

In benzonitrile the proton transfer rates in reaction (1) are correlated with the equilibrium constants. The fastest observed rates are diffusion controlled. Consequences of the kinetic results for the interpretation of properties of the two solvents will be discussed.

References

- 1 F. Strobusch, D. B. Marshall and E. M. Eyring, *J. Phys. Chem.*, **82**, 2447 (1978).

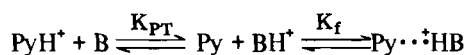
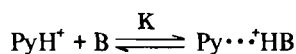
Complex $[\text{NHN}]^+$ Formation in Aprotic Media

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The proton transfer and tautomeric equilibria $[\text{NHN}]^+$ heterocomplexes in aprotic solution are considerably more complicated than those in the gas phase. A clear correlation in different solvents between acidity of $[\text{NH}]^+$, and formation constant $K_{[\text{NHN}]^+}$ N-bases is not established. The same holds for the relationships with the basicity of the proton acceptor N-base. The systems studied in the present work involve the interaction of pyridinium $[\text{PyH}]^+$, and imidazolium $[\text{ImH}]^+$ cation with N-bases, where $\text{p}K_a^{\text{H}_2\text{O}}$ N-bases ranges from 11 to -1. Three terms run through the investigations: (1) to establish the molecularity and formation constants $K_{[\text{NHN}]^+}$ homo-, and heterocomplexes in acetone and acetonitrile, (2) to estimate proton transfer constants K_{PT} for heterocomplexes where proton transfer occur and (3) to determine the acidity of protonated N-bases in acetone and acetonitrile media.

A general scheme for the formation of complexes may thus be written as



where K is overall equilibrium constant, K_{PT} , and K_f are the proton transfer (PT) and formation equilibrium constants.

The value of K and K_{PT} was derived from the following relationships

$$K = C_{\text{B}}R^2 - R(C_{\text{PyH}^+} + C_{\text{B}}) + C_{\text{PyH}^+}/R(C_{\text{B}} - C_{\text{PyH}^+})^2$$

where: C_{B} , and C_{PyH^+} = base and acid concentration

$$R = a_{\text{H}^+} f_{C_{\text{B}}} = C_{\text{PyH}^+} / a_{\text{H}^+} C_{\text{B}} = C_{\text{PyH}^+} \cdot f$$

$$K_{\text{PT}} = K_{a[\text{PyH}^+]}^{\text{acetone}} / K_{a[\text{BH}^+]}^{\text{acetone}}$$

Hence values of K_f , the equilibrium constant for the formation of hydrogen bonding complexes, can be found, since $K_f = K/K_{\text{PT}}$. In the case where K_{PT} equals unity (for homocomplexes), the overall equilibrium constant value K is equal to the equilibrium constant formation value $K = K_f$.

Heterobinuclear Complexes of L-Carnosine with Cu(II) and Cd(II) in Aqueous Solution

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The complex formation in aqueous solution between metal ions and peptides has been widely studied in recent years. Both binary (metal ion–peptide) and ternary (generally with an aminoacid as second ligand) systems have been investigated.

In previous papers [1–3] the formation was evidenced, of heterobinuclear complexes of polyfunctional ligands, such as L-histidine or citric acid (with Cu(II), Ni(II), Zn(II) and Cd(II)) and glutathione (with Zn(II), Ca(II) and La(III)). Owing to these results too, we thought to investigate the formation of heteronuclear species in solution of the dipeptide L-carnosine (car, β -alanil-L-histidine).

The study was performed at $t = 37 \pm 0.1$ °C and $I_c = 0.15$ mol dm⁻³ by potentiometric measurements of hydrogen ion concentration with glass electrode, in the presence of Cu(II) and Cd(II) ions.

First the stability constants were determined for the binary systems Cu(II)–car and Cd(II)–car. Concerning Cu(II) complexes a disagreement was noticed in the literature, as to the species present in solution [4, 5]: our data show a fairly good agreement with those reported by Perrin *et al.* [4]. The most important species in solution is $[\text{Cu}_2(\text{car})_2\text{H}_2]$, in which the amide hydrogen was very probably displaced.

The stability constants for the Cd(II)–car system have not yet been reported. Our measurements evidenced the presence in solution of the species $[\text{Cd}(\text{car})\text{H}]$, $[\text{Cd}(\text{car})]^+$ and $[\text{Cd}(\text{car})_2]$.

When considering the ternary Cu(II)–Cd(II)–car system the calculation of titration curves in agreement with the experimental data is possible only if we suppose that species other than binary com-

plexes are present in solution. We showed that ternary heterobinuclear complexes are present, of the type $[\text{CuCd}(\text{car})]^{3+}$, $[\text{CuCd}(\text{car})\text{H}_{-1}]^{2+}$, $[\text{CuCd}(\text{car})\text{H}_{-2}]^{+}$.

It is noticeable that the deprotonated species are the most relevant both for binary and ternary systems, but they are dimeric for binary and monomeric for ternary systems. In the complex $[\text{CuCd}(\text{car})\text{H}_{-2}]^{+}$ the second hydrogen ion displaced very probably comes from the pyrrole group of His-residue.

References

- 1 P. Amico, G. Arena, P. G. Daniele, G. Ostacoli, E. Rizzarelli and S. Sammartano, *Inorg. Chim. Acta*, 35, L383 (1979).
- 2 P. Amico, G. Arena, P. G. Daniele, G. Ostacoli, E. Rizzarelli and S. Sammartano, submitted to *Inorg. Chim. Acta* (1979).
- 3 M. L. D. Touche and D. R. Williams, *J. Chem. Soc. Dalton*, 1355 (1976).
- 4 R. P. Agarwal and D. D. Perrin, *J. Chem. Soc. Dalton*, 268 (1975).
- 5 G. Brookes and L. D. Pettit, *J. Chem. Soc. Dalton*, 2112 (1975).

Reactions Between Zinc(II) and Tetra-Azamacrocycles of Varying Sizes. ΔH° and ΔS° Contributions to the Macrocylic Effect

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Cyclic polyamines complexes with some first-row transition metal ions such as copper(II) and nickel(II)

are, in general, more stable than the equivalent complexes formed by the same metals with the corresponding non-cyclic polyamine ligands: the Macrocylic Effect [1]. Much published work exists on the thermodynamic interpretation of the Macrocylic Effect [2].

In the case of Zn(II) complexes, the thermodynamic interpretation is made more difficult by both the relative ease with which zinc can change its coordination geometry and by the impossibility of making use of the spectroscopic techniques which have proved so useful for the other metals. In this communication we are reporting both the enthalpy and the entropy contributions to the reaction between the zinc(II) ion and saturated cyclic polyazamacrocycles (Fig. 1) and will be comparing these values with the existing values for the analogous non-cyclic polyamines (see Table I).

It can be likewise generally stated that the macrocyclic zinc complexes are more stable than the corresponding complexes with non-cyclic polyamines. This extra stability is almost entirely due to a very

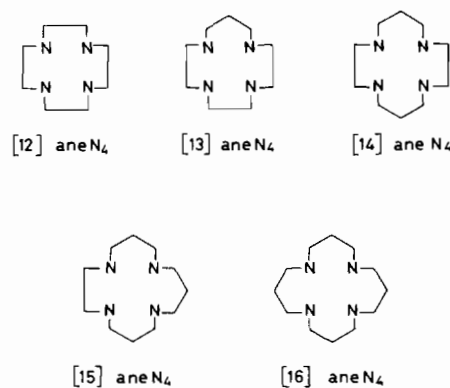


Fig. 1. Saturated tetra-azamacrocycles.

TABLE I. Thermodynamic Parameters for Macrocylic and non-Cyclic Tetra-Aza Ligand Complexes of Zn(II).

Ligand	Log _{ML}	$-\Delta H^\circ$ (kcal·mol ⁻¹)	ΔS° (cal·K ⁻¹ ·mol ⁻¹)
[12]aneN ₄	16.2	14.5	25.5
[13]aneN ₄	15.6	15.3	20.1
[14]aneN ₄	15.34	14.8	21.3
[15]aneN ₄	15.35	16.5	13.3
[16]aneN ₄	13.05	7.1	35.8
2,2,2-tet ³	12.02	8.9	25.0
2,3,2-tet ³	12.83	11.9	18.8
3,2,3-tet ³	11.25	10.6	15.9
3,3,3-tet ³	9.32	7.4	18.0