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The Kinetics of Cerium(IV) Sulfate Reaction with Citrate and the Thermodynamic Characteristics of Formation of Intermediate Complexes

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Abstract—Intermediate cerium(IV)–citrate complexes formed at the first stage of the oxidation of citric acid (Citr) with cerium(IV) were studied spectrophotometrically and pH-potentiometrically at ionic strength $I = 2$ (sulfate medium). Their composition and the form of the organic ligand present in them, the thermodynamic parameters of their formation, and the kinetic parameters of intramolecular redox decomposition were determined. A detailed scheme of the initial stages of the redox process in the $Ce^{4+}–SO_4^{2-}$ –Citr system was considered, and the law of its initial rate and intermediate mechanism were determined. The results were compared with the corresponding data on several oxycarboxylic acids and polyhydric alcohols. The inverse linear correlation was found between the logarithms of stability constants and the logarithms of rate constants for intramolecular redox decomposition of $[(CeOH)H_{-2}R]^+$ complexes with dibasic ligands of the type $R = H_2L$, $H(OH)L$, and $L(OH)_2$. The stabilizing role played by ligand oxy groups in these complexes was demonstrated.

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INTRODUCTION

Interactions of cerium(IV) with organic compounds are extensively studied [1–19]. These studies are of interest from both kinetic [1–22] and thermodynamic [5, 8, 23–26] points of view and are of considerable importance in relation to the problem of the stabilization of unstable oxidation states of metals [26–28] and numerous applications of cerium(IV) in various domains of chemistry as a complex-forming agent on the one hand and a one-electron oxidizer on the other [1, 25].

The oxidation of aliphatic organic substances with an active methylene group by cerium (the first stage of the Belousov–Zhabotinskii (BZh) autooscillating reaction) [1–4, 7, 9, 29–37] is of special interest. Concentration oscillations in the BZh reaction occur because of the alternation of two stages schematically written as

$$\mathrm{Ce(IV)} + \mathrm{R} = \mathrm{Ce(III)} + \mathrm{P}, \qquad (1)$$

$$\mathrm{Ce(III)} + \mathrm{BrO_3^-} = \mathrm{Ce(IV)} + \mathrm{P'}, \qquad (2)$$

where R is the reducing agent and P and P' are the reaction products [31]. Oxycarboxylic and dicarboxylic acid (citric [3, 29–31], malic [3, 30], oxalic [3, 7], malonic [2, 3], and methylmalonic [1, 4]), β-diketonates [28], saccharides [4], alcohols [6], etc. can play the role of reducing agents. Oxidizers can be cerium(IV) and one-electron oxidizers (e.g., Mn(III)) close to it in the redox potential value and the kinetics of redox reactions [30].

The detailed mechanism of the BZh reaction is very complex and includes dozens of intermediate compounds. Its study is based on the so-called Field–Koros–Noyes (FKN) theory [32] and its subsequent developments [33–35]; it was the object of numerous studies [1–4, 7, 9, 31–36]. The radical mechanism [2, 3] and the intermediate and final products of the oxidation of malonic acid $CH_2(COOH)_2$ [3, 4] and its derivatives [1, 4], oxalic $(COOH)_2$ [3, 7, 38], citric $HOOCCH_2C(OH)(COOH)CH_2COOH$ [18–21], malic $HOOCHC(OH)CH_2COOH$, tartaric $(CH(OH)COOH)_2$ [3, 5] and other carboxylic acids by cerium (IV) as the first stage of BZh reaction (1) have been actively studied. The possibility of formation of intermediate organocerium(IV) complexes in the BZh reaction was mentioned in several works [1, 4, 31, 32]. However, most of these complexes have not been identified and their structure, reactivity, and thermodynamic stability have not been determined.

It is known from kinetic studies that polar organic compounds (oxycarboxylic acids, alcohols, ketones, etc.) are oxidized by variable-valence metal ions (Ce(IV), Mn(III), …) according to the one-electron mechanism, which as a rule includes two stages. First, an organic compound enters into the coordination sphere of the ion-oxidizer in an equilibrium reaction, and a redox process then occurs in this complex, which is the rate-limiting stage [1, 4, 20–22, 31, 32],

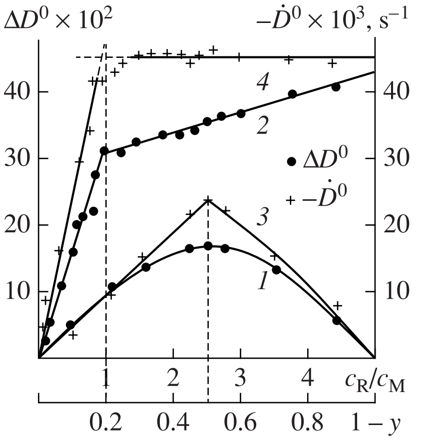

Fig. 1. (*1*, *2*) ΔD^0—composition and (*3*, *4*) $-\dot{D}^0$—composition diagrams: (*1*, *3*) isomolar series of solutions ($c = 1.00 \times 10^{-2}$ mol/l, pH 1.44, $I = 2$, $T = 23.0$°C, $\lambda = 400$ nm), y is the mole fraction of the ligand and (*2*, *4*) series of molar ratios ($c_M = 2.8 \times 10^{-3}$ mol/l, pH 2.23, $I = 2$, $T = 25.0$°C, $\lambda = 400$ nm).

$$\mathrm{M}^{n+1} + \mathrm{HR'} \overset{K'}{\rightleftharpoons} \mathrm{HR'}\ldots\mathrm{M}^{n+1} \xrightarrow{k} \mathrm{M}^{n+} + \cdot\mathrm{R'} + \mathrm{H}^+, \qquad (3)$$
$$K' = k_1/k_{-1}, \quad k_1 \gg k_{-1} > k.$$

However, kinetic data cannot be used to draw conclusions about the structure of this complex; we can only estimate the effective constants of its formation at a fixed pH value. These constants correspond to indefinite forms of the metal and ligand in the complex. Thermodynamic methods of study of preequilibrium (3) [23–25] cannot be used to determine the kinetic parameters of these complexes. Only kinetic generalizations of thermodynamic methods [5, 8], on the one hand, provide the possibility of directly determining the composition of intermediate complexes, the form in which organic ligands are present in them, and noneffective constants of their formation, which allows us to refine scheme (3). On the other hand, they can be used to study the reactivity of these complexes and the kinetics and mechanism of the initial stages of the redox process that occurs in the system.

In this work, this approach is applied to study the cerium(IV)–citrate reaction in a sulfuric acid medium. The results of earlier studies of the $\mathrm{Ce^{4+}}$–$\mathrm{SO_4^{2-}}$–Citr system were reported in [22–24]. In the context of more complex systems, this subsystem was considered in [3, 17–19, 29–31].

EXPERIMENTAL

We used doubly recrystallized citric acid of kh. ch. (chemically pure) grade and cerium(IV) sulfate $\mathrm{Ce(SO_4)_2 \cdot 4H_2O}$ of ch. d. a. (pure for analysis) grade. The $I = 2$ ionic strength of solutions was adjusted using ammonium sulfate of ch. d. a. grade. The concentration of solutions of the organic acid was refined by pH metric titration with a solution of NaOH which did not contain the $\mathrm{CO_3^{2-}}$ ion. The content of cerium(IV) in the salt and freshly prepared solution was determined by back titration with Mohr's salt in the presence of ferroin [39] before and after measurements. The optical density of solutions was recorded on a SPECORD UV VIS spectrophotometer in the extinction measurement mode at a constant wave number ($\lambda = 400$ nm) and a KF-5 photoelectrocolorimeter with a MEA-4 recording device. The reaction time was counted from the moment of turning a vessel-mixer, into which the initial components were placed.

The initial optical density of the reaction mixture of the metal and ligand D^0 was found by the linear extrapolation of kinetic curves in the $\log D$–τ semilogarithmic coordinates to the $\tau = 0$ time moment, because changes in the logarithm of the optical density in time obeyed a straight line equation. The initial rate of the observed redox process $-\dot{D}^0$ (s^{-1}) was estimated graphically in the same coordinates from the slope $\tan\alpha = (D^0 - D^i)/(\tau^0 - \tau^i) = \mathrm{const}$ and calculated by the method of least squares. Solutions were held at a constant temperature using a Wobser thermostat. pH of mixtures of components and solutions of cerium(IV) sulfate was measured by a DATA METER precision pH meter. Calculations were performed using the logarithms of protonization constants $B_i = [\mathrm{R}]/([\mathrm{H}_{-i}\mathrm{R}][\mathrm{H}]^i)$ of the citric acid ($\mathrm{H_{-2}R}$) anion, $\log B_1 = 4.17$ and $\log B_2 = 7.02$ [40].[1]

RESULTS AND DISCUSSION

The composition of intermediate complexes formed in the $\mathrm{Ce^{4+}}$–$\mathrm{SO_4^{2-}}$–Citr system at the moment of mixing reaction mixture components was determined from the property–composition diagrams by the generalized molar ratio and isomolar series methods [5, 8]. According to Fig. 1 (lines *1*, *2*), the position of an extremum on the axis of compositions corresponds to the formation in the system of a 1 : 1 cerium(IV)–citrate complex at the initial time. The initial rate of the redox process, which is a function of the yield of the complex,[2] was

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[1] Here and throughout, the index $-i(-x)$ in $\mathrm{H}_{-i}\mathrm{R}(\mathrm{H}_{-x}\mathrm{R})$ formulas denotes the number of dissociated protons (protons displaced from reducing molecule R by complex formation).

[2] Under the conditions of the predominance of one intermediate complex, the initial rate of the observed redox process is determined by the equation $-\dot{D}^0 = k_{\mathrm{obs}} c_C^0 = k_{\mathrm{obs}} \alpha_C^0 c_M$ at $c_M < c_R$ and $-\dot{D}^0 = k_{\mathrm{obs}} c_C^0 = k_{\mathrm{obs}} \alpha_C^0 c_R$ at $c_R < c_M$, where c_M and c_R are the initial concentrations of the metal ion and ligand; $\alpha_M^0 = \Delta D^0/(D_\infty^0 - D_M)$, c_C^0 is the yield and concentration of the complex at time $\tau = 0$; D_∞^0, and D_M are light absorption by the reaction mixture at $\alpha_C^0 = 1$ and metal, respectively; and $\Delta D^0 = D^0 - D_M$ [5].

determined by the generalized isomolar series and molar ratio methods. This rate reached a maximum simultaneously with the maximum yield of the complex at the stoichiometric ratio between the reagents. This was also evidence of the formation of a 1 : 1 intermediate complex in the system (Fig. 1, lines *3*, *4*). Note that the position of an extremum in the $-\dot{D}^0$, D^0—composition diagrams remains constant until the depth of the observed redox process reaches $\xi \sim 0.9$. The data on the composition of the complex are in agreement with the results obtained in [24] and can be considered a proof of the validity of the suggestion of the formation of a 1 : 1 intermediate complex in the oxidation of citric acid by cerium(IV) [22, 31].

The form in which the coordinated ligand was present in the complex and the stability constant of the complex were determined by analyzing the property–medium pH diagram (Fig. 2, lines *1*–*4*) and by additionally analyzing the kinetic data. The predominant form of cerium(IV) against the sulfate background at pH studied is the monohydroxo form $M^{n+1} = CeOH^{3+}$ [41–43]. The number of protons x displaced from the R = Citr molecule by the cerium(IV) ion when equilibrium

$$CeOH^{3+} + Citr \overset{K}{\rightleftharpoons} [(CeOH)H_{-x}Citr]^{3-x} + xH^+,$$
$$K = \frac{[(CeOH)H_{-x}Citr][H]^x}{[CeOH][Citr]} = \beta_{ef}[H]^x \qquad (4)$$

was established (charges are omitted for simplicity) was estimated graphically as the slope of the dependence of $\log\beta_{ef}$ on pH,

$$\log\beta_{ef} = \log K + x\text{pH}. \qquad (5)$$

It follows from an analysis of the dependence of $\log\beta_{ef}$ on pH (Fig. 2, line *3*) that the $CeOH^{3+}$ ion displaces two protons ($x = 2$) from the citric acid molecule as a result of complex formation. Most probably, two carboxylic groups of citric acid participate in complex formation. The result obtained for the form in which citric acid is present in the cerium(IV)–citrate complex proves the validity of the suggestion made in [22] of the chelate structure of the intermediate complex in the cerium(IV)–citrate reaction.

According to the data obtained, complex formation preequilibrium in the $Ce^{4+}–SO_4^{2-}$–Citr system can be represented as

$$CeOH^{3+} + H_{-2}Citr^{2-} \overset{\beta}{\rightleftharpoons} [(CeOH)H_{-2}Citr]^+. \qquad (6)$$

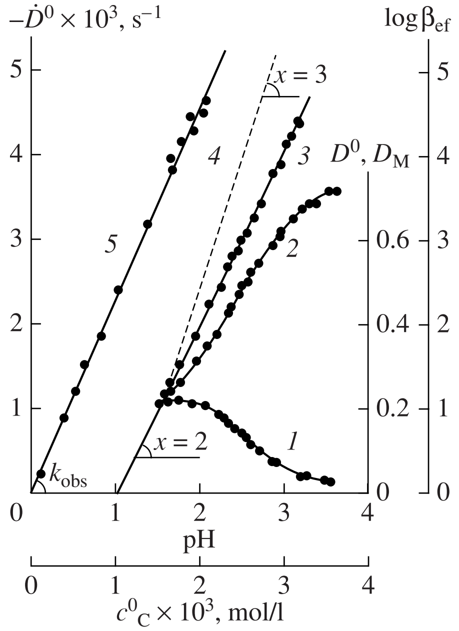


Fig. 2. (*1*) D_M – pH, (*2*) D^0 – pH, and (*3*) $\log\beta_{ef}$ – pH diagrams for the $Ce^{4+}–SO_4^{2-}$–Citr system ($c_M = 3.0 \times 10^{-3}$ mol/l, $c_R = 3.0 \times 10^{-3}$ mol/l, $I = 2$, $T = 25.0$°C, $\lambda = 400$ nm), (*4*) $\log\beta_{ef}$ – pH diagram for the $Ce^{4+}–SO_4^{2-}$–Malt system ($c_M = 2.1 \times 10^{-3}$ mol/l, $c_R = 2.0 \times 10^{-3}$ mol/l, $I = 2$, $T = 17.7$°C, $\lambda = 400$ nm), and (*5*) $\dot{D}^0 - c^0_C$ diagram for the $Ce^{4+}–SO_4^{2-}$–Citr system ($c_M = 2.8 \times 10^{-3}$ mol/l, pH 2.23, $I = 2$, $T = 25.0$°C, $\lambda = 400$ nm).

The corresponding equilibrium constant

$$\beta = \frac{[(CeOH)H_{-2}Citr]}{[CeOH][H_{-2}Citr]} = \frac{c^0_C}{(c_M - c^0_C)(c_R - c^0_C)} f_2$$
$$= \beta_{ef} f_2, \qquad (7)$$
$$f_2 = 1 + \sum_{i=1}^{2} B_i[H]^i,$$

was calculated for every point of the $\log\beta = \log\beta_{ef} + \log f_2$ dependence. The $\log\beta$ values were then averaged over D^0 – pH data series and the ascending portion of the molar ratio diagrams (table). The $\log\beta$ value found for the cerium(IV)–citrate complex against the sulfate background by the D^0 – pH and molar ratio methods was $\log\beta = 5.34 \pm 0.15$ (table). The $K_m = 0.67 \approx \beta_{ef}^{-1}$ value estimated in [30] is an effective value corresponding to an indefinite form of the presence of the reagents in the cerium(IV)–citrate complex. The $\log\beta$ value obtained for the $[(CeOH)H_{-x}R]^{3-x}$ com-

Stability constants and rate constant for the redox decomposition of the cerium(IV)–citrate complex

D^0	D_M	pH	$\log\beta_{ef}$	$\log\beta$	D^0	$-\log(-\dot{D}^0)$	c_R/c_M	$\log\beta$	$-\log k_C$
0.227	0.207	1.52	1.17	5.17	0.285	2.89	0.29	5.45	1.99
0.235	0.208	1.61	1.31	5.14	0.330	2.83	0.44	5.49	1.99
0.255	0.210	1.73	1.57	5.18	0.375	2.56	0.59	5.54	1.98
0.292	0.208	1.90	1.86	5.13	0.410	2.49	0.74	5.54	1.98
0.350	0.208	2.06	2.28	5.24	0.450	2.35	0.89	5.58	1.99
0.370	0.191	2.21	2.45	5.14	0.475	2.41	1.04	5.56	1.99
0.415	0.177	2.28	2.71	5.27	0.500	2.38	1.18	5.58	2.00
0.420	0.174	2.33	2.74	5.22	0.515	2.36	1.33	5.55	2.00
0.430	0.161	2.37	2.82	5.23	0.519	2.35	1.48	5.48	2.00
0.440	0.161	2.40	2.87	5.22	0.525	2.35	1.63	5.44	2.03
0.460	0.142	2.45	3.01	5.28	0.525	2.37	1.78	5.38	2.05
0.465	0.132	2.53	3.06	5.19	0.525	2.35	1.93	5.33	2.01
0.495	0.111	2.58	3.25	5.30	0.539	2.36	2.07	5.34	2.02
0.515	0.102	2.66	3.38	5.30	0.530	2.36	2.22	5.26	2.02
0.575	0.069	2.85	3.83	5.46	0.550	2.36	2.37	5.30	2.04
0.583	0.074	2.90	3.89	5.45	0.545	2.37	2.52	5.18	2.02
0.585	0.069	2.91	3.92	5.46	0.550	2.35	2.67	5.23	2.02

Note: $x = 2$, $\log\beta = 5.34 \pm 0.15$, and $\log k_C = -2.01 \pm 0.03$ (25.0°C).

plex with R = Citr and $x = 2$ (Fig. 2, line *3*) is much lower than the corresponding value $\log\beta = 18.39 \pm 0.18$ for the complex of cerium(IV) with malic acid (R = Malt, $x = 3$, Fig. 2, line *4*) [5]. The multiple-charge $CeOH^{3+}$ ion displaces the alcohol hydroxyl proton along with protons of two carboxyl groups from the malic acid molecule and forms a complex with the malate ion much more stable than the complex with the citrate ion. The difference in the structure and stability of cerium(IV)–citrate and cerium(IV)–malate intermediate complexes can be the reason for the well known difference between the oscillation regimes of the BZh reaction for citric and malic acids [30].

The rate constant for the redox decomposition of $[(CeOH)H_{-2}Citr]^+$ complexes was calculated from the $-\dot{D}^0$, $D^0 - c_R/c_M$ data series (table) using the equilibrium concentration of the complex at time $\tau = 0$ calculated from the $D^0 - c_R/c_M$ data series. The logarithm of the observed rate constant for the intramolecular redox decomposition of the complex was analytically calculated at each point of the dependence

$$\log k_{\text{obs}} = \log\dot{D}^0 - \log c_C^0 \quad (8)$$

with subsequent averaging of the $\log k_{\text{obs}}$ values (table). The k_{obs} value was also estimated graphically by the $-\dot{D}^0$, $D^0 - c_R/c_M$ method. For this purpose, the

$$-\dot{D}^0 = A + k_{\text{obs}}c_C^0 \quad (9)$$

dependence was plotted (Fig. 2, line *5*). Since the effective rate constant for the redox decomposition of the complex k_{obs}, l/(mol s), depends on the extinction coefficient ε_C ($k_{\text{obs}} = \varepsilon_C l k_C$, where l is the thickness of the absorbing solution layer), we also calculated the logarithm of the true rate constant k_C, s^{-1}, for the redox decomposition of the complex,

$$\log k_C = \log k_{\text{obs}} - \log\varepsilon_C l. \quad (10)$$

The extinction coefficient of the complex was determined by the Beneshi–Hildebrand method [42].

It follows from an analysis of the dependence of $-\dot{D}^0$ on the concentration of the complex c_C^0 (Fig. 2, line *5*) and the constant value of $\log k_C$ calculated from the $-\dot{D}^0$, $D^0 - c_R/c_M$ data series (table) that one intermediate complex predominates in the system. The equality to zero of the free term of Eq. (9) can be evidence of the absence of a bimolecular reaction contribution to the redox process (see Fig. 2, line *5*). It follows that the law of the rate of the observed redox reaction is

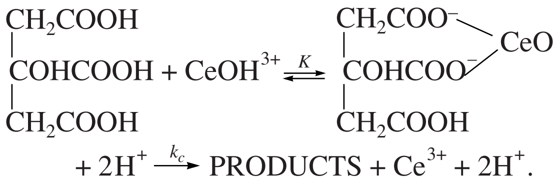
$$-\dot{D}^0 = \varepsilon_C l k_C c_C^0, \quad (11)$$

and the intermediate mechanism is the mechanism of the process.

Taking (4) and (7) into account, Eq. (11) can be rewritten as

$$-\frac{dc_M}{dt} = k_C K[CeOH^{3+}][Citr][H^+]^{-2} = k_C\beta[CeOH^{3+}][H_{-2}Citr^{2-}]. \quad (12)$$

Equation (12) establishes a functional dependence of the rate on the equilibrium concentration of hydrogen ions in solution. It is in agreement with the general form of the rate equation $-d[Ce(IV)]/dt = k'[Ce(IV)][Citr]$ [22] and the inverse quadratic dependence of the rate pseudoconstant k' on the equilibrium concentration of hydrogen ions in solution also obtained in [22]. According to (12), the latter dependence can be described by the equation $k' = k_C K/[H^+]^2$. The form of Eq. (12) shows that the form of the reagents participating in the elementary redox event is $R = H_{-2}Citr^{2-}$, $M^{n+1} = CeOH^{3+}$ rather than $R = Citr$, $M^{n+1} = Ce(OH)_2^{2+}$ as suggested in [22]. This modifies the reaction scheme suggested in [22] for the initial redox process stages as follows:



$$\begin{array}{l} CH_2COOH \\ | \\ COHCOOH \\ | \\ CH_2COOH \end{array} + CeOH^{3+} \overset{K}{\rightleftarrows} \begin{array}{l} CH_2COO^- \\ | \\ COHCOO^- \\ | \\ CH_2COOH \end{array} CeOH^{3+} + 2H^+ \xrightarrow{k_C} PRODUCTS + Ce^{3+} + 2H^+. \quad (13)$$

The $\log k_C = 1.99 \pm 0.03$ (25°C) value found for the $[(CeOH)H_{-2}Citr]^+$ complex coincides in the order of magnitude with the logarithm of the rate constant for the oxidation of malonic [32] and oxalic [38] dicarboxylic acids that do not contain oxy groups in molecules with cerium(IV), which substantiates the participation of just carboxyl groups in the formation of the cerium–citrate complex. This leads us to suggest a similar structure for the complex of cerium(IV) with malonic acid. This value is higher than $\log k_C = \bar{3}.40 \pm 0.04$ for cerium(IV) complexes with α-oxycarboxylic acids formed with the displacement of the alcohol hydroxyl proton [5] and is larger by two orders of magnitude than the $\log k_C = \bar{4}.2 \pm 0.1$ value for the corresponding $[(CeOH)H_{-2}R]^+$ complexes with aliphatic polyhydric alcohols ($R = Alk_n$, $n = \overline{3, 6}$) [8]. A comparison of the kinetic data on this series of organic substances additionally substantiates the suggestion that, as distinct from the α-oxycarboxylic acids considered earlier (malic, tartaric, lactic, etc.), citric acid interacts with cerium(IV) as a dicarboxylic acid.

The rate constants for the formation of intermediate cerium(IV) complexes with oxalic ($R = Ox$, $x = 2$, $\log\beta \sim 7.0$) [38], quinic ($R = Quin$, $x = 2$, $\log\beta \sim 15.0$), lactic ($R = Lact$, $x = 2$, $\log\beta \sim 15.0$), malic ($R = Malt$, $x = 3$, $\log\beta \sim 18.4$), and tartaric ($R = Tart$, $x = 4$, $\log\beta \sim 27.8$) carboxylic acids [5] and polyhydric alcohols ($R = Alk_n$, $n = \overline{3, 6}$, $x = 2$, $\log\beta \sim 22.4$) [8] and the $\log\beta$, and $\log k_C$ values obtained for the cerium(IV)–citrate complex allow us to establish an inverse linear correlation between the logarithms of stability constants and logarithms of the rate constants for the redox decomposition of the $[(CeOH)H_{-2}R]^+$ complexes with dibasic ligands of the type $R = H_2L$ = Citr, Ox; $R = H(OH)L$ = Lact, Quin; $R = L(OH)_2 = Alk_n$, $n = \overline{3, 6}$ (Fig. 3, I). This correlation demonstrates the stabilizing action of the oxy groups of ligands in complexes with the predominantly ionic character of bonds.[3] An increase in the basicity of oxycarboxylic acids above two ($x > 2$) and, as a consequence, an increase in the thermodynamic stability of complexes does not influence their reactivity (Fig. 3, II). The correlation equation for $x = 2$ has the form $\log k_C = -(1.3 + 0.1\log\beta)$. It should, however, be used with care because of the statistical spread of values.

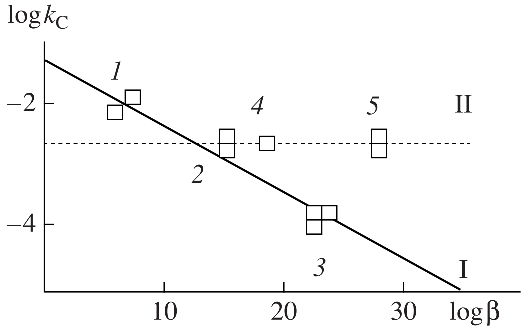


Fig. 3. $\log k_C - \log\beta$ correlation dependences: I, for complexes of the type $[(CeOH)H_{-2}R]^+$, R = (*1*) Citr and Ox, (*2*) R = Lact and Quin, and (*3*) $R = Alk_n$, and II, for complexes of the type $[(CeOH)H_{-x}R]^{3-x}$, $x > 2$, (*4*) R = Malt and (*5*) R = Tart.

The results obtained in this work lead us to suggest the existence of the corresponding correlations between the electrochemical and optical characteristics of $[(CeOH)H_{-x}R]^{3-x}$ complexes [27]. Studies of such correlations are currently at the initial stage but are well worth the effort.

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[3] For complexes with the predominantly covalent type of metal–ligand bonds ($M^{n+1} = Mn^{3+}$), the opposite dependence is observed [25].

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