KINETIC STABILITY OF COMPLEXES OF CONJUGATED MACROHETEROCYCLES WITH METALS IN A PROTON-DONOR MEDIUM

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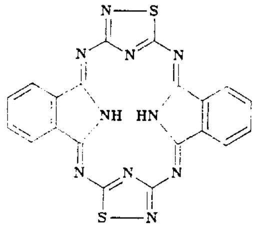
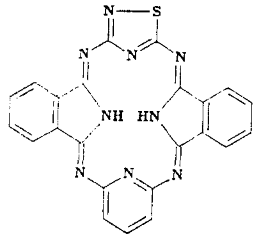
The rate of decomposition of conjugated macroheterocyclic ligands containing isoindole and 1,2,4-thiadiazole residues has been studied together with the rate of dissociation of their complexes with copper, cobalt, and zinc in a proton-donor medium at three temperatures. Rate constants and activation parameters have been determined for the decomposition of the macrocyclic ligands and the dissociation of their complexes.

Among the numerous groups of macrocycles with heteroatoms, conjugated azamacrocycles and macrocycles containing sulfur atoms in the conjugated system attract special interest because they are structural analogs of natural biologically active porphyrins and can be used as model molecules for their study.

For our study of stabilities in a proton-donor medium, we selected conjugated macroheterocyclic compounds (MHC) having isoindole, 1,2,4-thiadiazole, benzene, and pyridine fragments together with their copper, cobalt, and zinc complexes. The electronic absorption spectra are shown in Figs. 1 and 2 [1, 2].



I



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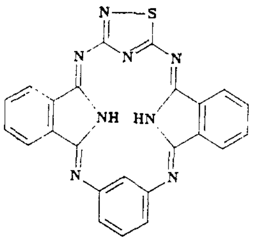

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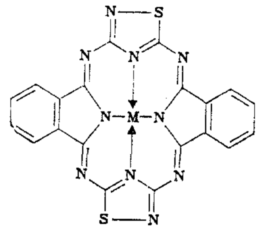
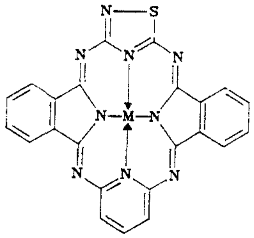
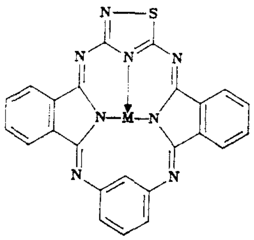


M=Cu^{2+}, Co^{2+}, Zn^{2+}





The spectral features of conjugated azamacrocycles and macroheterocycles containing a sulfur atom in the conjugated system have been elucidated previously [3].

With the object of studying the influence of the structural features of the molecule on its stability, a kinetic method was used to determine the rate of decomposition of the macroheterocycles and the rate of dissociation of their metal complexes.

It can be seen from the results in Table 1 that the effective rate constants for the breakdown of compounds I-III in a mixture of glacial acetic acid with H_2SO_4 monohydrate are practically the same. This is in agreement with the similarity of the electronic interactions in their conjugated systems.

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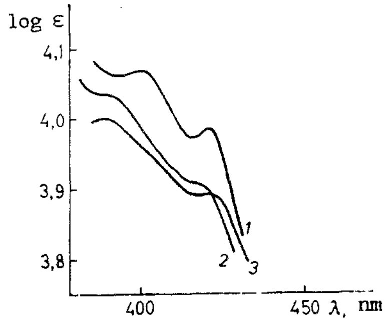


Fig. 1

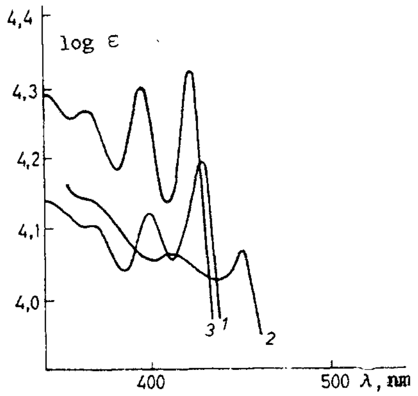


Fig. 2

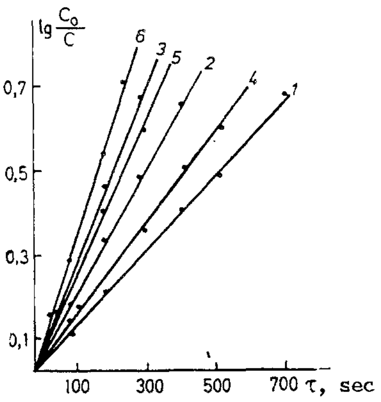


Fig. 3

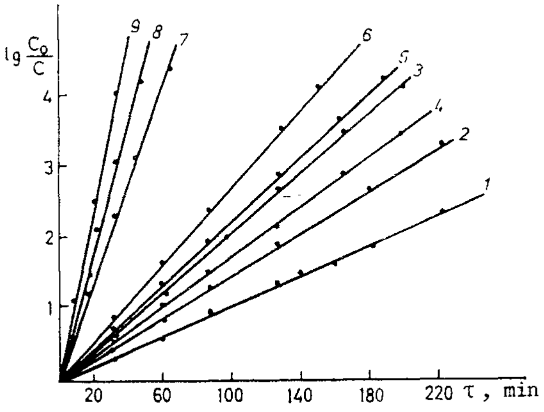


Fig. 4

Fig. 1. Electronic absorption spectra of macrocycles in pyridine: 1) MHC I; 2) MHC II; 3) MHC III.

Fig. 2. Electronic absorption spectra of MHC I complexes in pyridine: 1) Cu^{2+}; 2) Co^{2+}; 3) Zn^{2+}.

Fig. 3. Kinetics of the decomposition of MHC: 1, 2, 3) = II; 4, 5, 6) = I at 25, 35, and 45°C, respectively.

Fig. 4. Kinetics of the dissociation of complexes of I in HAc + H_2SO_4: 1, 2, 3) = Cu(I); 4, 5, 6) = Co(I); 7, 8, 9) = Zn(I) at 40, 50, and 60°C, respectively.

Breakdown of the macroheterocyclic ligands I-III apparently proceeds at a C=N bond [4]. The effective rate constant in the series I-III is independent of the nature of the conjugation in the macro-ring. Breakdown of macrocyclic ligands in a proton-donor medium is first order in ligand concentration (Fig. 3).

Dissociation of the complexes of MHC I-III takes place according to the equation

$$\underset{\text{Complex}}{MMHC} + \underset{\text{acid}}{2HA} \rightarrow \underset{\text{ligand}}{H_2MHC} + \underset{\text{metal acetate}}{MAc_2} \tag{1}$$

at a comparatively low rate, with small activation energy and very low activation entropy (Table 2).

Dissociation of the stable complexes of conjugated MHC with metals is a slow reaction and is first order in ligand concentration (Fig. 4).

The low rates of decomposition of the complexes are characteristic for aromatic and conjugated macrocycles. The rate constants (k_{ef}^{25}) characterize the kinetic stability of the complexes. In general, the kinetic stability of the complexes with aromatic macrocycles falls in the order Cu > Co > Zn [4].

TABLE 1. Kinetic Characteristics of the Decomposition of Macroheterocyclic Ligands

Compound	$k_{ef} \cdot 10^3$, sec^{-1}			E_{act}, kJ/mole	$\Delta S^{\neq}$, J/mole·K
	25 °C	35 °C	45 °C		
I	1,6±0,06	2,4±0,04	3,7±0,1	33±5	−196
II	1,3±0,09	1,9±0,07	2,9±0,1	32±5	−202
III	1,4±0,06	2,2±0,15	3,2±0,1	34±5	−199

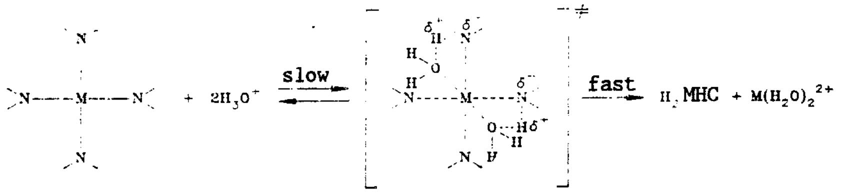
TABLE 2. Kinetic Parameters of the Dissociation of MHC Complexes in a Proton-Donor Medium

Compound	$k_{ef}^{25} \cdot 10^4$, sec^{-1}	E_{act} ±5, kJ/mole	$\Delta S^{\neq}$ ±8, J/mole
Cu(I)	0,9±0,11	31	−226
Co(I)	1,9±0,06	19	−261
Zn(I)	1,6±0,08	23	−229
Cu(II)	1,1±0,10	30	−228
Co(II)	1,8±0,08	23	−246
Zn(II)	2,6±0,07	31	−218
Cu(III)	5,3±0,06	25	−230
Co(III)	2,3±0,13	31	−220
Zn(III)	4,5±0,17	34	−204

TABLE 3. Location of the First Absorption Band in the Electronic Absorption Spectra of MHC I-III and Their Complexes in HAc + H_2SO_4 Mixture

Compound	λ, nm	Compound	λ, nm	Compound	λ, nm
I	405	II	400	III	398
Cu(I)	376	Cu(II)	370	Cu(III)	400
Co(I)	400	Co(II)	360	Co(III)	365
Zn(I)	366	Zn(II)	365	Zn(III)	365

The negative values of the activation entropy (Table 2) are the result of the high polarity of the transition state:



The low activation energies are apparently determined by the greater ease of activation of the MMHC + H_3O^+ reactants and the effective stabilization of the transition state as a result of solvation.

The activation entropies ($\Delta S^{\neq}$) of the dissociation of complexes of MHC I-III are 100 J/(mole·K) lower than for the corresponding porphyrins (Table 2). It can be conjectured that in the course of the dissociation the solvent more strongly solvates the transition state of complexes I-III than of porphyrins.

As can be seen from Tables 1 and 2, the rate of breakdown of the macrocyclic ligands is an order of magnitude greater than that of the complexes. This means that in the case of the complexes we are measuring a solvoprotolytic dissociation with the formation of ligand and M^{2+}. Under these conditions, the ligand is then decomposed with opening of the ring. The dependence of the effective dissociation rate constant on the nature of M^{2+} (Cu^{2+}, Co^{2+}, Zn^{2+}) fully supports the hypothesis made above. The kinetic stability Cu > Co > Zn corresponds to the strength of their bonding in complexes with nitrogen-containing ligands.

EXPERIMENTAL

The study of the decomposition of MHC was carried out in a proton-donor medium. Reaction rates were determined spectrophotometrically.

Kinetic Experiment Technique. A mixture of glacial acetic acid (HAc) with H_2SO_4 monohydrate was prepared. The concentration of the monohydrate in acetic acid was 2.68 mole/liter. The concentration of MHC and their metal complexes in solution amounted to 10^{-3} mole/liter. The colored solutions of MHC and their complexes in the HAc + H_2SO_4 mixture were placed in a 1 cm thick quartz cell with a ground stopper. The cell was thermostatted in the cell compartment of an SF-4A spectrophotometer in a specially constructed [5] block connected to a thermostat. Fluctuations in temperature did not exceed 0.1°C. Experiments were carried out for MHC at temperatures of 25, 35, and 45°C and for the complexes at 40, 50, and 60°C. Decolorizing of the solutions was observed in the course of the experiments. The change in optical density was measured over a determined period of time at the absorption maximum (Table 3). The constant k_{ef} was calculated as the average of the results of four experiments.

The spectral changes arising in the course of the decomposition were used for calculation of the effective constant [6]:

$$k_{ef} = \frac{1}{\tau} \ln \frac{D_0 - D_\infty}{D_\tau - D_\infty},$$

where D_0, D_τ, and D_∞ are the optical densities at the beginning of the experiment, after time τ, and at the end of the experiment, respectively.

The activation energy was calculated from the Arrhenius equation which in integral form can be written as [6]

$$E_{act} = 8.314 \frac{T_1 T_2}{T_2 - T_1} \ln \frac{k_2}{k_1}.$$

The relative values of the activation entropy were calculated from the equation [6]

$$\Delta S^{\neq} = 8.314 \ln k^{25} + \frac{E}{298} - 253.22.$$

LITERATURE CITED

1. G. R. Berezina, N. A. Kolesnikov, and R. P. Smirnov, Izv. Vuzov. Khim. Khim. Tekhnol., 29, 52 (1986).
2. G. R. Berezina, N. A. Kolesnikov, and R. P. Smirnov, Dep. with ONIITEkhim (Cherkassy), March 10, 1987, No. 229-XII-87.
3. R. P. Smirnov, G. R. Berezina, N. A. Kolesnikov, and B. D. Berezin, Izv. Vuzov. Khim. Khim. Tekhnol, 29, 3 (1986).
4. B. D. Berezin, Coordination Compounds of Porphyrins and Phthalocyanins [in Russian], Nauka, Moscow (1978).
5. O. A. Golubchikov, Kinetic Relationships in the Formation of Metal Porphyrins in Individual and Mixed Solvents [in Russian], Dissertation, Ivanovo (1974).
6. N. M. Émanuél and D. G. Knorre, Course in Chemical Kinetics [in Russian], Vysshaya Shkola, Moscow (1969).