

Reaction of macrocyclic complex $\text{Cu}(\text{TAAB})^{2+}$ with hydroxylamine

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The kinetics of the reduction of a copper(II) complex with the macrocyclic ligand tetrabenzo(*b,f,j,n*)(1,5,9,13)tetraazacyclohexadecine by hydroxylamine has been investigated both in anaerobic and aerobic medium. The results are compared with the parameters of ascorbic acid reaction with $\text{Cu}(\text{TAAB})^{2+}$ and the reaction mechanism is discussed.

Изучалась кинетика восстановления комплекса меди(II) с макроциклическим лигандом тетрабензо(*b,f,j,n*)(1,5,9,13)тетраазациклогексадеценом (ТААВ) гидроксиламином в анаэробных и аэробных условиях. Результаты сравниваются с параметрами реакции аскорбиновой кислоты с комплексом $\text{Cu}(\text{ТААВ})^{2+}$ и обсуждается механизм реакции.

Development of chemistry of coordination compounds with synthetic macrocyclic ligands is connected with the possibility of systematic changing their geometrical and electronic parameters as well as the respective thermodynamic and kinetic properties.

From the standpoint of good possibility of comparison of macrocyclic complexes with those formed by small molecules as ligands as well as from the standpoint of natural analogues modelling tetraazadonor macrocycles are widely studied. Among these tetrabenzo(*b,f,j,n*)(1,5,9,13)tetraazacyclohexadecine (TAAB) has special position owing to its thorough conjugation of unsaturated bonds. For the copper(II) complex this is expressed distinctively by easier reducibility with regard to other complexes with CuN_4 chromophore [1]. Systematic attention is paid, therefore, to $\text{Cu}(\text{TAAB})^{2+}$ complex [2—5] which represents the analogy to superoxidismutase [6].

The present paper treats of $\text{Cu}(\text{TAAB})^{2+}$ reaction with hydroxylamine both in anaerobic and aerobic medium with the aim to compare the course and kinetic parameters of this reaction with the reaction of this complex with ascorbic acid [4] and so to characterize more thoroughly the peculiarities of macrocyclic complex reactivity.

Experimental

$[\text{Cu}(\text{TAAB})](\text{NO}_3)_2$ was synthesized as described previously [7]. The hydroxylamine hydrochloride solutions (anal. grade; Lachema, Brno) were prepared immediately prior to

the experiment. The Britton—Robinson buffer solutions were prepared from anal. grade chemicals in redistilled water, the ionic strength was adjusted with KNO_3 ($I = 0.1 \text{ mol dm}^{-3}$). Argon was used as inert gas.

The reduction of the Cu(II) complex was monitored spectrophotometrically at the Cu(TAAB)^+ maximum absorption wavelength ($\lambda = 660 \text{ nm}$, $\epsilon = 5200 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$ [2]), at which the Cu(TAAB)^{2+} absorption can be neglected. The spectrometer Specord UV VIS (Zeiss, Jena) was employed. Measuring cells of the type Kleinküvette D 5 cm (GFR) were closed but provided with openings for filling and bubbling. For kinetic measurements all solutions were of constant temperature 25.0°C .

Changes of dioxygen and H_2O_2 concentrations in the course of the reaction were monitored polarographically at the potentials -0.45 V (O_2) and -1.1 V (H_2O_2), respectively. The OH-102 polarograph (Radelkis, Budapest) was used. Dropping mercury electrode ($t_1 = 5.4 \text{ s}$, $m_t = 7.7 \times 10^{-4} \text{ g s}^{-1}$, $h = 53 \text{ cm}$) served as the indicating electrode, the saturated calomel electrode (SCE) served as reference electrode and all potentials in this paper are referred to this electrode. The polarographic vessel was closed from the outer atmosphere and adjusted so as the solution could be bubbled through by inert gas.

The potentiometric measurements were carried out with the OP-201/2 pH-meter (Radelkis, Budapest) using the glass and calomel electrodes. The dissociation constants were determined in the CO_2 -free medium.

Results

The reaction in anaerobic medium

The reaction stoichiometry was determined by monitoring the spectrophotometric titration of Cu(TAAB)^{2+} with hydroxylamine in Britton—Robinson buffer solutions of pH 6.0 and 7.0, respectively. A one-electron reduction of 1 mol of Cu(TAAB)^{2+} requires 1 mol of hydroxylamine both under anaerobic and aerobic conditions. The gas bubbles on the walls of the photometric measuring cell indicate formation of a gaseous reaction product. The entire reaction can be, therefore, expressed as follows



The reacting forms of the reactants will be discussed in the next section.

The kinetics of the reaction was studied under minimally 50-fold excess of hydroxylamine against the Cu(TAAB)^{2+} concentration at pH = 6.0 up to pH = 7.5 and at three different initial concentrations of Cu-complex ($c_0/(\text{mol dm}^{-3})$): 1.5×10^{-5} , 3×10^{-5} , and 6×10^{-5} . First order of the reaction with respect to Cu(TAAB)^{2+} concentration has been proved by linear dependence of $\log(d c_0/d t)_t$ vs. $\log c_{0,t}$ with the slope equal to 1. The observed pseudo-first order rate constants

$k(\text{obs})$ were obtained from the dependence of $\ln(A_\infty - A_t)$ on time (where A_∞ is the absorbance after full reduction and A_t is that at the time t).

The $k(\text{obs})$ value increases in the investigated pH region with the increasing hydroxylamine concentration and reaches maximum at the mole ratio $n(\text{NH}_2\text{OH}) : n(\text{Cu}(\text{TAAB})^{2+}) \approx 100 : 1$. This dependence for four different temperatures is shown in Fig. 1. The value of $k(\text{obs})$ (for 1.5×10^{-3} mol dm $^{-3}$ and 3×10^{-3} mol dm $^{-3}$ hydroxylamine) decreases linearly with the increasing concentration of H^+ ions. For the region of lower excess of NH_2OH and for pH from 6.0 to 7.5 the reaction kinetics can be expressed by the following equation

$$k(\text{obs}) = k c(\text{NH}_2\text{OH} \cdot \text{HCl}) / c(\text{H}^+) \quad (1)$$

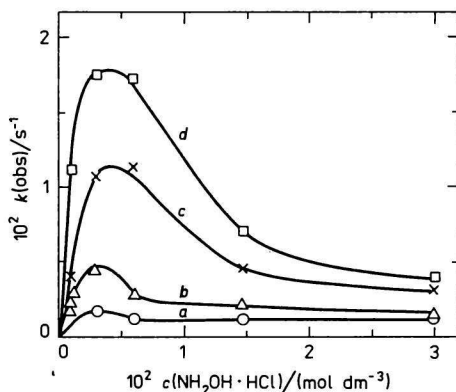


Fig. 1. Dependence of the observed rate constant $k(\text{obs})$ on total hydroxylamine concentration.

Anaerobic medium, Britton—Robinson buffer solution, pH=7.0, $I=0.1$ mol dm $^{-3}$ (KNO_3), $c(\text{Cu}(\text{TAAB})^{2+}) = 3 \times 10^{-5}$ mol dm $^{-3}$; θ : 16.5 °C (a), 25.0 °C (b), 35.0 °C (c), and 45.0 °C (d), respectively.

The dependence of the rate constant k (determined from the initial course of the curves in Fig. 1) on temperature is presented in Table 1.

The observed rate constant $k(\text{obs})$ decreases with the increasing ionic strength of the solution (adjusted with KNO_3). The obtained dependence is given in Table 1.

In view of the lack of literature data on the acid dissociation of hydroxylamine hydrochloride we investigated the NH_3OH^+ dissociation by the potentiometric titration with NaOH . In the range of pH from 3 to 13 the only potential jump was observed at the mole ratio $n(\text{NaOH}) : n(\text{NH}_3\text{OH}^+) = 1 : 1$. For the solutions with ionic strength 0.1 mol dm $^{-3}$ (KNO_3) following values of the dissociation constant $K_1/(\text{mol dm}^{-3})$ were found: 4.9×10^{-7} (16.5 °C), 8.4×10^{-7} (25.0 °C), 1.6×10^{-6} (35.0 °C), and 2.7×10^{-6} (45.0 °C), respectively.

In the same way the acidity (electrophilic properties) of $\text{Cu}(\text{TAAB})^{2+}$ complex was studied. At the range of pH from 6 to 10 one distinct potential jump was observed which leads to the following values of the equilibrium constant $K_2/(\text{mol dm}^{-3})$: 1.1×10^{-7} (20.0 °C), 1.4×10^{-7} (25.0 °C), and 2.1×10^{-7} (35.0 °C).

Table 1

Dependence of the rate constant k on temperature and dependence of the observed rate constant $k(\text{obs})$ on ionic strength (KNO_3)

Anaerobic medium, Britton—Robinson buffer solution, $\text{pH} = 7.0$
 $c(\text{Cu}(\text{TAAB})^{2+}) = 3 \times 10^{-5} \text{ mol dm}^{-3}$, $c(\text{NH}_2\text{OH} \cdot \text{HCl}) = 3 \times 10^{-3} \text{ mol dm}^{-3}$

$\theta/^\circ\text{C}$ ($I = 0.1 \text{ mol dm}^{-3}$)	16.5	25.0	35.0	45.0
$10^3 k/\text{s}^{-1}$	8.3	20	47	111
$I/(\text{mol dm}^{-3})$ ($\theta = 25.0 \text{ }^\circ\text{C}$)		0.1	0.5	1.0
$10^3 k(\text{obs})/\text{s}^{-1}$		5.1	3.0	1.2

The reaction in the presence of O_2

The observed rate of the $\text{Cu}(\text{TAAB})^{2+}$ reduction ($c = 3 \times 10^{-5} \text{ mol dm}^{-3}$) by hydroxylamine ($c = 3 \times 10^{-3} \text{ mol dm}^{-3}$) in the presence of dioxygen ($c = 2.4 \times 10^{-4} \text{ mol dm}^{-3}$ is given by the air solubility) is greater than that in the anaerobic medium. The rates difference increases with pH rise. While at $\text{pH} = 6.05$ the $k(\text{obs})$ has approximately the same value both for anaerobic and aerobic medium (at $25.0 \text{ }^\circ\text{C}$), at $\text{pH} = 7.0$ in the aerobic medium the $k(\text{obs})$ value makes the twofold of that in the absence of O_2 and the twofold is conserved also at the temperatures $35.0 \text{ }^\circ\text{C}$ and $45.0 \text{ }^\circ\text{C}$, respectively (Table 2).

Table 2

Dependence of the observed rate constant $k(\text{obs})$ on pH and on temperature
 Britton—Robinson buffer solution, $I = 0.1 \text{ mol dm}^{-3}$ (KNO_3), $c(\text{Cu}(\text{TAAB})^{2+}) = 3 \times 10^{-5} \text{ mol dm}^{-3}$,
 $c(\text{NH}_2\text{OH} \cdot \text{HCl}) = 3 \times 10^{-3} \text{ mol dm}^{-3}$

pH ($\theta = 25.0 \text{ }^\circ\text{C}$)	6.05	6.35	6.50	7.00
$10^4 k(\text{obs, anaerob.})/\text{s}^{-1}$	5.9	8.3	13.3	36.1
$10^4 k(\text{obs, aerob.})/\text{s}^{-1}$	5.9	9.7	15.2	73.6
$\theta/^\circ\text{C}$ ($\text{pH} = 7.00$)	16.5	25.0	35.0	45.0
$10^3 k(\text{obs, anaerob.})/\text{s}^{-1}$	2.1	3.6	8.5	19.1
$10^3 k(\text{obs, aerob.})/\text{s}^{-1}$	4.4	7.4	21.1	33.7

In the absence of the Cu-complex at pH = 7.0 and 25.0 °C the O₂ concentration does not change by the effect of hydroxylamine ($c = 3 \times 10^{-3}$ mol dm⁻³) during 1 h and at 35.0 °C very slow decrease of O₂ concentration is observed. In the presence of Cu(TAAB)²⁺ ($c = 3 \times 10^{-5}$ mol dm⁻³) the O₂ concentration decreases slowly and O₂ is consumed ca. during 1 h at pH = 7.0 and 35.0 °C. Cu(TAAB)²⁺ is completely reduced herewith to Cu(TAAB)⁺ already during the first phases of the reaction (ca. to the decrease of O₂ concentration by 1/6) and is deposited in the form of precipitate. H₂O₂ as a product of the O₂ reduction has been polarographically verified and so was its slow further reaction.

Discussion

From the literature [8—12] it is known that the course of hydroxylamine oxidation is complicated and more products are formed in accordance with the conditions of experiment. Copper salts serve as the vigorous oxidating agents of hydroxylamine and as the catalyst of its oxidation by the air dioxygen [13—15]. The course of the reactions depends on the concentration of reactants as well as on the temperature [16] and is slowed down by the copper-complexing agents [14].

Confronting these known facts with the behaviour of the Cu(TAAB)²⁺—hydroxylamine system, first it is necessary to decide in which form hydroxylamine and the complex react. The found value of the only NH₃OH⁺ dissociation constant ($K_1 = 8.4 \times 10^{-7}$ mol dm⁻³ at 25.0 °C) is in agreement with the published data $K_1 = 1 \times 10^{-6}$ mol dm⁻³ [17] and confirmed that NH₂OH is the reagent in the investigated pH region (6.0 up to 7.5). The introduction of the hydroxylamine deprotonized form concentration into the kinetic eqn (1) by the expression $(K_1 c(\text{NH}_2\text{OH} \cdot \text{HCl}) / (K_1 + c(\text{H}^+)))$ disturbs the stability of the constant k . The dependence of $k(\text{obs})$ on $c(\text{H}^+)$ therefore does not represent only the dissociation of NH₃OH⁺ similarly as it was in the case of the reaction of Cu(TAAB)²⁺ with the ascorbic acid in the range of pH > 3.5 [4]. Beside the type Cu(TAAB)²⁺ also its deprotonized form [18] will represent the reacting form of the copper complex. This deprotonized form reacts faster and its concentration increases with the pH value. In fact eqn (1) has more complicated form

$$k(\text{obs}) = \frac{k_1 K_1 c(\text{NH}_2\text{OH} \cdot \text{HCl})}{K_1 + c(\text{H}^+)} + \frac{k_2 K_1 K_2 c(\text{NH}_2\text{OH} \cdot \text{HCl})}{(K_1 + c(\text{H}^+))(K_2 + c(\text{H}^+))} \quad (2)$$

($k_2 = 2 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and k_1 is approximately by two orders of magnitude smaller than k_2 at 25.0 °C), which is in a satisfactory accordance with the experimental data. In the pH region > 7.5 another type of the alkaline catalysis is of use.

The $k(\text{obs})$ decrease with the increasing ionic strength is apparently in the contradiction with the participation of NH₂OH in the reaction (if a charge of one of

the reactants is equal to zero, the rate constant should not depend on the ionic strength). It is the fact that the decrease of the rate constant is more distinct at higher ionic strength value (1 mol dm^{-3}) and does not fulfill the linearity of the Debye—Hückel equation. The cause of the reaction rate decrease may be chemical — the presence of NO_3^- in the sixth coordination site of Cu. The linkage of axial ligand is obviously very weak in the case of $\text{Cu}(\text{TAAB})^{2+}$ [19] and its effect therefore will be expressed only at high concentration relative to that of $\text{Cu}(\text{TAAB})^{2+}$.

The determined stoichiometry of the reaction of $\text{Cu}(\text{TAAB})^{2+}$ with NH_2OH confirmed that the course of this redox reaction under anaerobic conditions with pH round 7 is usual for the hydroxylamine oxidation by weaker agents [12]. The experiments for the reaction stoichiometry determination have also shown that $\text{Cu}(\text{TAAB})^{2+}$ has not a significant catalytic effect on the NH_2OH decomposition in the neutral medium.

The complicated course of the $k(\text{obs})$ dependence on the hydroxylamine concentration follows from the already mentioned complexity of NH_2OH reactions and from the peculiarities of the copper macrocyclic complex. Moreover, both reactants react minimally in two protolytic forms. At low hydroxylamine concentrations relative to that of $\text{Cu}(\text{TAAB})^{2+}$ it obviously comes to the temporary weak association of $\text{Cu}(\text{TAAB})^{2+}$ and NH_2OH followed by the innercomplex exchange of the electron. $\text{Cu}(\text{TAAB})^+$ and $\cdot\text{NH}_2\text{OH}^+$ are formed, $\cdot\text{NH}_2\text{OH}^+$ being changed into $\cdot\text{NHOH}$ and reacting with the second particle of $\text{Cu}(\text{TAAB})^{2+}$. The reaction rate of the charge transfer is relatively low due to the redox stability of the 5-coordinated central atom. The rate is raised by temperature increase owing to overcoming the activation energy (the dissociation constants of NH_3OH^+ and $\text{Cu}(\text{TAAB})^{2+}$ as well as the stability constant of the associate of $\text{Cu}(\text{TAAB})^{2+}$ with NH_2OH are changed at the same time).

At higher hydroxylamine concentrations relative to that of $\text{Cu}(\text{TAAB})^{2+}$ the above described process is still realized (or is dominant) at the lower temperature. Higher temperatures help the process connected with greater redistribution of electron density. The next NH_2OH particle coming to the sixth coordination site of copper can cause the displacement of the electron in the complex particle $[\text{Cu}(\text{I})\text{N}_4(\text{L}_{\text{ax}}^+) (\text{L}_{\text{ax}})]^{2+}$ to $[\text{Cu}(\text{II})\text{N}_4(\text{L}_{\text{ax}}) (\text{L}_{\text{ax}})]^{2+}$. The axial ligand thus becomes oxidating agent. This process competes with $\text{Cu}(\text{TAAB})^+$ and $\cdot\text{NH}_2\text{OH}^+$ formation and the observed reaction rate decreases. The pursued process shows thus the effect of mutual influence of ligands (L_{ax} influences the redox properties of both central atom and ligands).

The study of the $\text{Cu}(\text{TAAB})^{2+}$ reaction with hydroxylamine in the aerobic medium also showed the peculiarities of macrocyclic complex reaction. The NH_2OH oxidation by dioxygen was, in fact, initiated by this complex but $\text{Cu}(\text{TAAB})^+$ was formed fast and irreversibly. The inability of $\text{Cu}(\text{TAAB})^+$ to be

reoxidized by air dioxygen directly as well as to form the ternary complex with the reducing agent and O_2 was observed already at the study of the catalytic oxidation of ascorbate anion [4]. In that case the high reactive superoxide radical $\cdot O_2^-$ formed in the reaction of ascorbate anion radical with O_2 was indicated as the originator of the fast reoxidation of $Cu(TAAB)^+$ as well as its deprotonized form. The primary product of the $Cu(TAAB)^{2+}$ reaction with NH_2OH , i.e. $\cdot NHOH$, is not obviously subject to such interaction with dioxygen. $Cu(TAAB)^+$ is therefore accumulated, compounds with higher oxidation state of nitrogen (N_2O and NO_2^-) are formed [12] and O_2 is changed to H_2O_2 . It was verified that $Cu(TAAB)^{2+}$ is reduced fast by the NO_2^- anion in the presence of NH_2OH , by which the greater rate of $Cu(TAAB)^+$ formation in the aerobic medium at higher pH values may be explained.

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