$ of the titrant was determined separately and corrections for it were applied to the measured enthalpies of reaction. The values found for $\Delta_{dil}H$ were -0.40 kJ mol^{-1} for 2,6-Br_2-4-NO_2ArOH, C_6Cl_5OH and $(CH_3)_3NOHClO_4$ and -0.30 kJ mol^{-1} for 2,4,6-Cl_3ArOH

The stoichiometry of the complexes (Ar_1O^-...HOAr) and $(CH_3)_3NOH^+Ar_1O^-$ was examined by addition of excess free acid. The thermometric titration curves clearly revealed the formation of a 1:1 complex. The enthalpy of hydrogen bond formation, $\Delta_{HB}H$, is related to the experimental enthalpy of reaction, $\Delta_{HB}H_{exp}$, by the expression:

$$\Delta_{HB}H = \Delta_{HB}H_{exp} / [\text{compl}]\, V \qquad (1)$$

where [compl] is the concentration, mol dm^{-3}, of the complex formed at equilibrium calculated from the formation equilibrium constant K_f, and V is the volume of the solution in dm^3. Values of K_f were obtained previously [2,6,9] from e.m.f. measurements. The log K_f values for $(ArOHOAr_1)^-$ and $(CH_3)_3NOH^+Ar_1O^-$ complexes in acetonitrile range from 2.0 to 4.8 and from 4.0 to 6.0, respectively.

RESULTS AND DISCUSSION

The calorimetric results $\Delta_{HB}H$ of the 12 systems studied are summarized in Table 1, and the pK_a^{AN} values of acids are given using an acetonitrile scale. Small enthalpy changes were detected when 2,4,6-Cl_3-ArOH reacted with the first five phenolates with $\Delta pK_a^{AN} < 0$.

The enthalpy data for the formation of the following two types of complexes

$$Ar_1O^- + ArOH \rightleftarrows (Ar_1OHOAr)^- \qquad (2)$$

$$Ar_1O^- + (CH_3)_3NOH^+ \rightleftarrows (CH_3)_3NOH^+Ar_1O^- \qquad (3)$$

show reaction (2) to be more exothermic than reaction (3). This indicates a larger decrease in the internal energy in the formation of hydrogen-bis-phenolates than in the formation of hydrogen-trimethyl-N-oxide phenolates.

The larger internal energy loss is reflected in a greater strength of the (-OHO-) than ($-NOH^+O^-$-) bridges.

In Table 2 are listed the thermodynamic data for the formation of two

TABLE 1

Acidity constants, pK_a^{AN}, of the phenols and enthalpies of hydrogen bonding formation, $\Delta_{HB}H$, of phenolate complexes with some proton donors in acetonitrile at 298.15 K.

			2,6-Br_2- -4-NO_2ArOH	C_6Cl_5OH	2,4,6-Cl_3ArOH	$(CH_3)_3NOH^+$ [e]
No.	Subsituted phenolate[a]	(pK_a^{AN}) [b]	-$\Delta_{HB}H$ / kJ mol^{-1} [d]			
1	2,6-Br_2-4-NO_2-	15.0	2.5	2.1^f	1.2^f	2.1^f
2	2,4-$(NO_2)_2$-	16.3	2.5	3.3^f	1.2^f	3.7^f
3	2,6-$(NO_2)_2$-	16.5	2.9	4.2	1.3^f	3.7^f
4	Cl_5-	16.5^c	2.9	4.6	1.4^f	4.6^f
5	3,4-$(NO_2)_2$-	17.7	5.0	6.3	1.5^f	3.7
6	2,5-$(NO_2)_2$-	18.4	7.1	12.5	2.1^f	6.7
7	2,4,6-I_3-	19.5	12.6	17.1	3.3^f	7.9
8	2,4,6-Cl_3-	20.4	18.8	23.8	3.7	7.9
9	4-NO_2-	21.1	22.6	30.1	9.2	9.2
10	2,6-Cl_2-	21.8	27.6	32.6	14.6	10.8
11	2-NO_2-	22.4	30.5	37.2	18.8	11.3
12	3-NO_2-	24.1	38.2	47.2	28.0	14.6

[a] Tetra-*n*-butylammonium phenolates; [b] From Ref. 6 ; [c] From Ref. 2; [d] Maximum Standard Deviation: ± 0.4 kJ mol^{-1}; [e] Perchlorate trimethyl-N-oxide, pK_a^{AN} $[(CH_3)_3NOH^+] = 16.9$; [f] $\Delta pK_a^{AN} < 0$.

families of complexes. The equilibrium constant for the $(CH_3)_3NOH^+Ar_1O^-$ is larger than that for Ar_1OHOAr^- [2,6,9]. One reasonable interpretation of the relative entropy change is that more "ordering" of the reactants takes place in the formation of the Ar_1OHOAr^- heterocomplexes than in the formation of the $(CH_3)_3NOH^+Ar_1O^-$ heterocomplexes.

In Fig.1 the enthalpies for hydrogen bonding $\Delta_{HB}H$ are plotted vs ΔpK_a^{AN}. For a series of bases, Ar_1O^-, with three phenols 2,6-Br_2-4-NO_2ArO^- ($\Delta pK_a^{AN} = 15.0$), pentachloro- ($\Delta pK_a^{AN} = 16.4$) and 2,4,6-Cl_3-phenol ($\Delta pK_a^{AN} =$ 20.4) showed essentially parallel lines for acid-base of common structural type $ArOHOAr_1^-$. A plot of $\Delta_{HB}H$ for $[(CH_3)_3NOH^+ + Ar_1O^-]$ has a shallower slope than [phenols + Ar_1O^-]. The slopes suggest that the bond strength increases nearly linearly with an increase of basicity of proton acceptor. The ratio of the slopes $Ar_1O^-/ArOH$ and $Ar_1O^-/(CH_3)_3NOH^+$ is about 2.5. A break-point is

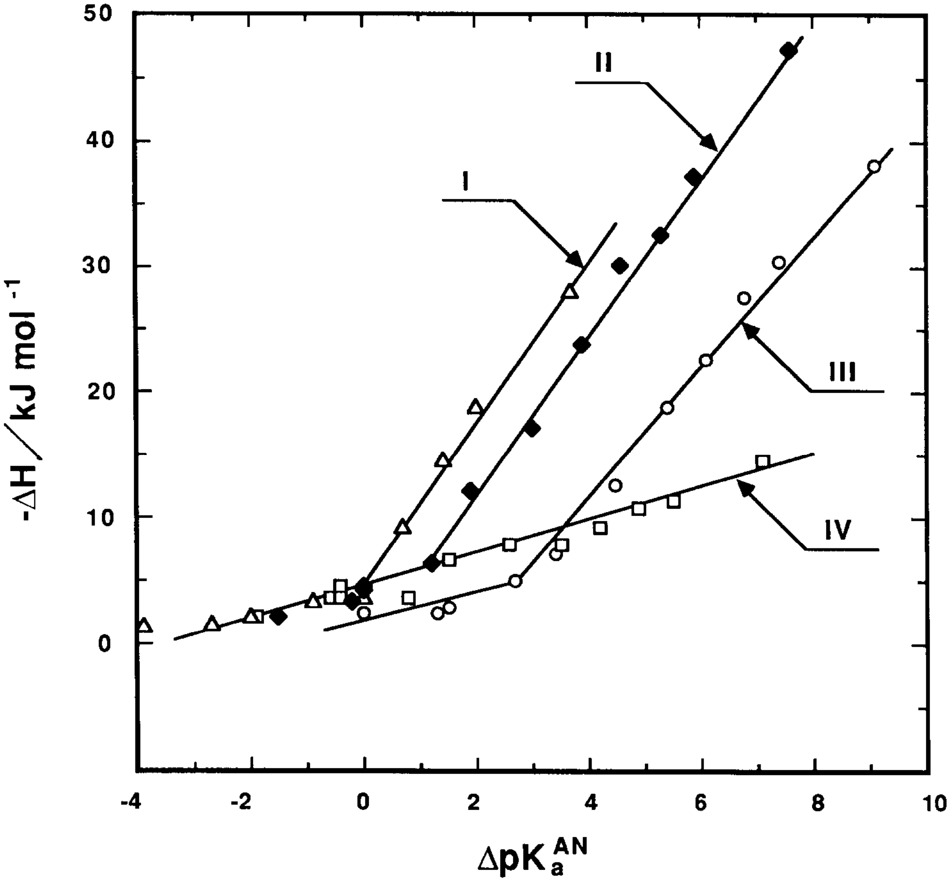

Fig. 1. Enthalpies of hydrogen-bond formation ($\Delta_{HB}H$) vs ΔpK_a^{AN} in acetonitrile for 12 phenolates, Ar_1O^-, with the proton donors: (I) 2,4,6-Cl_3ArOH; (II) C_6Cl_5OH; (III) 2,6-Br_2-4-NO_2ArOH; (IV) $(CH_3)_3NOH^+$.

TABLE 2

Thermodynamic data for the two types of complexes $(Ar_1OHOAr)^-$ and $(CH_3)_3NOH^+Ar_1O^-$ in acetonitrile at 298.15 K.

Type of complex	log K_f	ΔG	ΔH	ΔS
$(CH_3)_3NOH^+C_6Cl_5O^-$	4.20	-24.06	-4.60	65.20
$(C_6Cl_5OHOCl_5C_6)^-$	2.70	-15.48	-4.60	36.48

Units are: kJ mol^{-1} for ΔG and ΔH; J K^{-1} mol^{-1} for ΔS.

observed for three phenols around the $\Delta pK_a^{AN} = 0$ region, but no slope change is observed for the $[(CH_3)_3NOH^+ + Ar_1O^-]$ systems.

However, in view of the behaviour of these families of acids shown in Fig. 1, it seems quite likely that each of these base-acid $Ar_1O^-/ArOH$ and $Ar_1O^-/(CH_3)_3NOH^+$ systems would generate their own properties as a result of differing solvation energies of two families of complexes [1,7,8] (see Table 2). Differences in acid strength between proton donors and the protonated acceptor result more in a shift of the proton. The systems with the most negative enthalpy changes have $\Delta pK_a^{AN} > 0$ values (see Fig. 1).

This difference is illustrated by a comparison of systems numbered 1 and 4, both of which result in the formation of the same complex. The data for numbers 1 and 4 are:

2,6-dibromo-4-nitro-phenolate + pentachlorophenol:

$\Delta_{HB}H = 2.1$ kJ mol^{-1} $\quad\quad \Delta pK_a^{AN} = -1.5$

2,6-dibromo-4-nitro-phenol + pentachlorophenolate:

$\Delta_{HB}H = 2.9$ kJ mol^{-1} $\quad\quad \Delta pK_a^{AN} = +1.5$

Similar results were found for two other systems, namely numbers 4,8 and 1,8

pentachlorophenolate + 2,4,6-trichlorophenol:

$\Delta_{HB}H = 1.4$ kJ mol^{-1} $\quad\quad \Delta pK_a^{AN} = -3.9$

pentachlorophenol + 2,4,6-trichlorophenolate:

$\Delta_{HB}H = 23.8$ kJ mol^{-1} $\quad\quad \Delta pK_a^{AN} = +3.9$

2,6-dibromo-4-nitro-phenolate + 2,4,6-trichlorophenol:

$\Delta_{HB}H = 1.2$ kJ mol^{-1} $\quad\quad \Delta pK_a^{AN} = -5.4$

2,6-dibromo-4-nitro-phenol + 2,4,6-trichlorophenolate:

$\Delta_{HB}H = 18.8$ kJ mol^{-1} $\quad\quad \Delta pK_a^{AN} = +5.4$

The homoconjugation reactions 1, 4 and 8 (Table 1) between $2,6\text{-}Br_2\text{-}4\text{-}NO_2\text{-}ArO^-$, $C_6Cl_5O^-$, $2,4,6\text{-}Cl_3ArO^-$ and their phenols show hydrogen bond of relatively low enthalpy namely 2.5, 4.6 and 3.7 kJ mol^{-1}, respectively.

ACKNOWLEDGEMENTS

Financial support of this work by Professor R.M. Izatt, Department of Chemistry, Brigham Young University, Provo, Utah during sabbatical leave 1985/87 (Z.P.) is gratefully acknowledged. The assistance of Professors E. Winnicka and R.M. Izatt in the preparation of this manuscript is appreciated. This work was partly supported by grant from C.P.B.P. 01.15.

REFERENCES

1 Z. Pawlak and R.G. Bates, J. Chem. Thermodynamics, 14 (1982) 1035-1040.
2 Z. Pawlak, M. Tusk, S. Kuna, F. Strohbusch and M.F. Fox, J. Chem. Soc. Faraday Trans. I, 80 (1984) 1757-1768
3 E.M. Arnett, E.J. Mitchell and T.S.S.R. Murty, J. Am. Chem. Soc. 96 (1974) 3875-3891.
4 J.F. Coetzee, in A. Streitwieser Jr. and R.W. Taft (Eds.), Progress in Physical Organic Chemistry, Wiley, New York, 1967, Vol. 4, 45-92.
5 Z. Pawlak, R.A. Robinson and R.G. Bates, J. Solution Chem., 7 (1978) 631-638.
6 Z. Pawlak and J. Magonski, J. Chem. Soc. Faraday Trans. I, 78 (1982) 2807-2813.
7 R.W. Taft, D. Gurka, L. Joris, P.V. Schleyer and J.W. Rakshys, J. Am. Chem. Soc., 91 (1969) 4801-4812.
8 D.P.N. Satchell and R.S. Satchell, Quart. Rev., Chem. Soc., 25 (1971) 171-180.
9 Z. Pawlak, in preparation.