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Electron-transfer Reaction between Copper Macrocyclic Complex and Ascorbate Anion. Application of the Marcus Theory

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Abstract

The kinetics of the reduction of a copper(II) complex with a tetrabenzo(b,f,j,n) (1,5,9,13)tetraazacyclohexadecine (TAAB) by ascorbic acid has been investigated in aqueous buffer solutions of pH 2.8 up to 5.0. The polarographic half-wave potential of $Cu(TAAB)^{2+}$ reduction in aqueous media and acetonitrile and the acid equilibrium constant of $Cu(TAAB)^{2+}$ have been determined. The rate constant of the outer-sphere electron-transfer reaction is discussed in terms of the Marcus theory. The previously reported self-exchange kinetic parameters per one-electron couples $HA^{0/-}$ and $Cu(TAAB)^{2+/+}$ have been confirmed, and estimates of some other parameters of the electron self-exchange reactions and the cross-reactions are reported here.

Introduction

Electron-transfer reactions play an important role in many physical, chemical and biological processes. Consequently it is important to study the factors which determine their kinetic parameters. The results of such studies are usually interpreted by the Marcus theory, which serves as a theoretical model for outer-sphere electron transfer [1–5]. A general formula has also been devised in which the electron-transfer rate constant is expressed as the product of nuclear, electronic and frequency factors [6].

In connection with electron transfer, a series of complexes as well as metalloproteins [7] have been studied. But there are few studies that include complexes containing synthetic macrocyclic ligands, which are characterized by slow solvolysis and permit systematic variation of theoretically important parameters such as standard free energy and distances between atom centres in chromophore [8].

The present paper deals with the electron-transfer reaction for the Cu(II) complex of a relatively inflexible macrocyclic tetrabenzo(b,f,j,n) (1,5,9,13)-tetraazacyclohexadecine (TAAB) ligand which is an analog of superoxodismutase [9]. The application of the Marcus theory to the $Cu(TAAB)^{2+}$ complex redox reactions is of interest since, to our knowledge, this theory has not previously been used to explain redox processes of Cu(II) complexes. (The majority of these complexes, especially the non-chelate ones, are kinetically labile in the substitution reactions.) The $Cu(TAAB)^{2+}$ complex is also a convenient model because the axial interaction with its redox partner is weak and therefore meets the requirements of the outer-sphere electron transfer. The reaction partner is ascorbic acid, a widely occurring reagent in chemical and biological systems as well as in photoconversion. The aim of this work is to verify the applicability of the theoretical model to the mentioned system, especially in connection with the already existing description of ascorbic acid oxidation by a series of complexes using the Marcus approach [10, 11].

Experimental

L-ascorbic acid (Spofa, Prague) was used without further purification. $[Cu(TAAB)](NO_3)_2$ was prepared as described previously [12]. The other reagents employed were of analytical grade. The inert gas employed was incandescent lamp nitrogen.

The electron-transfer cross-reaction was studied by use of a Specord UV-Vis spectrophotometer (Zeiss, Jena). The $Cu(TAAB)^{2+}$ reduction was monitored at 658 nm. Solutions containing ascorbic acid were prepared immediately prior to use. An excess of ascorbic acid over Cu(II) complex concentration was employed. The Britton–Robinson buffer solutions with the ionic strength maintained at 0.1 M by the addition of KNO_3 were employed. The kinetic measurements were performed in anaerobic conditions and at three temperatures between 20 and 35 °C, with termostating (±0.1 °C) provided by an external water bath.

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Potentiometric measurements were made with a pH-meter, Type OP-201/2 (Radelkis, Budapest), using glass and saturated calomel electrodes. Voltammetric measurements were made with an OH-102 type polarograph (Radelkis, Budapest). A three compartment cell containing dropping mercury ($t_1 = 5.4$ s, $m_r = 7.7 \times 10^{-4}$ g s^{-1}, $h = 53$ cm), platinum counter, and saturated calomel reference electrodes was employed.

Results

The stoichiometry of the Cu(TAAB)$^{2+}$ reaction with ascorbic acid has been determined by monitoring the spectrophotometric titration of Cu(TAAB)$^{2+}$ with ascorbic acid in a buffer solution of pH = 3.5. A one-electron reduction of 1 mol of Cu(TAAB)$^{2+}$ requires 0.5 mol of ascorbic acid; thus the entire stoichiometry may be expressed as follows:

$$2\text{Cu(TAAB)}^{2+} + \text{H}_2\text{A} \longrightarrow \text{Cu(TAAB)}^{+} + \text{A} + 2\text{H}^{+} \quad (1)$$

where H_2A represents the ascorbic acid and A the dehydroascorbic acid.

The reaction kinetics were studied previously [13, 14]. From the dependence of $\ln(A_\infty - A_t)$ on time, the partial reaction order was determined, with regard to the Cu(TAAB)$^{2+}$ concentration, to be one, and observed rate constant values k_o have been calculated.

Evaluating the data of the k_o dependence on total ascorbic acid concentration ($c(H_2A) = 1.5 \times 10^{-3}$ up to 3.6×10^{-2} M) as well as on pH (2.8 up to 3.5), the following expression has been obtained:

$$k_o = \left(\frac{kK_{as}c(\text{H}_2\text{A})}{1 + K_{as}c(\text{H}_2\text{A})}\right)\left(\frac{1}{a(\text{H}^+)}\right) \quad (2)$$

where $k = 1.5 \times 10^{-6}$ M s^{-1}, $K_{as} = 350$ at 25.0 °C [13]. In the region of low H_2A concentrations [14], dependence k_o on $c(H_2A)$ is linear, and eqn. (2) is modified to the form

$$k_o = k_b c(\text{H}_2\text{A})/a(\text{H}^+) \quad (3)$$

The dependence of rate constants k_b on temperature is presented in Table I.

The dependence of the observed rate constant k_o on ionic strength μ within the range of μ between 0.1 and 1.0 M at pH = 3.0 and 25.0 °C was applied to the Debye–Hückel equation giving

$$\log k_o = -2.2 - \frac{2.1(\mu)^{1/2}}{1 + 1.4(\mu)^{1/2}} \quad (4)$$

(correlation coefficient $r = 0.9990$) [13]. The slope parameter of -2.1 in eqn. (4) is proof that oppositely-charged particles (2+ and 1–) do take part in the reaction.

TABLE I. Kinetic Parameters of the Electron-transfer Reaction between Cu(TAAB)$^{2+}$ Complex and Ascorbate Anion, $\mu = 0.1$ M.

T (°C)	$10^4 \times k_b$ (s^{-1})	k_{12} (M^{-1} s^{-1})	$H^{\neq}$ (kcal mol^{-1})	$S^{\neq}$ (cal mol^{-1} deg^{-1})
20.0	4.2	5.8		
25.0	5.3	7.1	6.2	−34
35.0	9.3	10.3		

The ascorbic acid dissociation constant $K_1 = 1.17 \times 10^{-4}$ has been determined at 35.0 °C and at ionic strength 0.1 M by potentiometric titration with NaOH. Acid (electrophilic) properties of the Cu(TAAB)$^{2+}$ complex have been studied by potentiometric titration with NaOH in the absence of CO_3^{2-} ions or CO_2 molecules. The monitored potential jump leads to the equilibrium constant value $K = 1.4 \times 10^{-7}$ at 25.0 °C.

Polarographic measurement was used to monitor Cu(TAAB)$^{2+}$ reduction in a Britton–Robinson buffer solution of pH = 3.5 (25.0 °C, $\mu = 0.1$ M). The electrode process of the first reduction step is quasi-reversible, and the value $E_{1/2} = 0.23$ V *vs.* SHE. The corresponding half-wave potential in acetonitrile $E_{1/2} = 0.37$ V *vs.* SHE, which is in agreement with the value obtained for the platinum electrode [15].

Discussion

Independent detailed studies [13, 16] have confirmed that when Cu(TAAB)$^{2+}$ reacts with ascorbic acid, it is reduced with the exchange of one electron, while the ascorbic acid is oxidized in two one-electron steps, including ascorbate radical, to preduce dehydroascorbic acid. This is in agreement with the stoichiometry determined here. The increase of the observed rate constant with H$^+$ reciprocal activity is generally taken as evidence that the ascorbate anion ($pK_1 = 4.04$ and $pK_2 = 11.3$ at 25.0 °C and 0.1 M ionic strength [17]) reacts in the rate determining step. The acid-dependent path is especially typcial for complexes with a low reduction potential [10] such as that of Cu(TAAB)$^{2+}$. The slope parameter of eqn. (4) confirms the ascorbate anion participation in the electron-transfer reaction.

At higher values of the H$^+$ ion activity, eqn. (3) may be rewritten in the form

$$k_o = \frac{k_{12}K_1c(\text{H}_2\text{A})}{K_1 + a(\text{H}^+)} \quad (5)$$

where k_{12} is the cross-reaction rate constant and K_1 is the ascorbic acid dissociation constant. Equation (5) must be corrected for pH > 3.5 in connection with the reaction of the other form of Cu-

(TAAB)$^{2+}$ (acid equilibrium constant K). Rate constant values k_{12} at various temperatures and calculated activation parameters are presented in Table I. In computing, use was made of dissociation constant K_1 values for the ionic strength of 0.1 M, *viz.* 3.1×10^{-5} at 20.0 °C [10], 9.12×10^{-5} at 25.0 °C [17] and 1.17×10^{-4} at 35.0 °C (determined in this paper). The values of the activation parameters, in accordance with the conclusions of refs. 10 and 11, manifest the outer-sphere electron-transfer pathway.

Within the Marcus theory [1–5] the relation between the self-exchange rate constants k_{11} and k_{22} and the rate constant of the cross-reaction k_{12} is expressed as follows:

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \tag{6}$$

where

$$\log f_{12} = (\log K_{12})^2/4\log(k_{11}k_{22}/Z^2) \tag{7}$$

Symbol K_{12} stands for the cross-reaction equilibrium constant. Z is the collision frequency between two uncharged reactants in a solution, and may be calculated from the masses of the reactants and the distance of the centers of reactants in the activated complex $\bar{r}$ (assumed to be the sum of their mean radii r_1 and r_2).

In connection with the further calculations, it appears necessary to consider the radii values of the reactants. Assuming the ascorbic acid molecule to be spherical in shape, the ascorbate anion radius r_1 may be calculated from the specific mass and the relative molecular mass. Utilizing $d = 1.7$ g cm^{-3} for ascorbic acid, it was possible to obtain the value of $r_1 = 341$ pm, which is close to 345 pm derived from the volume of the ascorbic acid crystallographic unit cell [18]. In determining the Cu(TAAB)$^{2+}$ ion radius r_2, it is possible to utilize reported structural parameters of complexes [Pd(TAAB)](BF$_4$)$_2$ [19] and [Ni(TAAB)](BF$_4$)$_2$ [20]. The TAAB ligand system in both cases is decidedly saddle-shaped, the two opposite benzene groups always forming a saddle-like cavity, 270 pm deep, above and below the MN$_4$ chromophore surface. The central atom is located in the center of the four nitrogen donor atoms. The value of $r = 545$ pm was calculated from the specific mass d of these complexes as well as from the volume of their unit cells, and it will be considered as r_2.

However, the structure of Cu(TAAB)$^{2+}$ is such that it actually enables the ascorbic acid anion to approach the copper atom in the activated complex axially relative to the macrocyclic ligand. The copper atom radius may be determined on the basis of its effective charge in the Cu(TAAB)$^{2+}$ particle. This charge q(Cu) is connected with the electron bonding energy E_b(Cu) in the 2p$_{3/2}$ orbital according to the expression

$$E_b(\text{Cu}) = 1.52q(\text{Cu}) + 932.2 \tag{8}$$

where the energy values are given in eV and the charge values in proton units [21]. Values $E_b(\text{Cu}) = 932.9 \pm 0.1$ eV and 935.4 ± 0.1 eV have been determined for the Cu(TAAB)$^+$ and Cu(TAAB)$^{2+}$ complexes, respectivley [22]; it follows that the copper atom charges are $q(\text{Cu}) \simeq 0.5$ and 2.0, respectively. Of the several Cu(II) complexes with N-donor ligands, the E_b(Cu) value is the highest for Cu(TAAB)$^{2+}$, and the central atom radius will evidently have the usual value for Cu^{2+}, *i.e.* 72 pm [23]. A small copper atom radius also follows from the comparison of Cu(TAAB)$^{2+}$ reduction potentials obtained in media with different dielectric constants ϵ (water and acetonitrile in this paper). According to the expression (9), obtained from the Born theory [24],

$$\Delta E \simeq -\frac{1.12 \times 10^{-6}}{r}\Delta\left(\frac{1}{\epsilon}\right) \tag{9}$$

the copper atom radius would be equal to 110 pm. All calculations in the present paper are based on the value of $\bar{r} = 345 + 72 = 417$ pm. The collision frequency in this case will be equal to 7×10^{10} M^{-1} s^{-1}. This value is close to $Z = 1 \times 10^{11}$ M^{-1} s^{-1}, which is usually taken for the second-order reaction and will also be used in this paper. Based on determined value of $\bar{r}$, the product $\beta\bar{r}$ in the Debye–Hückel equation can be theoretically calculated as $\beta\bar{r} = 1.37$ M$^{-1/2}$, which is close to the parameter 1.4 M$^{-1/2}$ of eqn. (4) and confirms the value of $\bar{r}$.

The explanation for the oxidation of ascorbic acid and its anions by inorganic complexes in terms of the Marcus theory [10, 11] has led to the estimation of the formal redox potentials and rate constants of the electron self-exchange reactions of one-electron couples H$_2$A$^{+/0}$, HA$^{0/-}$ and A$^{-/2-}$ (Table II). The Cu(TAAB)$^{2+}$ exchange rate constant $k_{22} = 5 \times 10^5$ M^{-1} s^{-1} was obtained independently [27]. The cross-reaction equilibrium constant K_{12} may be determined from the redox potentials. Assuming $E^0 \simeq E_{1/2}$, for values of $E_{1/2}(\text{Cu(TAAB)}^{2+}) = 0.23$ V and $E^0(\text{HA}^{0/-}) = 0.70$ V, we get $\log K_{12} = -7.905$, which is a very small but not unique value [10]. If we take the most probable value of $k_{11}(\text{HA}^{0/-})$ to be 1×10^5 M^{-1} s^{-1}, it then follows from eqns. (6) and (7) that at 25.0 °C the calculated value of k_{12} is 5.3 M^{-1} s^{-1}. This value is in good agreement with that derived experimentally, and can be taken as evidence for placing ascorbate anion oxidation by the Cu(TAAB)$^{2+}$ complex among the 34 cases of HA$^-$ oxidation by the Fe, Co, Ni, Os and Ir complex ions [11] (thermodynamic driving force function $\log(K_{12}f_{12})^{1/2} = -4.65$ and the corresponding $\log(k_{12},\ \exp/(k_{11}k_{22})^{1/2}) = -4.52$).

TABLE II. Parameters of the Self-exchange Electron-transfer Reaction of $HA^{0/-}$ and $Cu(TAAB)^{2+/+}$ Couples and of the Electron-transfer Cross-reaction between $Cu(TAAB)^{2+}$ Complex and HA^- at 25.0 °C and $\mu = 0.1$ M.

Reaction	r (pm)	k ($M^{-1}\ s^{-1}$)	E^o (V *vs.* SHE)	$\Delta G^{o\ g}$ (kcal mol^{-1})	ΔG^* (kcal mol^{-1})	w^j (kcal mol^{-1})	ΔG^{**} (kcal mol^{-1})
11	345^a	10^2–$10^{4\ b}$ $1 \times 10^{5\ c}$ $10^{6\ d}$	0.70^b 0.71^c 0.85–1.00^f	-16.2^g	8.2^h	0^j	8.2^k
22	545	$5.5 \times 10^{5\ e}$	0.23	-5.4^g	7.2^h	0.4^j	6.9^k
12	417	7.1	−0.47	10.8^g	13.5^i	-1.4^j	7.6^l

[a] Ref. 18. [b] Ref. 25. [c] Ref. 11. [d] Ref. 26. [e] Ref. 27. [f] Ref. 10. [g] Calculated from E^o values. [h] Calculated in the reverse manner from eqn. (10). [i] Calculated using eqn. (15). [j] Calculated using eqn. (13). [k] Calculated from ΔG^* and w values using eqn. (11). [l] Calculated using eqn. (14).

From the activation parameters in Table I, it follows that at 25.0 °C the value of activation free energy $\Delta G_{12}^{\neq}$ is equal to 16.3 kcal mol^{-1}. From this quantity, after correction for the loss in rotational and translational degrees of freedom in forming the activated complex, using the equation

$$\Delta G_{12}^* = \Delta G_{12}^{\neq} + RT\ \ln(hZ/k_BT) \tag{10}$$

the value of ΔG_{12}^* is found to be 13.9 kcal mol^{-1}.

The k_{12} rate constant and ΔG_{12}^* activation free energy relation-ship is defined by the outer-sphere electron-transfer theoretical model [4] as follows:

$$k_{12} = Z\ \exp(-\Delta G_{12}^*/RT) \tag{11}$$

$$\Delta G_{12}^* = w_{12} + \Delta G_{in}^* + \Delta G_{out}^* = w_{12} + \Delta G_{12}^{**} \tag{12}$$

The term w_{12} expresses the work required to bring the reactants to the position suitable for the reaction (distance $\bar{r}$) and terms ΔG_{in}^* and ΔG_{out}^* denote the energy contributions required for the reorganization of the inner coordination and outer solvation spheres of reactants, respectively, to obtain the configuration in which an electron may be transfered (often expressed as the reorganization parameter $\lambda = \lambda_{in} + \lambda_{out} = 4\Delta G_{12}^{**}$). The value of $w_{12} = -1.4$ kcal mol^{-1} is obtained when calculated using the equation

$$w = \frac{z_1 z_2 e^2 N}{D_s \bar{r}(1 + \kappa \bar{r})} \tag{13}$$

where the symbols z_1 and z_2 are used for formal charges of the reactants, e is the electron charge, D_s is the static dielectric constant of solvent, and $\kappa = 1.04 \times 10^7\ cm^{-1}$ is the reciprocal Debye radius. However, contributions of the reorganization energy are not easy to calculate directly because it is difficult to determine the real radii and breathing force constants of the given reactants.

At the same time, the reorganization energy contribution ΔG_{12}^{**} may be expressed as

$$\Delta G_{12}^{**} = (\Delta G_{11}^{**} + \Delta G_{22}^{**})/2 = (\lambda_{11} + \lambda_{22})/8 \tag{14}$$

where ΔG_{11}^{**} (= $\Delta G_{11}^* - w_{11}$) and ΔG_{22}^{**} (= $\Delta G_{22}^* - w_{22}$) are reorganization contributions to the activation energy of the electron self-exchange reactions. Using the independent data for k_{11} and k_{22} (Table II), the values $\Delta G_{11}^* = 8.2$ kcal mol^{-1} and $\Delta G_{22}^* = 7.2$ kcal mol^{-1} were calculated in the reverse manner from eqn. (10). Assuming the work terms $w_{11} = 0$ (0-charge of $HA^{\bullet}$ radical) and $w_{22} = 0.4$ kcal mol^{-1} ($r_2 = 545$ pm), we get $\Delta G_{11}^{**} = 8.2$ kcal mol^{-1} and $\Delta G_{22}^{**} = 6.9$ kcal mol^{-1}. The reorganization energy $\Delta G_{12}^{**} = 7.6$ kcal mol^{-1} can be calculated according to eqn. (14); *i.e.* $\lambda = 30.2$ kcal mol^{-1}.

The activation free energy ΔG_{12}^* may be calculated from the values of parameter λ and from the net change of free energy ΔG_{12}^o (= $\Delta G_{12}^* - \Delta G_{21}^*$) using the Marcus equation

$$\Delta G_{12}^* = w_{12} + \lambda[1 + (\Delta G_{12}^o + w_{21} + w_{12})/\lambda]^2/4 \tag{15}$$

The work term $w_{21} = 0$ with respect to the 0-charge of the $HA^{\bullet}$ radical. Starting from the known redox potential values (Table II), we get $\Delta G_{12}^o = 10.8$ kcal mol^{-1} and $\Delta G_{12}^* = 13.5$ kcal mol^{-1}.

The values of ΔG_{11}^{**} and λ obtained here are somewhat higher than those previously reported for ascorbate anion oxidation (4 kcal mol^{-1} and 11–26 kcal mol^{-1}, respectively [10]). However, the comparison between the ΔG_{12}^* value calculated from the parameter λ and that of ΔG_{12}^* obtained experimentally is satisfactory. From the eqn. (11) we get $k_{12,calc} = 12.5\ M^{-1}\ s^{-1}$, which is very close to that of $k_{12,exp}$ (Table I).

The investigation of the kinetic behavior of ascorbic acid toward the Cu(II)–macrocyclic complex has confirmed that the Marcus theory may also be used for the interpretation of electron transfer between non-spherical particles.

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