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Short Communication

Kinetics of *EDTA* Substitution of N,N′-Ethylenedisalicylamidato Cuprate(II) in Alkaline Media

Sreelekha D. Bhattamisra* and **Sanjukta Tripathy**

Department of Chemistry, Berhampur University, Berhampur 760007, Orissa, India

Summary. The kinetics of *EDTA* reaction with N,N′-ethylenedisalicylamidato cuprate(II) is followed at 30°C in borate buffer and is found to be first order in each reactant. The reaction is *pH* dependent and involves protonation of a deprotonated peptide nitrogen followed by nucleophilic attack by *EDTA*.

Keywords. Copper(II); *EDTA*; N,N′-Ethylenedisalicylamide; Protonation; Rate constant; Substitution.

Kinetik der *EDTA*-Substitution von N,N′-Ethylendisalizylamidatokupfer(II) in alkalischem Medium (Kurze Mitt.)

Zusammenfassung. Die Kinetik der *EDTA*-Reaktion mit N,N′-Ethylendisalizylamidatokupfer(II) wurde bei 30°C in Borat-Puffer verfolgt. Es wurde erste Ordnung bezüglich jedes Reaktanden festgestellt. Die *pH*-abhängige Reaktion beinhaltet die Protonierung eines deprotonierten Peptid-Stickstoffs, gefolgt von einem nucleophilen Angriff eines *EDTA*-Moleküls.

Introduction

Studies on copper complexes of di- and polypeptides have established the deprotonation and subsequent co-ordination of the peptide nitrogen to the metal [1]. The kinetics and mechanism for the proton transfer reaction of the peptide proton has also been investigated [2, 3]. The present work involves a tetradentate ligand, N,N′-ethylenedisalicylamide (LH_2) with two peptide linkages, but in contrast to the copper(II) peptide complexes this ligand lacks both the amine and the carboxylate terminals. Therefore it was considered interesting to study the kinetic properties of its copper complex, especially in view of the presence of two phenolic OH groups. Ligands with phenolic OH groups have been reported [4] to act as effective metal carriers in biological systems.

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* Present address: School of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland

Experimental

All the chemicals used were of AR quality. N,N'-ethylene disalicylamide was prepared by the literature method [5]. The copper chelate was prepared by adding calculated amounts of freshly precipitated $Cu(OH)_2$ to a slurry of the ligand in 0.5 *M* KOH. Found: C 36.2, H 4.2, N 5.3. Calculated for $K_2Cu[C_{16}H_{12}N_2O_4(5\,H_2O)]$ C 36.38, H 4.16, N 5.3%. The complex has identical IR and visible spectra as described elsewhere [5]. Disodium *EDTA* was standardised by the usual procedure [6]. The kinetics of *EDTA* substitution of the copper chelate was studied spectrophotometrically using the AIMIL spectrophotometer with microprocessor in ethanol water medium (50% *v/v*) at 30°C and $I = 0.125\,\text{mol}\,\text{dm}^{-3}$ using borate buffer. The rate of disappearance of $K_2[CuLH_{-2}5\,H_2O]$ was followed at 575 nm under second order conditions and the rate constants were calculated from conventional plots that yielded good straight lines up to four half lives.

Results and Discussion

N,N'-ethylenedisalicylamide reacts with copper(II) and releases four protons in base to form $[CuLH_{-2}]^{2-}$. Analytical *pH*-metric and spectral data are consistent with a structure having two deprotonated nitrogen and two oxygen atoms in a planar arrangement about copper(II) [7]. From the distribution of various species at different *pH* it is seen that above *pH* 7 $CuLH_{-2}$ is the predominant species. In borate buffer the rate of reaction of $[CuLH_{-2}5\,H_2O]^{2-}$ with *EDTA* was very fast under pseudo first-order conditions and as such the rate data were collected under second order conditions. However, using various *EDTA* concentrations at *pH* 9.25 ± 0.06, it was found that the reaction is first order in each reactant (Table 1). The rate law is given by Eq. (1),

$$-\frac{\mathrm{d}\,Cu\,(LH_{-2})}{\mathrm{d}t} = k_{\text{obs}}[Cu(LH_{-2})][EDTA]_T, \qquad (1)$$

Table 1. Rate constants for the reaction of disodium *EDTA* with copper(II)-bis-salicylamido ethane. $I = 0.125\,\text{mol}\,\text{dm}^{-3}$, temp. = 30°C, [borate] = $0.025\,\text{mol}\,\text{dm}^{-3}$

$10^3\,[Cu(LH_{-2})5\,H_2O]^{2-}$ [$\text{mol}\,\text{dm}^{-3}$]	$10^3\,[EDTA]^{2-}$ [$\text{mol}\,\text{dm}^{-3}$]	$10^2\,k_{\text{obs}}$ [$\text{mol}\,\text{dm}^{-3}\,\text{s}^{-1}$]
1.250	1.250	28.1
	1.313	29.5
	1.413	29.0
	1.563	30.2
	1.725	28.3
	1.875	30.4
2.500	2.500	28.7
	2.600	26.6
	2.800	28.9
	3.125	29.8
	3.440	30.4
	3.750	28.8
3.800	3.800	29.1
	3.875	29.4
	4.250	30.6
	4.687	31.3

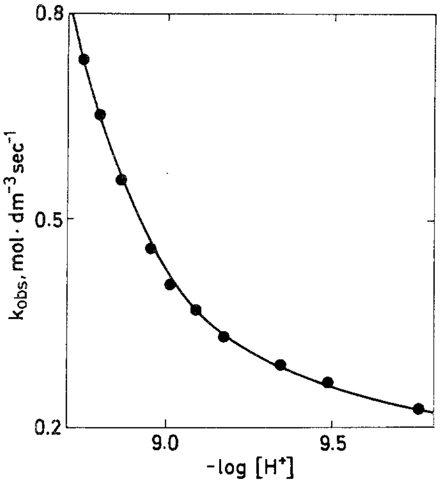

Fig. 1. Dependence of the *EDTA* reaction from the H^+-concentration

where $[EDTA]_T = [H_2EDTA]^{2-} + [HEDTA]^{3-} + [EDTA]^{4-}$ and the charges as well as the co-ordinated water molecules are omitted for clarity.

The hydrogen ion dependence of the *EDTA* reaction is shown in Fig. 1. The rate constant decreases exponentially with increase in *pH*. Considering the relative nucleophilic reactivity of the various *EDTA* species as $EDTA^{4-} > HEDTA^{3-} > H_2EDTA^{2-}$, it is obvious that the nucleophilic path is characterised by increasing rate with increase in *pH*. However, as observed in the present system, an inverse dependence of rate on the *pH* value rules out the possibility of any direct nucleophilic attack by *EDTA*. It is therefore likely that the protonation of the substrate, followed by attack by an *EDTA* species, constitutes the reaction mechanism, Eqs. (2)–(6).

$$[Cu(LH_{-2})]^{2-} + H^+ \overset{K_H}{\rightleftharpoons} [CuLH_{-1}]^{-1}, \qquad (2)$$

$$[Cu(LH_{-1})]^{-1} + [H_2EDTA]^{2-} \xrightarrow{k_{H_2EDTA}} [CuEDTA]^{2-} + [LH]^{-1}, \qquad (3)$$

$$[Cu(LH_{-1})]^{-1} + [HEDTA]^{3-} \xrightarrow{k_{HEDTA}} [CuEDTA]^{2-} + [L]^{2-}, \qquad (4)$$

$$[Cu(LH_{-1})]^{-1} + [EDTA]^{4-} \xrightarrow{k_{EDTA}} [CuEDTA]^{2-} + [LH_{-1}]^{3-}, \qquad (5)$$

$$(LH_n)^{n-2}_{(n=1,0,-1)} + (2-n)H_2O \xrightarrow{\text{fast}} LH_2 + (2-n)OH^{-1},$$

$$\text{Rate} = [CuLH_{-1}]\{k_{H_2EDTA}[H_2EDTA] + k_{HEDTA}[HEDTA] + k_{EDTA}[EDTA]\}, \qquad (6)$$

and

$$k_{obs} = \frac{k_{H_2EDTA}[H^+]^2 + k_{HEDTA}[H^+]k_{E1} + k_{EDTA}k_{E1}k_{E2}}{[H^+]^2 + k_{E1}k_{E2}} \frac{K_H[H^+]}{1 + K_H[H^+]}, \qquad (7)$$

where k_{E1} and k_{E2} are $6.31 \cdot 10^{-7}$ and $5.01 \cdot 10^{-11}$, the dissociation constants of disodium *EDTA* and $K_H = 6.76 \cdot 10^8$ [7]. The values of k_{H_2EDTA}, k_{HEDTA}, k_{EDTA} are calculated from Eq. (7) using an iterative least square method and are found to be

Table 2. Calculated and observed rate constants for the *EDTA* reaction with CuLH_{-2} at 30°C and $I = 0.125\,\mathrm{mol\,dm^{-3}}$ ($k_{\mathrm{H_2}EDTA} = 3.864 \cdot 10^2\,\mathrm{mol\,dm^{-3}\,s^{-1}}$, $k_{\mathrm{H}EDTA} = 3.46 \cdot 10^{-3}\,\mathrm{mol\,dm^{-3}\,s^{-1}}$, $k_{EDTA} = 9.8\,\mathrm{mol\,dm^{-3}\,s^{-1}}$)

pH	$10^2\,k_{\mathrm{obs}}$ [$\mathrm{mol\,dm^{-3}\,s^{-1}}$]	$10^2\,k_{\mathrm{cal}}$ [$\mathrm{mol\,dm^{-3}\,s^{-1}}$]
9.49	26.5	26.7
9.35	28.9	28.6
9.18	33.3	33.0
9.09	37.0	36.9
9.01	41.1	41.7
8.96	45.6	45.6
8.86	55.5	55.7
8.80	65.0	64.2
8.75	72.8	72.3

$3.864 \cdot 10^2$, $3.46 \cdot 10^{-3}$, and $9.8\,\mathrm{mol\,dm^{-3}\,s^{-1}}$, respectively. Using these values the overall rate constant at each *pH* was calculated. As is seen from Table 2, there is good agreement between the experimental and calculated rate constant values justifying the postulated reaction steps, Eqs. (2)–(7).

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