Thermodynamic and Kinetic Parameters of Cerium(IV) Complexes with Some Dicarboxylic Acids

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Applications

The study of the thermodynamic parameters of the formation and the kinetic parameters of the redox decomposition of cerium(IV) complexes with organic ligands, as well as of related regularities, is of theoretical and practical interest. This is due to the widespread use of compounds of cerium(IV) in various fields of chemistry and technologies as a complexing agent, a one-electron oxidant, and a reaction catalyst[1]. The results obtained in the course of such studies have an independent significance and are fundamentally connected with the solution of direct problems of chemical equilibria and kinetics, the formation of kinetic and thermodynamic databases for modeling chemical reactions, and the invention and development of innovative chemical technologies.

- For instance, nanotechnology for the preparation of ultra-small cerium(IV) dioxide particles implemented through the intermediate stage of the formation of cerium(IV) complexes with polybasic acids, like succinic acid, is of great practical importance. Methods for the preparation of homogeneous cerium(IV) containing catalysts, catalytic compositions with cerium(IV) ions, and cerium (IV) oxide catalysts from process solutions containing cerium(IV) complexes with glutaric, succinic, malonic, and other dicarboxylic acids are patented[2].

[1] *Cerium: Molecular Structure, Technological Applications and Health Effects*, A. Izyumov and G. Plaksin, Eds., New York: Nova Science Publishers, Inc, 2013

[2] US Patent no. 7504357 B2, 2009; WO Patent no. 2014121813 A1, 2014

• Through the stage of the formation of a cerium(IV) complex with oxalic acid, innovative technologies for the production of high-purity cerium(IV) nitrate and high-purity cerium(IV) oxide (as the final product of selective separation of cerium(IV) from rare earth concentrate) are performed[3].

• The separation of cerium in the +4 oxidation state from rare earth elements in the +3 oxidation state is closely related to the problem of stabilization of unstable oxidation states of metals. Despite the urgency and great importance of finding a solution to this problem, no kinetic criteria for stabilizing the oxidation state of metals through complexation, unlike thermodynamic criteria, have yet been developed. Determination of the rate constants of the intramolecular redox decomposition of transition metal complexes creates the necessary basis for the development of these criteria.

• The systems Ce^{4+}–$(CH_2)_r(COOH)_2$, r=0-7, are used as initiators of radical polymerization of acrylamide, graft copolymerization of vinyl monomers, and block copolymerization of polyacrylonitrile with polyacrylamide[4]. It is assumed in this case that the redox decomposition of intermediate complexes $[CeH_2L]^{4+}$ is the common mechanism for the generation of primary free radicals by redox pairs cerium(IV)–organic acid (H_2L) Nevertheless, there are no available references that disclose the kinetic and thermodynamic characteristics, for example, for cerium(IV) succinate and cerium (IV) glutarate intermediate complexes.

[3] RF Patent no. 0002601763, 2016; RF Patent no. 0002576763, 2016

[4] C. Özeroglu and S. Sezgin, *Express Polym. Lett.*, 2007, vol. 1, no. 3, p. 132

• The quantitative determination of dicarboxylic acids (such as glutaric, succinic, methyl- and ethylmalonic, and oxalic) is demanded for the analysis of biomaterials[5] and drugs[6]. However, despite the widespread use of cerimetry in clinical and pharmaceutical analysis, there are no cerimetric methods for $\mathrm{H_2Glut}$ or $\mathrm{H_2Suc}$ (in contrast to $\mathrm{H_2Mal}$ and $\mathrm{H_2Ox}$). This can be explained by the well-known[7] assumption that ceric sulfate does not oxidize succinic and glutaric acids[8].

• The involvement of di- and tricarboxylic acids ($\mathrm{H_2Glut}$, $\mathrm{H_2Suc}$, $\mathrm{H_2Mal}$, etc.) in the Krebs cycle also predetermines the importance of developing inorganic models for their oxidation, in particular, using ceric sulfate, as was initiated in the works of B. Belousov and A. Zhabotinsky[9]. But whereas the main features of the 'inorganic subset' of the Belousov–Zhabotinsky reaction are rather clear, there are still some unknown details in its 'organic subset'. The formation of intermediate cerium(IV) complexes with dicarboxylic acids in the 'organic subset' of the BZ reaction had been long postulated. However, the later authors made no efforts to identify and characterize these species.

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[5] M.P. Narayanan et al., *Indian J. Clin. Biochem.*, 2011, vol. 26, no. 4, p. 347

[6] *Encyclopedia of Toxicology*, Amsterdam: Academic Press, 2014, vol. 3, p. 76

[7] I.M. Kolthoff, R. Belcher, V.A. Stanger, and G. Matsuyama, *Volumetric Analysis*, New York: Interscience, 1957

[8] N.N. Sharma and R.C. Mehrotra, *Anal. Chim. Acta*, 1954, vol. 11, p. 507

[9] In *Oscillations and Traveling Waves in Chemical Systems*, R.G. Field and M. Burger, Eds., New York: Interscience, 1985

• It is known from kinetic studies[10] that polar organic compounds (dicarboxylic acids, alcohols, ketones, etc.), $\mathrm{R = HL}$, are oxidized by variable-valence metal ions (Ce(IV), Mn(III), etc.) according to the one-electron mechanism, which as a rule includes two stages. First, an organic compound enters in the coordination sphere of the ion-oxidizer in an equilibrium reaction, and a intramolecular redox process then occurs in this intermediate, which is the rate-determining stage[11],

$$\begin{aligned} \mathrm{M^{q+} + HL} &\overset{\beta_1^{ef}}{\rightleftharpoons} \mathrm{HL \ldots M^{q+}} \overset{\mathrm{k_1}}{\rightarrow} \mathrm{M^{q-1} + H^+ + {\cdot}L}\,, \qquad (1) \\ \beta_1^{ef} &= k_{+1}/k_{-1}, \quad k_{-1} \gg k_{+1} \gg k_1\,. \end{aligned}$$

There is much data indicate that a intermediate complexes in this reaction certainly formed but there is little experimental evidence concerning the actual nature and features of these intermediate complexes. Kinetic data cannot be used to draw conclusions about the structure of this complex. They allow us only estimate the effective constants of its formation. Thermodynamic methods for studying the preequilibrium of (1) cannot be used to determine the kinetic parameters of these complexes.

[10] J.P. Candlin, K.A. Taylor, and D.T. Thompson, *Reactions of Transition Metal-Complexes*, Amsterdam: Elsevier, 1968; *Organic Reaction Mechanisms*, A.S. Knipe and W.E. Watts, Eds., Chichester: Wiley, 1981

[11] E.T. Denisov, *Rate Constants of Homolytic Liquid-Phase Reactions*; Science: Moscow, 1971

In view of the lack of accurate information on the intermediate complexes formed, of interest are some generalization for the methods commonly used to investigate the composition and stability of the complexes with cations in a stable oxidation state (OS) to the case of the complexes with cations in an unstable OS as well as their application to determining the composition of such complexes, the speciation of organic ligands in them, specified stability constants, intramolecular rate constants, and mechanism of numerous redox processes, for which the rate-determining step is the decay of an intermediate complex[12].

In the present work, we develop these techniques and apply them to a comparative study of the intermediate complexes formed in the cerium (IV) oxidation of some dicarboxylic (oxalic H_2Ox, malonic H_2Mal, succinic H_2Suc, and glutaric H_2Glut) acids at an ionic strength $I = 2$ in the pH range 0.4–1.6 of a sulfate medium, and a temperature of 20° C by UV-Vis spectroscopy and pH-measurements with the aid of the of integral kinetic methods.

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[12] O. O. Voskresenskaya and N. A. Skorik, *Thermodynamic and Kinetic Aspects of the Formation and Redox Decomposition of Cerium(IV) Complexes with a Series of Hydroxyl-containing Organic Ligands* (NTL, Tomsk, 2011)

Olga Voskresenskaya, *Kinetic and Thermodynamic Stability of Cerium(IV) Complexes with a Series of Aliphatic Organic Compounds* (Nova Science Publ., New York, 2013)

Composition of intermediate complexes

Determination of the composition of the complexes formed in the systems Ce^{4+}–H_2L at the moment of mixing of the reactants by the molar ratio method (Fig. 1) shows that in all systems, complexes characterized by a metal : ligand molar ratio of 1 : 1 are formed at the point $\tau = 0$.

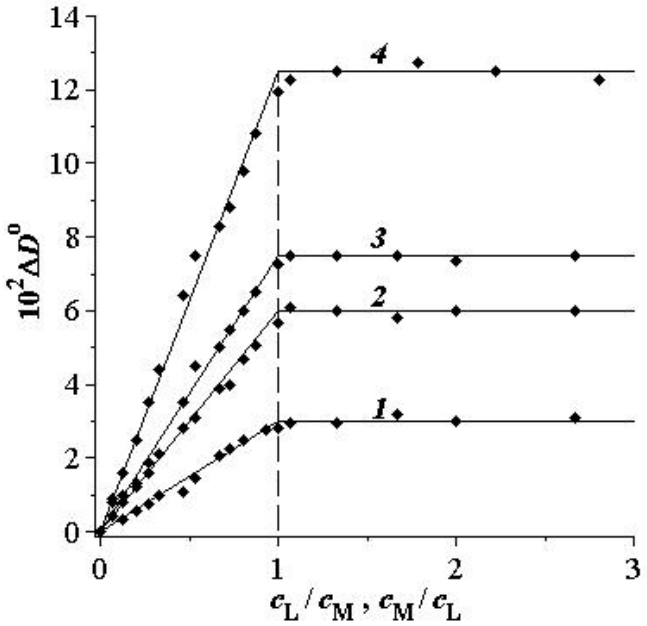


Figure 1: The dependence of the increment of the optical density on the c_L/c_M (c_M/c_L) ratio in the systems Ce^{4+}–H_2L at $\lambda = 400$ nm, pH 0.9–1.3, c_M 1.65–2.29 10^{-3} mol/L: $H_2L = H_2Glut$ (*1*), H_2Suc (*2*), H_2Mal (*3*), and H_2Ox (*4*).

Ligand speciation

The number of protons (z) displaced from $\mathrm{H_2L}$ molecules by a $\mathrm{CeOH^{3+}}$ ion at the establishment of the complexation equilibria

$$\mathrm{CeOH^{3+} + H_2L \overset{K_1}{\leftrightarrow} [CeOHH_{2-z}L]^{(3-z)+} + zH^+},$$

$$K_1 = \frac{[\mathrm{CeOHH_{2-z}L^{(3-z)+}}][\mathrm{H^+}]^z}{[\mathrm{CeOH^{3+}}][\mathrm{H_2L}]} = \beta_1^{\mathrm{ef}}[\mathrm{H^+}]^z \qquad (2)$$

was found as the slope of the linear dependence

$$\log \beta_1^{ef} = \log K_1 + zpH$$

as a result of the comparison of two or three $D^0 - pH$ data sets.

The examination of the $\log \beta_1^{ef}$ versus pH curves (Fig. 2) shows that the highly charged $\mathrm{CeOH^{3+}}$ ion displaces in the course of complexation two protons ($z = 2$) from the dicarboxylic acid molecules.

The latter can be accompanied by the formation of chelate complexes of the general formula $[\mathrm{CeOHL}]^+$ and the closure of the cycles: 5-membered in $[\mathrm{CeOHOx}]^+$, 6-membered in $[\mathrm{CeOHMal}]^+$, 7-membered in $[\mathrm{CeOHSuc}]^+$, and 8-membered in $[\mathrm{CeOHGlut}]^+$.

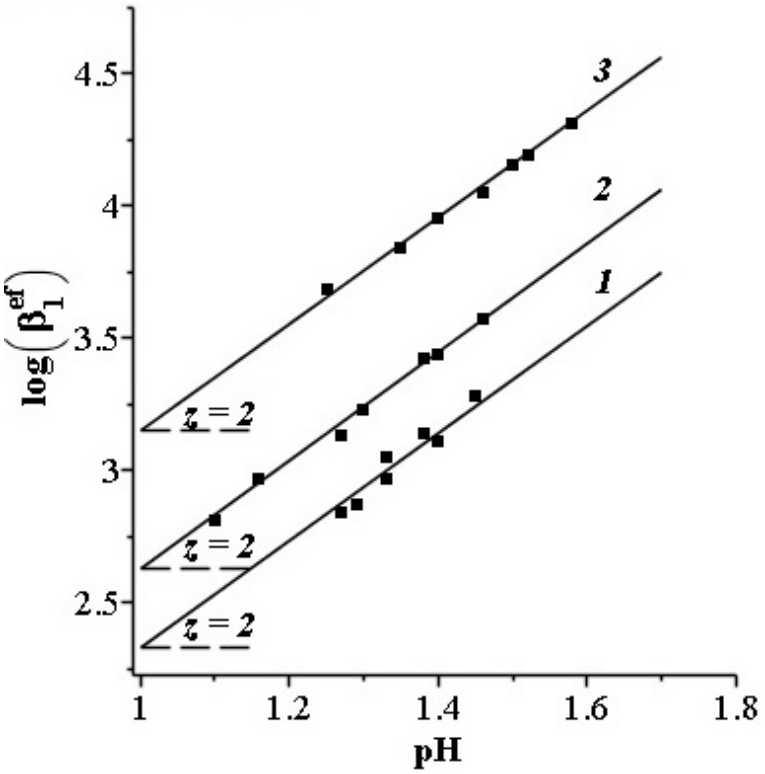


Figure 2: Diagrams of the dependence of the logarithm of the effective stability constant of complexes on the pH of the solution for systems Ce^{4+}–H_2L at $\lambda = 400$ nm and $c_M = c_L = 2.27 - 2.37\,10^{-3}$ mol/L: (*1*) $H_2L = H_2Glut$; (*2*) $H_2L = H_2Suc$; and (*3*) $H_2L = H_2Mal$.

An increase in the values of $\log \beta_1^{ef}$ in the series of complexes $[CeOHGlut]^+$, $[CeOHSuc]^+$, $[CeOHMal]^+$, and $[CeOHOx]^+$ can be associated with an increase in the stability of the cycle in these chelates during the transition from the 8-membered cycle in $[CeOHGlut]^+$ to the 5-membered cycle in $[CeOHOx]^+$.

Formation constants and redox decomposition rate constants

Table 1. The thermodynamic and kinetic parameters of the $[CeOHGlut]^+$ complex determined using integral kinetic method based on spectrophotometry and pH-potentiometry

D^0	D_M	$(\log D)'_\tau, s^{-1}$	pH	$\log k_1$	$\log \beta_1^{ef}$	$\log \beta_1$	$\log K_1$
0.363	0.340	$-3.41 \cdot 10^{-3}$	1.25	−2.10	2.82	9.92	0.32
0.363	0.340	$-3.42 \cdot 10^{-3}$	1.26	−2.10	2.82	9.91	0.30
0.364	0.341	$-3.45 \cdot 10^{-3}$	1.29	−2.10	2.85	9.88	0.27
0.368	0.343	$-3.71 \cdot 10^{-3}$	1.35	−2.07	3.07	9.98	0.37
0.372	0.344	$-3.70 \cdot 10^{-3}$	1.36	−2.07	2.98	9.87	0.26
0.375	0.345	$-3.80 \cdot 10^{-3}$	1.38	−2.06	3.14	9.99	0.38
0.380	0.349	$-4.21 \cdot 10^{-3}$	1.40	−2.01	3.11	9.92	0.31
0.389	0.352	$-4.21 \cdot 10^{-3}$	1.46	−2.01	3.32	10.01	0.40

* $\log \beta_1 = 9.93 \pm 0.05$, $\log K_1 = 0.33 \pm 0.05$, $\log k_1 = -2.07 \pm 0.03$
($\log k_1 = -2.09 \pm 0.04$ – by Ardon's method)

Tables 1, 2, 3, and 4 show the values of the formation constants and redox decomposition rate constants calculated from the data of the $D^0, (\log D)'_\tau - pH$ series in accordance with the procedure described in the section 'Experimental'.

Table 2. The thermodynamic and kinetic parameters of the $[\mathrm{CeOHSuc}]^+$ complex determined using integral kinetic method based on spectrophotometry and pH-potentiometry

D^0	D_M	$(\log D)'_\tau, s^{-1}$	pH	$\log k_1$	$\log \beta_1^{ef}$	$\log \beta_1$	$\log K_1$
0.364	0.339	$-3.59 \cdot 10^{-3}$	1.10	-2.08	2.82	9.83	0.62
0.369	0.340	$-4.10 \cdot 10^{-3}$	1.18	-2.03	2.98	9.84	0.62
0.375	0.340	$-4.23 \cdot 10^{-3}$	1.27	-2.01	3.14	9.81	0.60
0.378	0.341	$-4.21 \cdot 10^{-3}$	1.30	-2.11	3.27	9.88	0.66
0.383	0.347	$-4.37 \cdot 10^{-3}$	1.38	-2.00	3.42	9.87	0.67
0.384	0.349	$-4.25 \cdot 10^{-3}$	1.40	-2.01	3.44	9.85	0.64
0.385	0.352	$-4.51 \cdot 10^{-3}$	1.46	-1.98	3.57	9.86	0.65

$^*\log \beta_1 = 9.85 \pm 0.02$, $\log K_1 = 0.64 \pm 0.02$, $\log k_1 = -2.02 \pm 0.05$
($\log k_1 = -2.05 \pm 0.05$ – by Ardon's method)

The rate constants of the intracomplex redox decomposition of the first time order with respect to the complex $[\mathrm{CeOHL}]^+$, $k_1 = k_{n_\tau=1}$, determined from the data of series $(\log D)'_\tau - pH$, $(\log D)'_\tau - c_L/c_M$, and $(\log D)'_\tau - c_M/c_L$, where $(\log D)'_\tau$ is the derivative by time, and those obtained by Ardon's method (Fig. 3), agree well with one another.

Table 3. The thermodynamic and kinetic parameters of the $[CeOHMal]^+$ complex determined using integral kinetic method based on spectrophotometry and pH-potentiometry

D^0	D_M	$(\log D)'_\tau, s^{-1}$	pH	$\log k_1$	$\log \beta_1^{ef}$	$\log \beta_1$	$\log K_1$
0.396	0.340	$-4.51 \cdot 10^{-3}$	1.25	−1.99	3.69	9.25	1.19
0.399	0.343	$-4.80 \cdot 10^{-3}$	1.35	−1.96	3.83	9.20	1.13
0.402	0.348	$-5.24 \cdot 10^{-3}$	1.40	−1.92	3.96	9.21	1.16
0.404	0.350	$-5.37 \cdot 10^{-3}$	1.46	−1.91	4.09	9.22	1.17
0.405	0.353	$-5.61 \cdot 10^{-3}$	1.50	−1.98	4.14	9.21	1.14
0.406	0.354	$-5.77 \cdot 10^{-3}$	1.52	−1.88	4.22	9.25	1.18
0.407	0.354	$-5.80 \cdot 10^{-3}$	1.58	−1.87	4.33	9.25	1.17

$^*\log \beta_1 = 9.23 \pm 0.03$, $\log K_1 = 1.16 \pm 0.02$, $\log k_1 = -1.92 \pm 0.04$
($\log k_1 = -1.87 \pm 0.01$ – by differential method)

The values of $\log \beta_1$, determined from the data of the D^0–pH series, agree within the limits of the experimental error with the values obtained by the molar ratio method (for example, for $[CeOHMal]^+$ the molar ratio method yields: $\log \beta_1 = 9.22 \pm 0.06$). The consistency of the results of various methods for determining the stability constants serves as clear evidence of the correct consideration of the major equilibria in the solution.

Table 4. The thermodynamic and kinetic parameters of the complex $[\mathrm{CeOHOx}]^+$ determined using integral kinetic method based on spectrophotometry and pH-potentiometry

D^0	D_M	$(\log D)'_\tau, s^{-1}$	pH	$\log k_1$	$\log \beta_1^{ef}$	$\log \beta_1$	$\log K_1$
0.406	0.302	$-9.20 \cdot 10^{-3}$	0.39	-1.67	3.19	7.79	2.41
0.408	0.298	$-9.10 \cdot 10^{-3}$	0.55	-1.68	3.25	7.54	2.15
0.412	0.298	$-9.30 \cdot 10^{-3}$	0.63	-1.67	3.42	7.57	2.16
0.417	0.300	$-9.40 \cdot 10^{-3}$	0.71	-1.67	3.74	7.73	2.32
0.310	0.185	$-9.10 \cdot 10^{-3}$	0.33	-1.68	3.10	7.85	2.44
0.330	0.183	$-9.10 \cdot 10^{-3}$	0.54	-1.68	3.30	7.80	2.24
0.341	0.183	$-9.20 \cdot 10^{-3}$	0.65	-1.67	3.41	7.48	2.11
0.349	0.180	$-9.40 \cdot 10^{-3}$	0.78	-1.67	3.87	7.75	2.27

$^*\log \beta_1 = 7.67 \pm 0.14$, $\log K_1 = 2.27 \pm 0.13$, $\log k_1 = -1.68 \pm 0.01$
($\log k_1 = -1.70 \pm 0.05$ – by differential method)

For $[\mathrm{CeOHMal}]^+$ and $[\mathrm{CeOHOx}]^+$, the values of the rate constants k_1 (s^{-1}) determined by the integral method agree within the experimental error with the values of k_1 (s^{-1}) found by the differential kinetic method (see tables 4 and 3).

Michaelis–Menten kinetics

The consistency of the redox process occurring in the systems with Ardon's equation[13] (Fig. 3), a special case of the Briggs–Haldane equation describing the Michaelis–Menten kinetics, confirms the mechanism through intermediate of the redox process with the formation of an 1 : 1 intermediate complex.

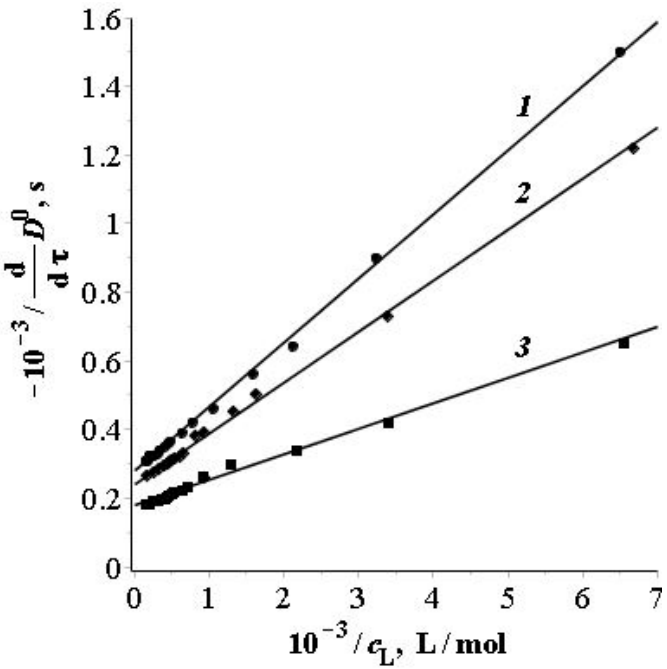


Figure 3: Dependence of the inverse initial rate of the complex redox decomposition on the initial inverse concentration of H_2L at pH 0.9–1.35 and c_M 2.28–2.37 10^{-3} mol/L for systems Ce^{4+}– H_2L: (*1*) $H_2L = H_2Glut$; (*2*) $H_2L = H_2Mal$; and (*3*) $H_2L = H_2Suc$.

[13] M. Ardon. *J. Chem. Soc.*, 4, 81 (1957)

Overall rate law

In view of (2), the concentration rate law $\partial[\mathrm{CeOHL^+}]/\partial\tau = \mathrm{k_1}[\mathrm{CeOHL^+}]$ for the oxidation of dicarboxylic acids by cerium(IV) can be represented as follows

$$-\frac{\partial[\mathrm{CeOHL^+}]}{\partial\tau} = k_1 \frac{K_1}{[\mathrm{H^+}]^2}[\mathrm{CeOH^{3+}}][\mathrm{H_2L}] = \beta_1[\mathrm{CeOH^{3+}}][\mathrm{L^{2-}}]\,. \tag{3}$$

Taking into account cerium(IV) complexation with background anions, it can be rewritten as

$$\frac{\partial[\mathrm{CeOH(SO_4)_3L^{5-}}]}{\partial\tau} = k_1\beta_1[\mathrm{CeOH(SO_4)_3^{3-}}][\mathrm{L^{2-}}]\,. \tag{4}$$

The latter equation can be converted to the form

$$\begin{aligned}\frac{\partial[\mathrm{CeOH(SO_4)_3L^{5-}}]}{\partial\tau} &= k_1\beta_1 \frac{\kappa_{1SO_4}\kappa_{2SO_4}\kappa_{3SO_4}\beta_{1h}K_w[\mathrm{H_2O}]}{(1 + B_1[\mathrm{H}] + \mathrm{B_2}[\mathrm{H}]^2)[\mathrm{H}]} \\ &\times \left(\frac{c_{SO_4}}{1 + B_{1SO_4}[\mathrm{H}]}\right)^3 [\mathrm{Ce^{4+}}][\mathrm{H_2L}]\end{aligned} \tag{5}$$

that considers all the main preequilibria and subsequent nonequilibrium processes within the investigated systems.

Model of the initial stages in the oxidation reactions investigated

The reaction mechanism associated with the above rate law (5) can be described by the set of the following equations

$$H_2O \overset{K_w}{\longleftrightarrow} H^+ + OH^-$$

$$SO_4^{2-} + H^+ \overset{B_{1so_4}}{\longleftrightarrow} HSO_4^-$$

$$L^{2-} + H^+ \overset{B_1}{\longleftrightarrow} HL^-$$

$$L^{2-} + 2H^+ \overset{B_2}{\longleftrightarrow} H_2L$$

$$Ce^{4+} + SO_4^{2-} \overset{\kappa_{1so_4}}{\longleftrightarrow} [CeSO_4]^{2+}$$

$$[CeSO_4]^{2+} + SO_4^{2-} \overset{\kappa_{2so_4}}{\longleftrightarrow} [Ce(SO_4)_2]$$

$$[Ce(SO_4)_2] + SO_4^{2-} \overset{\kappa_{3so_4}}{\longleftrightarrow} [Ce(SO_4)_3]^{2-}$$

$$[Ce(SO_4)_3]^{2-} + OH^- \overset{\beta_{1h}}{\longleftrightarrow} [CeOH(SO_4)_3]^{3-}$$

$$[CeOH(SO_4)_3]^{3-} + L^{2-} \overset{K_1}{\longleftrightarrow} [CeOH(SO_4)_3L]^{5-}$$

$$[CeOH(SO_4)_3L]^{5-} \overset{k_1}{\longrightarrow} [Ce(SO_4)_2]^- + \text{PRODUCTS}$$

with the model parameters pK_w 15.74, $\log B_{1SO_4}$ 1.00, $\log \kappa_{1SO_4}$ 4.54, $\log \kappa_{2SO_4}$ 2.30, $\log \kappa_{3SO_4}$ 1.33, $\log \beta_{1h}$ 13.90, the values of $\log B_i$ ($i = 1, 2$) indicated above, and the values of $\log \beta_1$ and $\log k_1$ determined in the present study.

Solution of a direct problem

The solution of the direct problem of chemical equilibria on the basis of the reaction model obtained demonstrates that, whereas the dominance of the investigated intermediate complexes under the conditions of the BZ reaction is retained for the malonic and oxalic acids, the yield of the complex is small for H_2Suc and H_2Glut under the same conditions (Fig. 4). The latter can contribute to better chances of occurrence of H_2Suc and H_2Glut oxidation by cerium(IV) sulfate along the free-radical path.

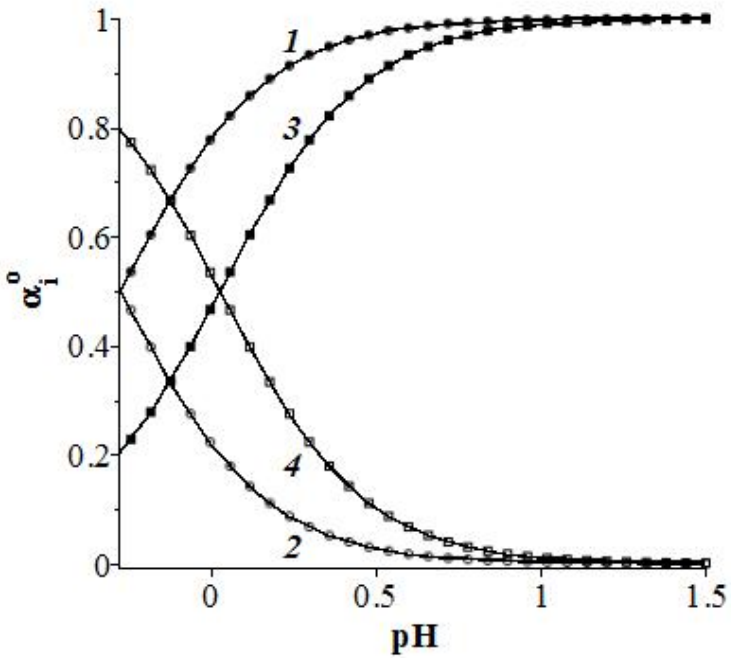


Figure 4: Diagrams of the particles yield: (*1*) $[CeOHMal]^+$ and (*2*) $CeOH^{3+}$ at c_L 0.25 mol/L, (*3*) $[CeOHSuc]^+$ and (*4*) $CeOH^{3+}$ at c_L 0.20 mol/L.

Correlations between the thermodynamic and kinetic parameters of the complexes

- Between the logarithm of the intracomplex redox decay rate constant $\log k_1$ and the logarithm of the equilibrium constant $\log K_1$, there is a direct linear correlation with the coefficients $\log k_{01} \approx -2.15$, $\rho_1 \approx 0.20$ (Fig. 5). It can be interpreted as a kinetic manifestation of the chelate effect (an increase in $\log k_1$ with a greater $\log K_1$) in the series of complexes $[\mathrm{CeOHGlut}]^+$, $[\mathrm{CeOHSuc}]^+$, $[\mathrm{CeOHMal}]^+$, and $[\mathrm{CeOHOx}]^+$.

$$\log k_1 = \log k_{01} + \rho_1 \log K_1. \qquad (6)$$

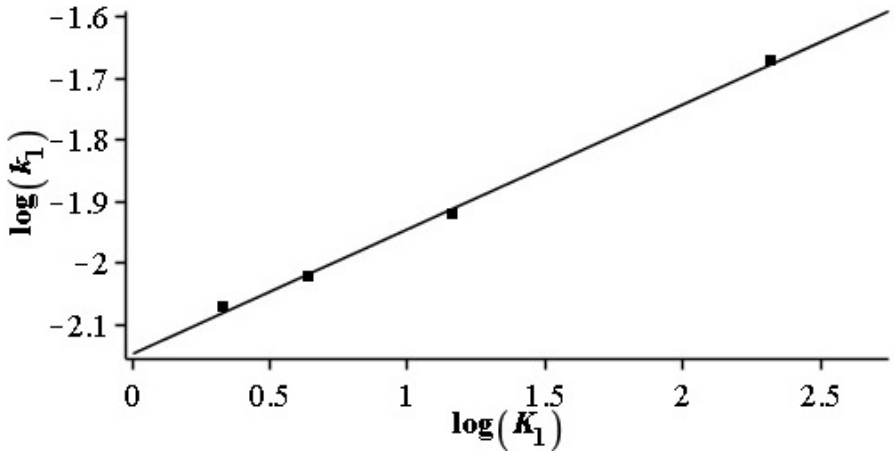


Figure 5: Direct linear correlation between the logarithm of the intracomplex redox decomposition rate constant and the logarithm of the equilibrium constant $\log K_1$ for systems Ce^{4+}–$\mathrm{H_2L}$, $\mathrm{H_2L} = \mathrm{H_2Glut}$, $\mathrm{H_2Suc}$, $\mathrm{H_2Mal}$, and $\mathrm{H_2Ox}$ (left to right).

- There is also another independent linear correlation between $\log K_1$ and the logarithm of the first dissociation constant of a dicarboxylic acid $\log K_{a,1}$

$$\log K_1 = \log K_{01} + \rho_2 \log K_{a,1}. \tag{7}$$

Evaluation of the coefficients of this equation yields in $\log K_{01} \approx 3.15$ and $\rho_2 \approx 0.64$ (Fig. 6). Taking into account the relation $K_1 = k_{+1}[H^+]^z/k_{-1}$, this equation can be transformed into

$$\log k_{+1} = \log k_{01} + \rho_2 \log K_{a,1}, \tag{8}$$

where $\log k_{01} = \log[(K_{01}k_{-1})/[\mathrm{H}^+]^2]$. It can be regarded in this form as an analog of the Brønsted equation for acid catalysis $\log k_a = \log k_0 + \alpha \log K_a$ with the rate constant of the catalytic process k_a and the Brønsted constant α. In terms of the Brønsted equation, the dependence of the complex formation rate constant k_{+1} on $K_{a,1}$ means that the transfer of the proton from the ligand to the water molecule catalyzes (accelerates) the process of complex formation.

- The Brønsted equation is closely related to the Taft equation $\log k = \log k_0 + \rho^{\sigma} \sigma^*$, since the Taft constants σ^*, as a quantitative measure of the inductive effect of the substituent in the series of aliphatic compounds (I-effect) are linearly related to the K_a values. In these terms, the enhancement of the negative I-effect in the carboxylic groups of acids $\mathrm{H_2Glut}$, $\mathrm{H_2Suc}$, $\mathrm{H_2Mal}$, and $\mathrm{H_2Ox}$, leading to an increase in the acidity of a dicarboxylic acid (a decrease in $pK_{a,1}$: $4.34 > 4.00 > 2.76 > 1.48$) and a growth in K_1 and k_{+1} in accordance with (7) and (8) .

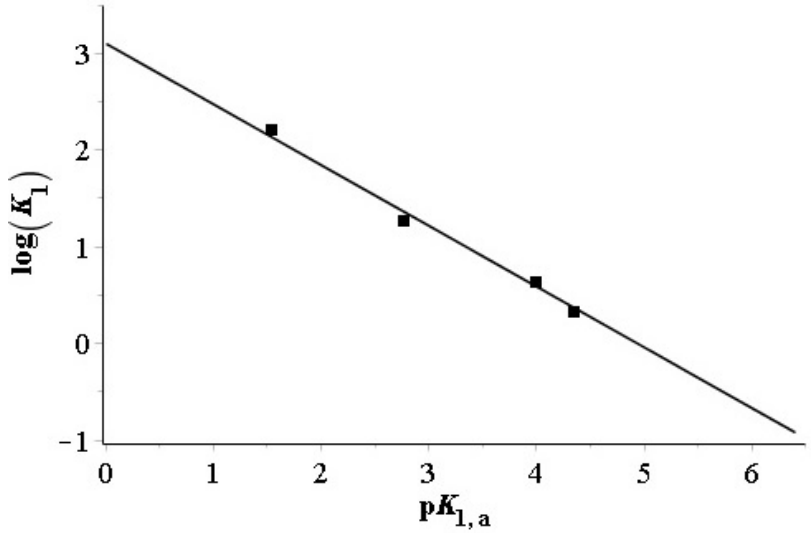


Figure 6: Correlation between the logarithm of the complex formation equilibrium constant and the negative logarithm of the first dissociation constant of $\mathrm{H_2L}$ for systems $\mathrm{Ce^{4+}}$–$\mathrm{H_2L}$, $\mathrm{H_2L} = \mathrm{H_2Ox}$, $\mathrm{H_2Mal}$, $\mathrm{H_2Suc}$, and $\mathrm{H_2Glut}$ (left to right).

- The direct linear correlation established between $\log k_1$ and the logarithm of the first dissociation constant of a dicarboxylic acid $\log K_{a,1}$

$$\log k_1 = \log K_{02} + \rho_3 \log K_{a,1}. \tag{9}$$

with the coefficients $\log K_{02} \approx 1.50$ and $\rho_3 \approx 0.14$ (Fig. 7) can also be considered as an analog of the Brønsted equation for describing the reactions of oxidation of organic compounds with ions of transition metals. The analysis shows that the correlation (9) is a consequence of Eqs. (6) and (7). It demonstrates that the intracomplex redox decay rate constant, $\log k_1$, is a complex function of $\log K_{a,1}$, $\log k_1 = F[\log K_1(\log K_{a,1})]$.

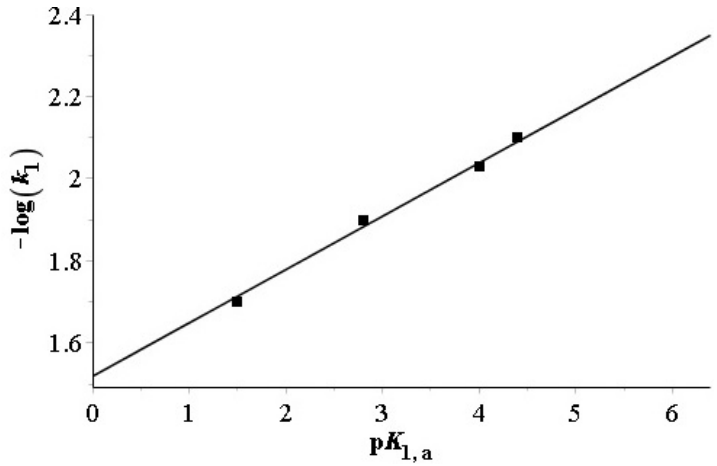


Figure 7: Correlation between the negative logarithms of intracomplex redox decomposition rate constant and first dissociation constant of dicarboxylic acid for systems Ce^{4+}–H_2L, $H_2L = H_2Ox$, H_2Mal, H_2Suc, and H_2Glut (left to right).

- Another consequence of eqs. (6) and (7) is the following correlation between the logarithms of the observed second-order rate constant $k_{obs} = k_1 K_1/[H^+]^z$ (see (3)), which was observed in some papers[14], and $K_{1,a}$ of a dicarboxylic acid

$$\log k_{obs} = \log K_{03} + \rho_4 \log K_{a,1}. \qquad (10)$$

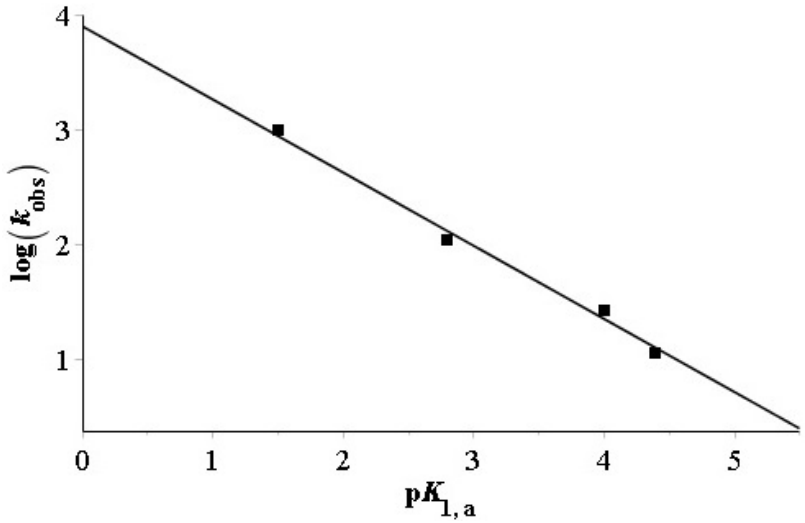


Figure 8: Correlation between the logarithm of the observed oxidation rate constant and $pK_{1,a}$ for systems Ce^{4+}–H_2L, $H_2L = H_2Ox$, H_2Mal, H_2Suc, and H_2Glut (left to right).

This equation can also be used to describe oxidation of organic compounds by variable-valence metal ions in coordination chemistry.

[14] R.N. Mehrotra and S. Gosh. *Z. Phys. Chem.*, **224**, 57 (1963)
O. Voskresenskaya and N. Skorik. *Russ. J. Phys. Chem.* A, **83**, 945 (2009)

Summary and outlook

- The compositions of the complexes like $[(\mathrm{CeOH})_m(\mathrm{H_{2-z}L})_n]^{3m-zn}$ with glutaric, succinic, malonic, and oxalic acids, the thermodynamic parameters of their formation, and the kinetic parameters of the intramolecular redox decomposition were determined.
- The relationship between chemical structures, stability and reactivity of these complexes was also analyzed. An increase in the values of the equilibrium constant $K_1 = [\mathrm{CeOHL^+}][\mathrm{H^+}]^2/([\mathrm{CeOH^{3+}}][\mathrm{H_2L}])$ in the series of the complexes $[\mathrm{CeOHGlut}]^+$, $[\mathrm{CeOHSuc}]^+$, $[\mathrm{CeOHMal}]^+$, and $[\mathrm{CeOHOx}]^+$, as well as a simultaneous increase in the intracomplex redox decomposition rate constant k_1 (s^{-1}), can be associated with an increase in the stability of the cycle in these chelate complexes during the transition from the 8- and 7-membered cycles in $[\mathrm{CeOHGlut}]^+$ and $[\mathrm{CeOHSuc}]^+$ to the 6- and 5-membered cycles in $[\mathrm{CeOHMal}]^+$ and $[\mathrm{CeOHOx}]^+$.

- Several types of linear correlations between the found thermodynamic and kinetic parameters of the examined complexes were also obtained. The found direct correlation $\log k_1 = \log k_{01} + \rho_1 \log K_1$ is interpreted as a kinetic manifestation of the chelate effect (an increase in $\log k_1$ with a greater $\log K_1$) in this series of complexes.
- The established correlations $\log K_1 = \log K_{01} + \rho_2 \log K_{a,1}$ (its equivalent form $\log k_{+1} = \log k_{01} + \rho_2 \log K_{a,1}$), $\log k_1 = \log k_{02} + \rho_3 \log K_{a,1}$, and $\log k_{obs} = \log k_{03} + \rho_4 \log K_{a,1}$) were treated as analogs of the Brønsted equation for describing the reactions of complexation and oxidation of organic compounds by ions of transition metals in coordination chemistry.
- A general model of the interaction of components in the systems $\mathrm{Ce^{4+}}$–$\mathrm{H_2L}$ was proposed, the thermodynamic and kinetic parameters of which can be used for mathematical modeling of the 'organic subset' of the Belousov–Zhabotinsky reaction mechanism involving the dicarboxylic acids in question and for resolving direct problems of calculating the initial and current concentrations of the studied intermediate complexes in technology of solutions containing these compounds.

Materials

Dicarboxylic acids (glutaric, succinic, malonic, and oxalic) of the chemically pure grade and cerium(IV) sulfate tetrahydrate of analytical reagent grade were used as starting materials. In all solutions, a ionic strength of I = 2 mol/L [$(NH_4)_2SO_4$]) = 0.67 mol/L was generated with AR grade ammonium sulfate. The acid solutions concentration was refined by pH-metric titration with a $NaOH$ solution containing no CO_3^{2-} ion. The content of cerium(IV) in a freshly prepared solution of cerium(IV) sulfate was determined by back titration with Mohr's salt in the presence of ferroin before and after an experiment.

The optical density was recorded in time using a SPECORD UV VIS recording spectrophotometer equipped with a temperature-controlled cell holder for rectangular quartz cells with an optical path length $l = 1$ cm and a KF-5 photoelectric colorimeter with a MEA-4 recording device and a temperature-controlled case for standard cells with I $(10.00 \pm 0.01) \times 10^{-1}$ cm. The pH of the reaction mixture was measured with a DATA METER precision pH meter.

Kinetic measurements

Kinetic measurements were carried out at 440 nm (H_2Glut, H_2Suc, H_2Mal) and 400 nm (H_2Ox), where the greatest increase in the difference $\Delta D^0 = D^0 - D_M$ was observed (D^0 is the optical density of the reaction mixture at the time $\tau = 0$, and D_M the optical density of the metal ion) with increasing pH. The instant at which the mixing vessel whereto the starting components were placed was turned upside down, was taken as the time of reaction onset, $\tau = 0$. The initial values of the optical density D^0 was found by linear extrapolation of the kinetic curves in the coordinates log D–τ, where their linearity took place, to the initial time $\tau = 0$.

Instrumental analysis

The initial equilibrium concentration c_n^0 of a intermediate complex with the metal : ligand ratio of 1 : n was determined according to the formulas

$$c_n^0 = c_M(D^0 - D_M)/(D_\infty^0 - D_M) \text{ at } c_M \leq c_L\,,$$

$$c_n^0 = c_L(D^0 - D_M)/(D_\infty^0 - D_M) \text{ at } c_L \leq c_M\,,$$

where D_∞^0 is the initial optical density corresponding to 100% yield of the complex.

Stoichiometry determination

Metal-ligand ratio

The metal-ligand ratio in the complex formed at the time of mixing the solutions was established by the molar ratio method (the saturation curve method) based on the diagrams ΔD^0–c_L/c_M, ΔD^0–c_M/c_L [where c_M and c_L are initial concentrations of cerium(IV) sulfate and a dicarboxylic acid in the reaction mixture of solutions], adapted to the study of metal complexes with an unstable degree of oxidation. Adaptation of this and other applied methods consisted in using, for plotting the diagrams and for subsequent thermodynamic calculations, the initial values of the optical density D^0 at the initial time $\tau = 0$.

Number of displaced protons

To determine the form of existence of dicarboxylic acids in the complexes, the number of protons displaced from the $\mathrm{H_2L}$ molecules by a cerium(IV) ion in establishing the preequilibria of complexation was estimated numerically and graphically by the slope of the $\log \beta_1^{ef}$ versus pH plot as a result of comparison of the data of two or three D^0–pH series. The effective stability constants β_1^{ef} were calculated for each pH value of the D^0–pH series and from the ascending part of the saturation curves from the expression $\beta_1^{ef} = c_1^0/[(c_M - c_1^0)(c_L - c_1^0)]$. The monohydroxoform $\mathrm{CeOH^{3+}}$ was adopted as the dominant form of cerium (IV) in a sulfate medium in the pH range 1–2, according to the data of[15]

[15] O. O. Voskresenskaya, N. A. Skorik, and Yu. V. Yuzhakova. *Russ. J. Phys. Chem.*, **A91**, 627 (2017)

Calculations

Calculation of the stability constants

For complexation preequilibria

$$\mathrm{CeOH^{3+} + H_2L \overset{K_1}{\leftrightarrow} [CeOHH_{2-z}L]^{(3-z)+} + zH^+},$$

$$\mathrm{CeOH^{3+} + H_{2-z}L^{z-} \overset{\beta_1}{\leftrightarrow} [CeOHH_{2-z}L]^{(3-z)+}}$$

the concentration equilibrium constants $K_1 = \beta_1^{ef}[\mathrm{H^+}]^z$ and $\beta_1 = \beta_1^{ef} f_z$ with the protonation function $f_z = \sum_{i=1}^{z} B_i[\mathrm{H^+}]^i$ were calculated for each point of the functions $\log K_1 = \log \beta_1^{ef} - zpH$, $\log \beta_1 = \log \beta_1^{ef} + \log f_z$, followed by averaging the obtained values from the $D^0 - pH$, $D^0 - c_L/\ c_M$, and $D^0 - c_M/c_L$ series data. In the calculations, the log overall protonation constants of anions $\mathrm{L^{2-}}$, $\log B_1 = 5.27$, $\log B_2 = 9.61$ ($\mathrm{Glut^{2-}}$), $\log B_1 = 5.21$, $\log B_2 = 9.21$ ($\mathrm{Suc^{2-}}$), $\log B_1 = 5.29$, $\log B_2 = 8.05$ ($\mathrm{Mal^{2-}}$), $\log B_1 = 3.87$, and $\log B_2 = 5.35$ ($\mathrm{Ox^{2-}}$)[16], were used. The confidence interval for averaged values of the thermodynamic and kinetic quantities was calculated at a sample size of $N = 33 - 36$ with a confidence level of 0.95 using the STATOBRABOTKA program[17].

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[16] A.E. Martell, R.M. Smith, and R.G. Montekaitis. *NIST Critically Selected Stability Constants of the Complexes Database: Version 8.0, Gaithersburg: National Inst. of Standards and Technology, 2004*

[17] N. A. Skorik and E. B. Chernov, *Computer Computations in Complex Compounds Chemistry* (Tomsk. Gos. Univ., Tomsk, 2009)

Calculations of the redox-decomposition rate constants

The rate constants of the redox decomposition of the first time order complexes with respect to the complex $k_1 \equiv k_{n_\tau=1} = -2.303(\log D)'_\tau$ (s^{-1}) were determined by the integral kinetic method from the data of the $(\log D)'_\tau - pH$, $(\log D)'_\tau - c_L/c_M$, and $(\log D)'_\tau - c_M/c_L$ series, followed by averaging the $\log k_1$ values (see, for example, the tables 1–4) under the dominance of $[\mathrm{CeOHL}]^+$ complex. The conditional velocity $(\log D)'_\tau = (\log D^0 - logD^i)/(\tau^0 - \tau^i) = \tan\gamma = const$ (s^{-1}) was estimated by the method of finite differences by the slope of the line in the semilogarithmic coordinates, and also calculated by means of linear least squares method.

The advantage of the integral kinetic method of determining the rate constants $k_{n_\tau=1}$ (s^{-1}), as compared to the differential method is no need to preliminarily determine the extinction coefficient of the complex ε_1 (L $\mathrm{mol}^{-1}\mathrm{cm}^{-1}$), since it has no effect on $(\log D)'_\tau$ and $k_{n_\tau=1}$ (s^{-1}).

The values of k_1 were also estimated by Ardon's method in accordance with $-1/\dot{D}^0 = 1/(\varepsilon_1 k_1 c_M) + 1/(\varepsilon_1 k_1 c_M \beta_1^{ef} \cdot c_L)$, where, $-\dot{D}^0 \equiv \partial D/\partial\tau$ (s^{-1}) is the initial velocity of the redox process observed in the systems, found by the initial velocity method using the formula $-\dot{D}^0 = (D^0 - D^i)\ /(\tau^0 - \tau^i) = const$ on a semilogarithmic grid; and l (cm) is the thickness of the absorbing layer of the solution.