



Scientific article

UDC 547.979.733:544.164:544.42

DOI: 10.52957/27821900_2022_01_113

THE ROLE OF THE ENTROPY FACTOR IN THE KINETICS OF COMPLEX FORMATION OF NON-PLANAR PORPHYRINS WITH LOCALIZED AND DELOCALIZED NH BONDS

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Keywords:
tetrapyrrole macroheterocyclic compounds; porphyrins; complexing reaction; chemical activity of NH bonds; activation entropy

Abstract. The paper concerns NH-bonds chemical activity exhibiting in porphyrin molecules typical of macrocycles with planar or non-planar polarized structures. It is not limited by the increasing rate of their metal complexing indicator reaction in proton-donating media in comparison with proton-donating ones. The work dwells on the entropy of the process towards more positive values as the electron-donating properties of the solvent increase. It is due to the formation of molecular complexes "porphyrin - electron-donor" increasing the solvation of the initial state of the complexing reaction. The deformation of the planar structure of the H₂P macrocycle expressed by the example of N- and dodeca-substituted porphyrin accompanying by an appreciable polarization of the molecule does not lead to the appearance of NH-bonds chemical activity.

For citation:

Berezin, D.B. (2022) The role of the entropy factor in the kinetics of complex formation of non-planar porphyrins with localized and delocalized NH bonds, *From Chemistry Towards Technology Step-By-Step*, 3(1), pp. 113-122 [online]. Available at: <http://chemintech.ru/index.php/tor/2022tom3no1>

Introduction

Most of the physico-chemical properties of porphyrins (H₂P) and their porphyrinoid analogues (H_nP_n), especially those related to the reactivity of the coordination cavity of the molecules, are controlled by the macrocyclic effect (MCE) [1, 2]. MCE is exhibited in solvation processes of macroheterocycles [3, 4], their complexing reaction [5-7], dissociation processes of metal complexes [8, 9] as well as in changes of NH-acidity compounds in processes of total proton transfer [10-13] and unfinished [14-18] acid-base interaction.

The macrocyclic effect of aromatic macroheterocycles (MHC) is not only the effect of spatial screening of the reaction centres of molecules, lowering their reactivity. It has also [1] the effect of π-electron influence, which can counteract with the steric effect in changing the reactivity of molecules in some cases [2]. The dependence of some, in particular the acidic and complexing properties of MHCs, on the molecular structure proved to be unusual (non-linear) by this reason. For example, the change of NH-acidity occurs in accordance with various structural



factors leading to its polarisation. For example, the increase of H₂P NH-acidity took place both with the increase of aromaticity of molecules, in particular, at the transition from porphyrins to their *meso*-aza analogues [2], and, on the contrary, with the increase of their non-planarity but only in case of nonplanar macrocycle was in polarized "saddle" conformation having dipole moment at least 1.5 D [19, 20]. The nature of the polarization of the "saddle-non-flat" MHC is shown in Fig. 1.

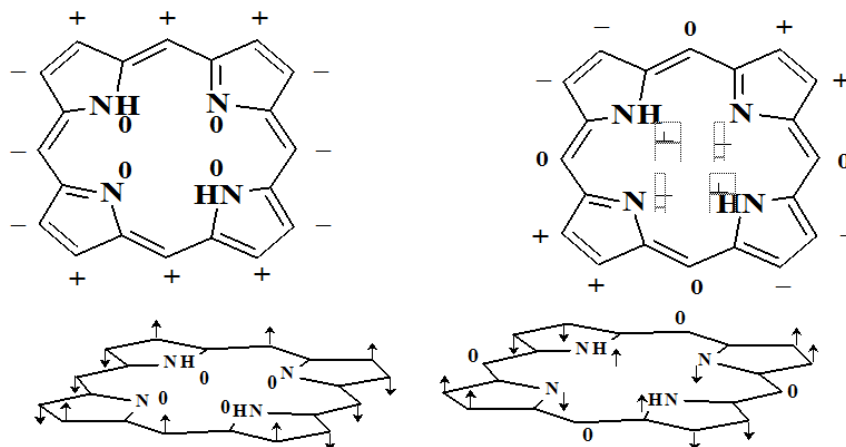


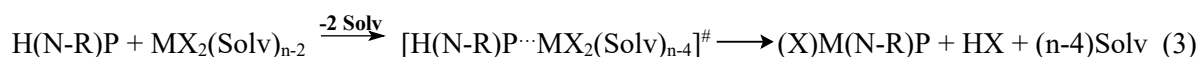
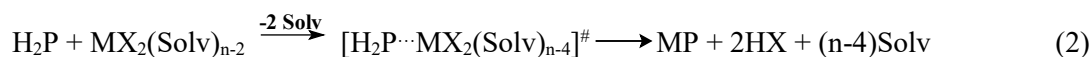
Fig. 1. The basic - fluted (left, $\mu=0$) and saddle (right, $\mu\neq 0$) are non-planar conformations of porphyrins ("+", "-" and "0" symbolise the position of atoms above, below and in the plane of the macrocycle respectively)

Such structural changes of planar structure led not only to the increase of NH-acidity of MHC molecules in general, but also to the increase of so called chemical activity of NH-bonds [2, 16], which is revealed in ability of molecules to interact with weak organic bases (DMF, DMSO, etc.) with formation of H-bonded molecular complexes (1) [14, 15, 17, 18].



The formation of such complexes was proved experimentally by electron, fluorescence and NMR spectroscopy, thermogravimetry, calorimetry [17, 18, 21, 22] and by quantum chemical methods of analysis (DFT, NBO) [18, 23].

The polarization of NH-bonds in H₂P molecule leading to their delocalization is one of the most important factors lowering its activation barrier and increasing the speed of the process by to the mechanism of the MHCs complexing reaction (2) [5, 24]. The monoanionic ligands of N-substituted porphyrin analogues (compounds 1, 2) transform the equation (2) into (3):



Often the increase of the chemical activity of NH-bonds in reaction (2) exhibits in the violation of the kinetic compensation effect (KCE) characteristic of reactions involving H₂P, i.e. linear dependence of the process activation parameters - activation energy (E_a , kJ·mol⁻¹ or ΔH^\ddagger) and entropy change (ΔS^\ddagger , J·mol⁻¹·K⁻¹) in the transition state formation of reaction (1) [24-26]. Supposedly, the polarisation of NH-bonds within the macrocyclic ligand leads to an increase in ΔS^\ddagger during reaction (2), which indicates an increase in the transition state solvation efficiency with polarised NH-bonds [24]. The nature of KCE was interpreted by different authors (2, 5, 24). A typical example of the deviation of the dependence $\Delta S^\ddagger = f(E_a)$ was found in [27].



It was observed an individual type of direct KCE in each group of NH-active MHCs, in particular non-planar and, conversely, high-aromatic ones (Fig. 2). Moreover, the increase of ΔS^\ddagger of reaction (2) occurs in the transition from classical porphyrins proper both as the flat structure of the molecule distorts and as its rigidity increases, because both factors cause an increase in the chemical activity of NH-bonds.

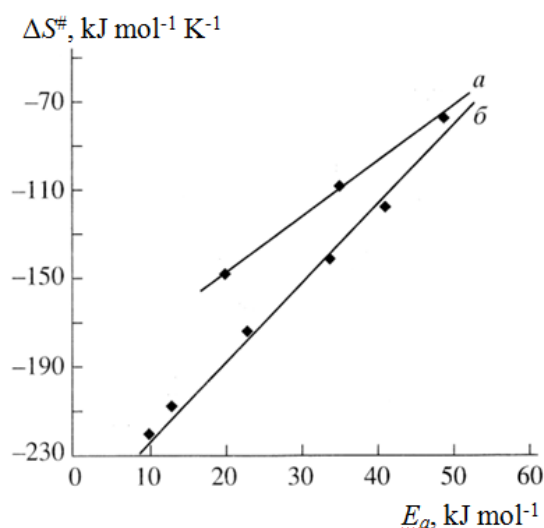


Fig. 2. Kinetic compensation effect of the complexing reaction of (2, Zn(OAc)₂, CH₃CN) spatially distorted (a) and rigid (b) porphyrins with chemically active NH-bonds [27]

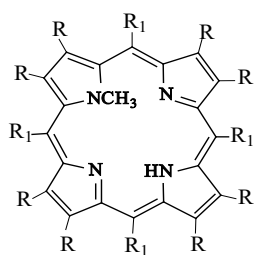
The macrocyclic effect extends not only to porphyrins proper but also to all cyclic porphyrin-like compounds, in particular aromatic derivatives of vitamin B₁₂ corrollys [28]. Thus, by the analysis of experimental data, basic criteria for the detection of the chemical activity of NH-bonds in porphyrin molecules [2, 15] and later their analogues [18] were formulated. The chemical activity of NH-bonds in aromatic MHC molecules can be achieved if several conditions are satisfied by:

- change of the macrocycle structure to a rigid aromatic or to a strongly flattened ones if the molecule is polarized;
- presence of electron-accepting groups or groups of different electronic nature in the molecule, leading to polarisation of the π -chromophore through a "push-pull" effect;
- change of the medium the properties promoting polarisation of the NH-bonds of the H₂P molecule through solvation, e.g. by molecules of electron-donating solvents.

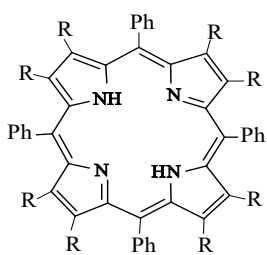
This work dwells on the analysis of kinetic parameters of the indicator reaction of metal complex formation (2) by the example of non-flat N-substituted porphyrin analogues (compounds 1-2) as well as H₂P (compounds 3-6) with zinc (II) and cobalt (II) salts in benzene and DMF medium to discover new facts of the chemical activation of NH-bonds influenced by electron donor solvent molecules in the entropic characteristics of reaction (2).

Experimental part

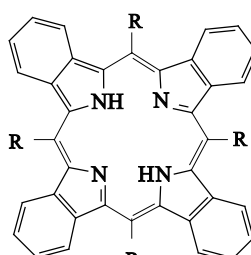
Porphyrins 1-6 were synthesised and spectrally identified according to existing methods [29, 30].



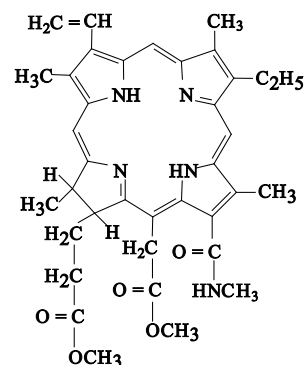
1 R = Et; R₁ = H
2 R = H; R₁ = Ph



3 R = H
4 R = Et
5 R = Ph
6 R = Br



7 R = H
8 R = Ph



9

The solvents acetone (Me_2CO , *pure*), benzene (C_6H_6 , *analytic grade*), dimethylformamide (DMF, *analytic grade*), dimethylsulfoxide (DMSO, *pure*), pyridine (Py, *pure*) 1-propanol (*n*-PrOH, *analytic grade*) were further purified as recommended [31]. The water content of the solvents was monitored by the Fischer method. Acetates and acetylacetonates of zinc(II) and cobalt(II) "*chemically pure*" were dried in the desiccator over P_2O_5 and used without further purification.

Kinetic measurements of the complexation reaction (2, 3) were performed in the temperature range of 298-318 K in DMF and C_6H_6 medium. The concentration of the macrocyclic ligand in all cases was $2 \cdot 10^{-5}$ mol/l and the reaction was carried out in 100 times excess molar quantity of salt. The H_2P and salt solutions were thermostatted before the experiment, combined and quickly placed in the thermostatted spectrophotometer chamber. During the reaction (2), the optical density of the pigment depending on the type of ligand was recorded at the operating wavelength of 620-720 nm at regular intervals. A detailed description of the experimental procedure and the calculation of the kinetic parameters of reaction (2) are in [32].

Results and Discussion

An effective mean to control the reactivity of the coordination cavity (N_4H_2) of porphyrins and their analogues is the regulation of the chemical activity (degree of delocalization) of intracyclic NH-bonds [2]. As for their π -electronic and geometrical structure, the azaporphyrins are better correspond under the definition of NH-active H_2P , possessing rigid macrocycle [2, 6, 10, 14], and nonplanar due to their overloading with bulk substituents at molecule periphery *dodeca*-substituted porphyrins [2, 7, 13, 15], and also some their derivatives, porphyrinoids with asymmetrically polarized molecular structure [18, 28].

The nature of the reaction (2) of the complexing of porphyrins with metal salts strongly depends on the nature of the solvent and, in particular, its donor-acceptor properties and polarity [2, 5, 7, 16]. At the same time chemical activation of NH-bonds of porphyrins with the help of electron-donating solvent molecules influences more significantly on the reaction (2), than structure and strength of coordination sphere of the salt, involved in the process of complexing [16].



Porphyrins with high NH-bond activity can be easily distinguished by comparing their ESP in any inert or low-solvent (benzene) and electron-donor (DMF) solvents, since in the medium of the latter they form spectrally distinct molecular complexes with partial transfer of the MHC NH-proton to the molecule of the electron-donating component of the solution (1) (Fig. 3). Dodecamerated H₂P (compounds 5 and 6, Fig. 3) can interact not only with such strong electron donors as Ry and DMF, but also with acetone and 1-propanol.

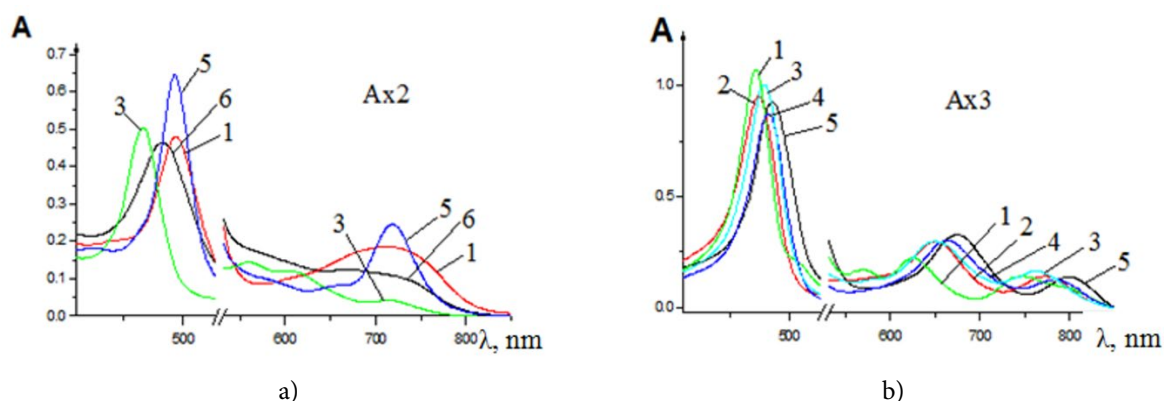


Fig. 3. Electronic absorption spectra H₂(β -Ph)₈TPP (compound 5) (a) and H₂(β -Br)₈TPP (compound 6) (b) in organic solvents: 1 – DMSO; 2 – Me₂CO; 3 – C₆H₆; 4 – DMF; 5 – Py; 6 – *n*-PrOH

The kinetic criterion of NH-activity can be applied for more detailed evaluation of the ability of H₂P to delocalise NH-bonds [15]. According to it porphyrin is chemically NH-active if its coordination rate in an electron-donating solvent (DMF, DMSO, Ry) in comparable conditions is higher than the reaction rate in proton-donating solvent (NOAs) or it increases with increasing electron-donating capacity and/or dielectric constant of ϵ . The both non-flat (e.g. pre-dodecamined) and rigid (e.g. porphyrazines) "non-classical" porphyrins are agree with this data.

Regular changes of the reaction rate (2) of porphyrins with classical and non-classical properties at replacement of solvent were observed earlier in many works, devoted to investigations of complexation kinetics of porphyrazines [6, 10], benzoporphyrins [2, 33, 34] or dodec substituted H₂P [7, 16]. Thus, the addition of proton donors (NOAs) inhibited the NH-activity and reduced the reaction rate (2) (33). In contrast, the transition from pure pyridine to the Py - 1M Et₂NH system increased the rate of reaction (2) with zinc acetate at 298 K by a factor of 120 and 40, respectively [34]. We found the linear dependence of the value of the rate constant k_v on the concentration of diethylamine (Fig. 4). In contrast, the reaction rate of H₂P with localized type of NH-bonds (compound 3) decreased approximately 5-fold in the presence of 1M Et₂NH [34].

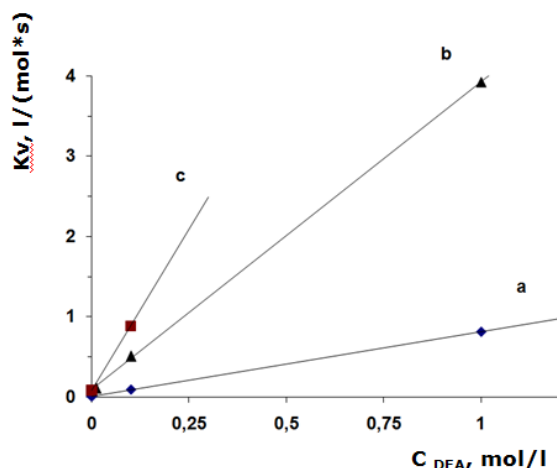


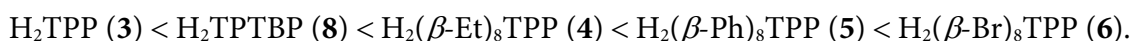
Fig. 4. Dependence of the true reaction rate constant (2) (k_v^{298} , $l \cdot mol^{-1} \cdot s^{-1}$) in concentration Et_2NH (DEA, with C_{DEA} , $mol \cdot l^{-1}$) for H_2TBP (compound **7**) in the system “Py ÷ Et_2NH ” (a), $H_2TBP(Ph)_4$ (compound **8**) in the system “Py ÷ Et_2NH ” (b) and $H_2TBP(Ph)_4$ in the system “DMSO ÷ Et_2NH ” (c)

Similarly, the addition of diethylamine to dimethylformamide solution of natural, chemically modified chlorine **9** influenced the rate of its reaction with copper(II) acetate [35], which increased 1.5 times in the presence of 0.1M Et_2NH , while the corresponding phorbine derivative of chlorophyll *a*, in contrast, decreased twice.

Although none of the above mentioned MHCs (compounds **7-9**) change their electronic spectrum in electron-donating media the kinetic measurements of the complexing reaction (2) in the presence of an electron donor allow revealing even a weakly expressed NH-activity.

It can be assumed that N-substituted porphyrinoids (e.g. compounds **1, 2**) are not typical NH-active H_2Ps as they do not change their ESP in electron-donating media. A kinetic study of reaction (3) offers an opportunity to confirm or disprove this statement for the N-substituted ligands. By experimental data [2], the complexing rates of N-substituted compounds **1** and **2** with zinc salts decrease with increasing electron-donating solvent: $n\text{-PrOH} > \text{DMF} > \text{DMSO} > \text{Py}$, which corresponds to the behavior of classical porphyrins with localized NH-bond. But the small additions of a proton donor (1 vol% NOAs) to a solution of porphyrin and zinc acetate in DMF or DMSO completely block the coordination reaction, or to shift it to an equilibrium state. The reasons are the high basicity of the N-substituted porphyrin ligands (the dication formed in an acidic environment is inactive in reaction (3)) as well as the low stability of the corresponding zinc complexes [2]. Thus, the complexing reaction behavior of N-substituted porphyrins is typical for classical, non-chemically active H_2P bonds such as *meso*-tetraphenylporphine (H_2TPP , compound **3**).

Most of the dodecadec substituted porphyrins, e.g. octabromtetraphenylporphine ($H_2(\beta\text{-Br})_8TPP$, **6**), octabromtetraphenylporphine ($H_2(\beta\text{-Et})_8TPP$, **4**), dodecaphenylporphine ($H_2(\beta\text{-Ph})_8TPP$, **5**), tetraphenyltetrabenzoporphine (H_2TPTBP , **8**) exhibit typical "non-classical behaviour" in reaction (2), satisfying the NH-activity kinetic criterion of H_2P [15]. These compounds can be ranked in order of increasing chemical activity of NH-bonds as follows:





The I band in the ESP of these compounds registered in DMF is shifted in a similar series:

$$647 \text{ nm (3)} < 697 \text{ nm (8)} < 717 \text{ nm (4)} < 718 \text{ nm (5)} < 784 \text{ nm (6)}.$$

The degree of the chemical activity of NH-bonds in non-planar porphyrin molecules is influenced not only by strong saddle in the symmetrical molecule leading to the appearance of a dipole moment [2], but also by the presence of electron-donating and (or) electron-accepting substituents in the molecule polarizing the chromophore. For example, the molecule of octabromotetraphenylporphyrin **6** having approximately the same degree of nonplanarity as other dodeca-substituted H₂P (compounds **4**, **5**) in crystal and solution [15], shows greater chemical NH-activity as presence of eight bromine atoms in β -positions causes the appearance of its "push-pull" effect.

We consider the arrangement of non-planar dodeca- and N-substituted porphyrins in a series of rates of complexation in DMF medium (Table 1). By Table 1 we can conclude that with the majority of investigated salts under identical concentration conditions NH-active pre-deconverted H₂P (compounds **4**, **5**) react slower than non-planar, but having a localized NH-bond of N-substituted porphyrins (compounds **1**, **2**). The flatter H(N-Me) β (-Et)₈P (**1**) tends to react slower in DMF than the deformed H(N-Me)TPP (**2**) [36]. In [10, 14] NH-delocalized structures of azaporphyrins in basic media were investigated and it was shown that activation of NH-bond in the macrocycle favors the reaction (2) only up to a certain limit. If stable structures with a stable axial screening of the H₂P reaction centre arise in the molecular H-bonded complex with the transfer of the porphyrin NH-proton to the electron-donating solvent molecule, reaction (2) can also slow down considerably.

Table 1. Reaction rate changes (2, 3) of non-planar porphyrins (**1**, **2**, **4**, **5**) in DMF - MX₂ system

3d metal salt	Series of reaction rates (2, 3)
Cu(OAc) ₂	1 < 5 < 4 < 2
Cu(Acac) ₂	1 < 5 < 4 < 2
Cd(OAc) ₂	4, 5 << 1 < 2
Cd(Acac) ₂	5, 4 << 1 < 2
Zn(OAc) ₂	4, 5 << 1 < 2
Zn(Acac) ₂	5 \approx 4 < 2 < 1
Co(OAc) ₂	4 < 5
Co(Acac) ₂	5 < 4

We found significant differences in the kinetic parameters of the complexing reaction (2, 3) of N- (compounds **1**, **2**) and dodeca- (compounds **4**, **5**) substituted porphyrin molecules taking in solution nonplanar, mostly saddle, but differing in symmetry and degree of conformation deformation. In accordance with Table 2 the entropy change ΔS^\ddagger during the activation of the reaction reagents (2, 3) is always more positive for the undeconverted than for the N-substituted porphyrins, but only in the electron-donating solvent (DMF).

**Table 2.** Influence of the porphyrin nature (compounds 1, 2, 4, 5) on the change of activation parameters of reaction (2, 3) with Zn(II) and Co(II) salts in C₆H₆ and DMF

Porphyrin	Salt	Solvent	k_v^{298} , l/mol*s	E_a , kJ/mol	ΔS^\ddagger , J/mol*K
H(N-Me)(β -Et) ₈ P (1)	Co(OAc) ₂	DMF	30.94±1.39	53.6±1.3	-63±2
	Co(Acac) ₂		18.13±0.69	59.7±1.8	-29±1
	Co(Acac) ₂	C ₆ H ₆	Very slowly		
H(N-Me)TPP (2)	Zn(OAc) ₂	DMF	6.14±0.41	34.1±0.9	-124±6
	Zn(Acac) ₂		12.51±0.50	40.2±1.2	-97±3
	Zn(Acac) ₂	C ₆ H ₆	Very slowly		
H ₂ (β -Et) ₈ TPP (4)	Zn(OAc) ₂	DMF	9.66±0.11	62.6±0.7	-24±1
	Zn(Acac) ₂		4.01±0.21	88.9±4.0	56±2
	Co(OAc) ₂		17.55±0.47	60.0±2.2	-26±1
H ₂ P(β -Ph) ₈ TPP (5)	Zn(OAc) ₂	DMF	1.81±0.05	93.2±2.3	64±1
	Zn(Acac) ₂	DMF	5.29±0.21	68.5±2.1	-9±1
	Zn(Acac) ₂	C ₆ H ₆	83.79±2.18	32.5±1.3	-108±4
	Co(OAc) ₂	DMF	5.39±0.30	77.8±1.8	22±1
	Co(Acac) ₂	DMF		77.1±3.6	13±1
	Co(Acac) ₂	C ₆ H ₆	10.48±0.56	79.3±3.1	-32±1

The change of the reaction entropy takes place in solution without a change in the mole number of the substance is related to the change in the solvation of the particles during the formation of the transition state [5, 24]. In terms of the increase of ΔS^\ddagger in reactions (2, 3) can be explained either by desolvation of the transition state, which is unlikely, or by additional (under certain conditions) solvation of the starting reagents. We possess the increase of ΔS^\ddagger of the complexing reaction of NH-active undeconverted porphyrins in the electron-donating solvent is directly related to their ability to form H-bonded molecular complexes with electron-donors. In case of non-polar media or NH-inactive compounds there is no increase of ΔS^\ddagger in reaction (2).

The formation of the molecular complex leads to an increase of the initial H₂P solvation in reaction (2) and an acceleration of this reaction due to its activation of NH-bonds compared to the NH- inactive porphyrins. By [2, 5, 24], the most energy-intensive contributions to the total energy of reaction (2) is the dissociation of the NH bonds of the H₂P ligand. The activation of NH-bonds and the formation of the complex with the electron donor are characteristic for the H₂P (compounds 4-6, 8) and are not characteristic for N-substituted porphyrin analogues (compounds 1, 2) which is reflected in their metal complexing reaction activation parameters (Table 2).

Thus, this work shows the exhibition of the chemical activity of NH-bonds of porphyrin molecules, characteristic for MHC with flat or flat polarized structure, is not limited to the increase in the rate of the indicator reaction of their metal complex formation (2) in the electron-donor compared with proton-donor media. But it also exhibits a change of ΔS^\ddagger towards more positive values as the electron-donating properties of the solvent intensify, which is caused by the formation of "H₂P-electron-donor" molecular complexes increasing the solvation of the reaction initial state (2). Using the example of N- and dodec substituted porphyrins, it is



demonstrated that deformation of the plane structure of the H₂P macrocycle, not accompanied by noticeable polarization of the molecule, does not lead to the appearance of chemical activity of NH bonds.

Acknowledgements

The assistance provided by Semeykin A.S., Doctor of Chemistry, Professor was greatly appreciated. This work was supported by Ivanovo State University of Chemistry and Technology, Ivanovo, Russia Centre for the Collective Use of Scientific Equipment (the Russian Ministry of Education and Science, Agreement No. 075-15-2021-671)

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Received 14.03.2022

Approved after reviewing 21.03.2022

Accepted 22.03.2022