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Complexation and Intramolecular Redox Decomposition of Cerium(IV) Hydroxo Complexes with Oxycarboxylic Acids

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Abstract—Spectrophotometry, pH-metry, and kinetic method were applied to study the complexation and redox decomposition of cerium hydroxo complexes formed in the systems $Ce^{4+}–SO_4^{2-}–H_mL$, where H_mL (m = 2, 3, 4) are, respectively lactic, malic, and tartaric acids.

A study of thermodynamic and kinetic characteristics of complexation and redox decomposition of complexes formed in the first stage of oxidation by cerium(IV) of polar organic compounds is of theoretical and practical interest. It is rather important in connection with the problem of stabilization of unstable oxidation states of metals [1–4] and use of these systems as a source of radicals in radical polymerization [5, 6], and also in view of their other applications—analytical [7], in a theoretical study of the electron transfer rates in intermediate complexes [8], and in separation of a mixture of rare-earth elements [1–3].

For example, separation of a mixture of rare-earth elements is based on the ability of cerium to form compounds in which it is in oxidation state +4. This leads to a pronounced difference between the properties of cerium compounds and those with rare-earth elements in oxidation state +3 and improves the efficiency of methods for separation of rare-earth elements. However, the problem of cerium stabilization in this “anomalous” oxidation state, especially in complexation with oxyacids, has been studied insufficiently.

Previously, the influence exerted by the stability constants of complexes, reducing ability of ligands, their denticity, and other factors on the rate of the redox interaction in systems containing cerium(IV) and organic ligands (carboxyl-containing complexons, oxycarboxylic acids, etc.) [3]. It has been established that there is a correlation between the rate of the redox interaction in the systems and the instability constant of cerium(IV) complexes. No simple relationship could be revealed between the stability of the complexes and the rate and apparent activation energy of the redox interaction in cerium(IV) complexation with oxyacids [3]. It has been shown that intramolecular redox interaction cannot be completely eliminated in systems of this kind, with only its partial suppression possible [3, 4].

As characteristics of the redox interaction were employed the conditional rate of the redox process, its apparent activation energy, and reducing power of an organic ligand [3]. Such a direct characteristic of the kinetic activity of the complexes as rate constant of their intracomplex redox decomposition was not determined in the previous studies mentioned here. It is also evident that such a property of an organic ligand as its reducing capacity may play an important part in the case of a bimolecular (free-radical), but not intermediate, mechanism occurring in oxidation of oxy acids by cerium(IV) [9]. A study of the problem of stabilization in the given context is inseparable from a study of the mechanism and kinetics of the redox process occurring in the systems.

The kinetics of oxidation of oxycarboxylic acids by cerium(IV) was studied in [5, 9–13]. In [10–12], a mechanism of the redox process was postulated, in which an intermediate complex is formed and the decomposition of this complex is the rate-determining stage of the process. However, it has been noticed that kinetic data are insufficient for confirming the formation of such an intermediate complex [11]. A synergistic effect of the carboxylic and hydroxy groups of α oxyacids, and also intermediate and free-radical mechanisms of oxidation of organic ligand by ceri-

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um(IV) for, respectively, oxy acids and succinic dicarboxylic acids have been noted [9]. A bridge mechanism of electron transfer in such an intermediate has been suggested and necessity for revealing the states in which the metal and ligand are present in this complex has been indicated [13].

It is noteworthy that the complexation pre-equilibrium in the redox process has not been studied specially, being either postulated or studied using methods yielding only effective complexation constants related to a fixed pH value and indeterminate form of the ligand and metal in the complex. At the same time, the kinetic dependences themselves were interpreted on the basis of assumptions about the composition, structure, and reactivity of the complexes and characterized by effective rate constants. Data on the rate constants of intramolecular decomposition of cerium(IV) complexes with organic ligands are unavailable in the literature. Of interest in this regard are generalized methods for investigation of complexation, proposed in this study, and their application to analysis of the kinetics and thermodynamics of the initial stages of the processes mentioned, the mechanism of these processes, and the reactivity of intermediate complexes involved.

A comparative evaluation of the effective formation constants of intermediate cerium(IV) complexes with lactic α oxyacid and other hydroxyl-containing compounds in a perchlorate medium was made in [5]. The composition and stability of complexes have been studied in a nitrate medium for the malate complex $[Ce(NO_3)_zMalt]^{2-z}$ [3, 14] and binuclear tartrate complex of cerium(IV) $[Ce_2(NO_3)_zTart]^{6-z}$ [3, 15]. Other researchers [3, 14, 15] could not study the complexation in a sulfate medium in the systems we investigated.

In the present study, the methods commonly used to investigate complexation and generalized to the case of kinetically active complexes were applied to determine in a sulfate medium the composition, stability constants β_1, rate constants k_2, and activation energy of intramolecular redox decomposition of lactate, malate, and tartrate hydroxo complexes of cerium(IV) $[CeOH\,H_{m-x}L]^{3-x}$ (m = 2, 3, 4) formed in the first stage of oxidation by cerium(IV) of the above-mentioned organic ligands:

$$CeOH^{3+} + H_{m-x}L^{x-} \overset{\beta_1}{\rightleftarrows} [CeOHH_{m-x}L]^{3-x}$$

$$\xrightarrow{k_2} Ce^{3+} + \cdot LH^{x-}_{m=1-x} + H_2O, \qquad (1)$$

$$\beta_1 = k_1/k_{-1}, \quad k_1 >> k_{-1} >> k_2.$$

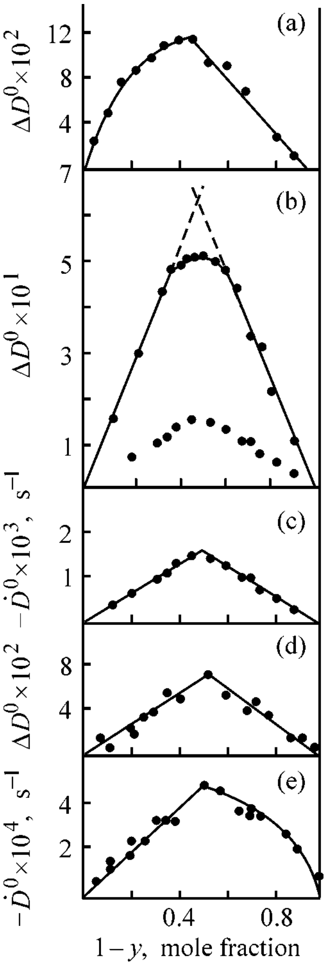


Fig. 1. (a, b, d) ΔD^0–composition and (c, e) $-\dot{D}^0$–composition diagrams for isomolar series of solutions. (y) Content of ligand. System: (a) Ce(IV)–SO_4^{2-}–H_2Lact (c_{tot} = 2.46 × 10^{-2} M, pH 2.87, I = 2, T = 25.0°C, λ = 400 nm), (b–e) Ce(IV)–SO_4^{2-}–H_4Tart [(b, c) c_{tot} = 1.17 × 10^{-2} M, pH 2.24, I = 2, T = 24.0°C, λ = 400 nm; (d, e) c_{tot} = 1.03 × 10^{-3} M, pH 2.3, I = 2, T = 25.0°C, λ = 340 nm].

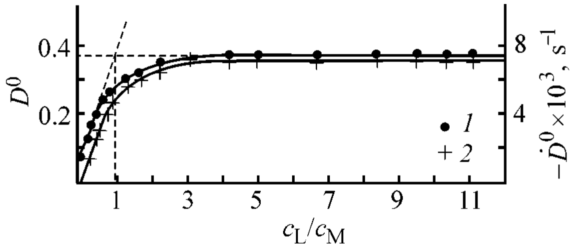


Fig. 2. (*1*) D^0–c_L/c_M and (*2*) $-\dot{D}^0$–c_L/c_M diagrams for the system Ce^{4+}–SO_4^{2-}–H_3Malt. c_M = 1.88 × 10^{-3}, c_L = 3.00 × 10^{-4}–2.11 × 10^{-2} M; pH 2.70; I = 2; T = 18.0°C; λ = 400 nm; D^0_∞ = 0.376; D_M = 0.09.

The number x of protons displaced from the ligand H_mL in complexation was determined. The mechanism of the redox process observed in the systems

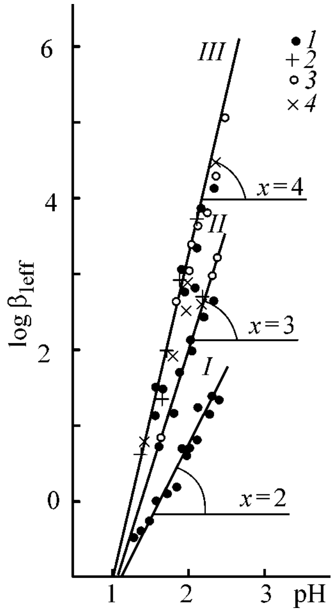


Fig. 3. log $\beta_{1\text{eff}}$–pH diagrams. System: (*I*) Ce^{4+}–SO_4^{2-}–H_2Lact (c_M = 6.0 × 10^{-3}, c_L = 3.0 × 10^{-2} M; I = 2; T = 18.0°C; λ = 400 nm); (*II*) Ce^{4+}–SO_4^{2-}–H_3Malt [(*1*) c_M = 2.14 × 10^{-3}, c_L = 2.00 × 10^{-3} M; T = 17.7°C; (*2*) c_M = 2.04 × 10^{-3}, c_L = 2.00 × 10^{-3} M; T = 28.0°C; and (*3*) c_M = 3.21 × 10^{-3}, c_L = 3.00 × 10^{-3} M; T = 27.0°C; I = 2, λ = 400 nm]; (*III*) Ce^{4+}–SO_4^{2-}–H_4Tart [(*1*) c_M = 1.22 × 10^{-3}, c_L=1.20 × 10^{-3} M; T = 28.0°C; (*2*) c_M = c_L = 2.14 × 10^{-3} M; T = 28.0°C; (*3*) c_M = 2.04 × 10^{-3}, c_L = 2.00 × 10^{-3} M; T = 28.0°C; and (*4*) c_M = 3.02 × 10^{-3}, c_L = 1.65 × 10^{-3} M; T = 24.0°C; I = 2, λ = 400 nm].

was studied, and the law governing its rate was established.

The composition of intermediate complexes formed in the systems Ce^{4+}–SO_4^{2-}–H_mL at the instant of mixing of the reaction mixture components was studied by the methods of isomolar series (Fig. 1) and molar ratios (Fig. 2). The results obtained indicate that 1 : 1 complexes are predominant in all the systems in the pH range studied. The formation of complexes with 1 : 1 composition in the systems studied was additionally confirmed by using kinetic analogues of the above methods [Figs. 1c and 1e; Fig. 2, curve *2*; Eq. (16)], which are particularly appropriate in the cases of low yield or low light absorption by the complexes.

The data on the composition of the complexes, obtained in the present study, is in agreement with the assumption that an intermediate cerium tartrate complex of composition 1 : 1 is formed in oxidation of tartaric acid by cerium(IV) [10, 12] and also with the conclusions of [5] that the 1 : 1 composition of intermediate organocerium complexes is independent of the denticity of the organic ligand and can be regarded as their proof. The composition of the malate complex of cerium(IV) in a sulfate medium coincides with that in a nitrate medium, established in [3. 14].

The form in which a coordinated ligand is present in the complexes and their stability constants were determined using the *D*–pH method [16]. As the dominant form of cerium(IV) in the pH range studied was taken the monohydroxo form $CeOH^{3+}$ [17].

The number x of protons displaced from the ligand molecule H_mL by metal ion in attainment of equilibrium

Table 1. Stability constant and rate constant of redox decomposition of lactate complex with cerium(IV) by the $\dot{D}^0$–pH* method (c_M = 6 × 10^{-3}, c_L = 3 × 10^{-2} M; I = 2; T = 18.0°C; λ = 400 nm; D^0_∞ = 0.610)

D^0	D_M	$-\dot{D}^0$, s^{-1}	pH	$c^0_K \times 10^3$, M	log $\beta_{1\text{eff}}$	log $\beta_{1\text{eff}} f$	log k_{app}	log k_2
0.307	0.300	1.0 × 10^{-5}	1.24	0.059	–0.48	15.35	$\bar{1}.23$	$\bar{3}.23$
0.304	0.300	1.5 × 10^{-5}	1.35	0.077	–0.36	15.25	$\bar{1}.28$	$\bar{3}.28$
0.304	0.299	3.0 × 10^{-5}	1.50	0.097	–0.26	15.05	$\bar{1}.49$	$\bar{3}.49$
0.309	0.300	4.0 × 10^{-5}	1.61	0.174	0.00	15.09	$\bar{1}.36$	$\bar{3}.36$
0.311	0.301	4.5 × 10^{-5}	1.70	0.194	0.05	14.96	$\bar{1}.37$	$\bar{3}.37$
0.311	0.297	8.5 × 10^{-5}	1.83	0.268	0.20	14.85	$\bar{1}.50$	$\bar{3}.50$
0.322	0.294	1.6 × 10^{-4}	1.94	0.532	0.52	14.95	$\bar{1}.48$	$\bar{3}.48$
0.332	0.294	1.5 × 10^{-4}	1.94	0.720	0.68	15.12	$\bar{1}.32$	$\bar{3}.32$
0.328	0.277	1.8 × 10^{-4}	2.03	0.864	0.74	15.00	$\bar{1}.32$	$\bar{3}.32$
0.327	0.284	2.7 × 10^{-4}	2.06	0.792	0.72	14.91	$\bar{1}.53$	$\bar{3}.53$
0.331	0.298	3.2 × 10^{-4}	2.12	0.900	0.81	14.89	$\bar{1}.56$	$\bar{3}.56$
0.339	0.274	4.3 × 10^{-4}	2.20	1.302	0.98	14.90	$\bar{1}.52$	$\bar{3}.52$
0.347	0.215	4.2 × 10^{-4}	2.27	1.896	1.22	15.00	$\bar{1}.35$	$\bar{3}.35$
0.357	0.217	4.4 × 10^{-4}	2.33	1.956	1.38	15.05	$\bar{1}.35$	$\bar{3}.35$
0.342	0.175	4.5 × 10^{-4}	2.43	2.184	1.33	14.86	$\bar{1}.31$	$\bar{3}.31$

* log β_1 = 14.97 ± 0.18, log k_2 = $\bar{3}.40$ ± 0.10 (18°C).

Table 2. Stability constants, rate constant, and activation energy of malate complex with cerium(IV), determined by the D^0, $\dot{D}^0$–pH* method [$c_M = 2.14 \times 10^{-3}$, $c_L = 2.00 \times 10^{-3}$ M; $I = 2$; $T = 17.7°C$; $\lambda = 400$ nm; $D^0_\infty = 0.310$ (run no. 1); $c_M = 3.21 \times 10^{-3}$, $c_L = 3.00 \times 10^{-3}$ M; $I = 2$; $T = 27.0°C$; $\lambda = 400$ nm; $D^0_\infty = 0.246$ (run no. 2)]

D^0	D_M	$-\dot{D}^0 \times 10^4$, s^{-1}	pH	$c^0_K \times 10^3$, M	log k_{app}	log k_2	log β_{1eff}	log β_1
				Run no. 1				
0.228	0.227	0.4	1.67	0.024	$\bar{1}.23$	$\bar{3}.23$	0.76	18.31
0.231	0.228	0.3	1.79	0.073	$\bar{1}.61$	$\bar{3}.61$	1.26	18.45
0.229	0.220	0.9	1.90	0.200	$\bar{1}.65$	$\bar{3}.65$	1.76	18.61
0.230	0.215	1.1	2.05	0.316	$\bar{1}.54$	$\bar{3}.55$	2.01	18.64
0.244	0.210	2.1	2.27	0.680	$\bar{1}.49$	$\bar{3}.49$	2.55	18.34
0.250	0.212	2.7	2.42	0.775	$\bar{1}.54$	$\bar{3}.55$	2.67	18.01
0.262	0.208	3.2	2.38	1.060	$\bar{1}.48$	$\bar{3}.48$	3.02	18.48
0.309	0.128	5.0	2.69	1.988	$\bar{1}.40$	$\bar{3}.40$	–	–
0.310	0.111	4.9	2.75	2.000	$\bar{1}.39$	$\bar{3}.39$	–	–
0.305	0.094	5.0	2.85	1.954	$\bar{1}.40$	$\bar{3}.40$	–	–
0.315	0.085	5.0	2.96	2.000	$\bar{1}.40$	$\bar{3}.40$	–	–
0.306	0.066	5.1	3.07	1.967	$\bar{1}.41$	$\bar{3}.41$	–	–
				Run no. 2				
0.158	0.155	1.0	1.68	0.095	0.02	$\bar{2}.20$	1.02	18.54
0.160	0.155	2.0	1.85	0.158	0.10	$\bar{2}.28$	1.26	18.28
0.162	0.150	3.7	1.96	0.360	0.01	$\bar{2}.19$	1.68	18.38
0.162	0.148	5.0	2.06	0.412	0.08	$\bar{2}.26$	1.75	18.15
0.167	0.148	5.1	2.06	0.559	$\bar{1}.96$	$\bar{2}.14$	1.94	18.34
0.185	0.140	7.8	2.20	1.227	$\bar{1}.80$	$\bar{2}.00$	2.85	18.83

* log $\beta_1 = 18.39 \pm 0.18$, log $k_2 = \bar{3}.43 \pm 0.10$ (17.7°C) (run no. 1); log $\beta_1 = 18.42 \pm 0.24$, log $k_2 = \bar{2}.17 \pm 0.10$ (27°C), $E = 133.0 \pm 1.3$ kJ mol^{-1} (run no. 2).

Table 3. Stability constant and rate constant of redox decomposition of tartrate complex with cerium(IV), determined by the D^0, $\dot{D}^0$–pH* method ($c_M = 1.22 \times 10^{-3}$, $c_L = 1.20 \times 10^{-3}$ M; $I = 2$; $T = 28.0°C$; $\lambda = 400$ nm; $D^0_\infty = 0.317$)

D^0	D_M	$-\dot{D}^0 \times 10^3$, s^{-1}	pH	$c^0_K \times 10^3$, M	log β_{1eff}	log k_{app}	log k_2
0.170	0.155	0.20	1.74	5.18×10^{-5}	28.25	3.86	$\bar{3}.98$
0.163	0.150	0.30	1.79	9.34×10^{-5}	27.97	3.21	$\bar{3}.90$
0.167	0.154	0.35	1.80	9.57×10^{-5}	27.95	3.66	$\bar{3}.96$
0.173	0.156	0.40	1.81	1.27×10^{-4}	28.05	3.12	$\bar{3}.89$
0.171	0.151	0.45	1.90	1.45×10^{-4}	27.76	3.10	$\bar{3}.88$
0.172	0.153	0.45	1.98	1.33×10^{-4}	27.44	3.36	$\bar{3}.92$
0.217	0.155	1.70	2.22	4.59×10^{-4}	27.34	3.70	$\bar{3}.96$
0.238	0.146	1.50	2.35	6.46×10^{-4}	27.24	–	–
0.273	0.152	1.60	2.38	8.78×10^{-4}	27.72	–	–
0.279	0.150	1.25	2.44	9.27×10^{-4}	27.67	–	–
0.292	0.121	1.30	2.50	1.05×10^{-3}	27.98	–	–

* log $\beta_1 = 27.76 \pm 0.32$, log $k_2 = \bar{3}.93 \pm 0.04$ (28°C).

$$\mathrm{CeOH^{3+}} + \mathrm{H}_m\mathrm{L} \overset{R_1}{\rightleftarrows} [\mathrm{CeOHH}_{m-x}\mathrm{L}]^{3-x} + x\mathrm{H}^+, \quad (2)$$

$$R_1 = \frac{[\mathrm{CeOHH}_{m-x}\mathrm{L}][\mathrm{H}]^x}{[\mathrm{CeOH}][\mathrm{H}_m\mathrm{L}]} = \beta_{1\mathrm{eff}}[\mathrm{H}]^x, \quad (3)$$

was evaluated graphically as the slope of the plot of log β_{1eff} against pH

$$\log \beta_{1\mathrm{eff}} = \log R_1 + x\mathrm{pH} \quad (4)$$

by comparing the D^0–pH data of series nos. 2–4 (D^0 is light absorption by the reaction mixture at instant of time $\tau = 0$).

As follows from analysis of the dependence of log β_{1eff} on pH (Fig. 3, Tables 1–3), the high-charge

Table 4. Stability constant and rate constant of redox decomposition of malate complex with cerium(IV), determined by the D^0, $\dot{D}^0$–c_L/c_M* method ($c_M = 1.88 \times 10^{-3}$, $c_L = 3.00 \times 10^{-4}$–$2.11 \times 10^{-2}$ M; pH 2.70; $I = 2$; T = 18.0°C; λ = 400 nm; $D^0_\infty = 0.376$; $D_M = 0.090$)

D^0	$-\dot{D}^0 \times 10^3$, s^{-1}	c_L/c_M	$c^0_K \times 10^3$, M	log k_{app}	log k_2	log β_1
0.132	1.5	0.16	0.296	$\bar{1}.70$	$\bar{3}.52$	19.08
0.180	2.5	0.32	0.592	$\bar{1}.63$	$\bar{3}.45$	19.17
0.215	3.1	0.48	0.822	$\bar{1}.58$	$\bar{3}.40$	18.50
0.240	4.0	0.64	0.986	$\bar{1}.61$	$\bar{3}.43$	18.22
0.260	4.5	0.80	1.117	$\bar{1}.60$	$\bar{3}.42$	18.09
0.279	5.0	0.96	1.243	$\bar{1}.60$	$\bar{3}.42$	18.05
0.306	5.5	1.27	1.420	$\bar{1}.59$	$\bar{3}.41$	18.01
0.327	6.0	1.60	1.558	$\bar{1}.59$	$\bar{3}.41$	18.03
0.350	6.5	2.23	1.709	$\bar{1}.58$	$\bar{3}.40$	18.11
0.364	7.0	3.19	1.801	$\bar{1}.59$	$\bar{3}.41$	18.24
0.370	7.0	4.15	1.841	$\bar{1}.58$	$\bar{3}.40$	18.41
0.374	7.4	5.10	1.866	$\bar{1}.60$	$\bar{3}.42$	18.75
0.374	7.3	6.70	1.866	$\bar{1}.59$	$\bar{3}.41$	18.60
0.375	7.5	8.45	1.873	$\bar{1}.60$	$\bar{3}.42$	18.76
0.379	7.6	9.55	1.880	$\bar{1}.61$	$\bar{3}.43$	–
0.375	7.5	10.40	1.873	$\bar{1}.60$	$\bar{3}.42$	18.73
0.377	7.5	11.20	1.880	$\bar{1}.60$	$\bar{3}.42$	–

* log β_1 = 18.45 ± 0.34, log k_2 = $\bar{3}.42 \pm 0.03$ (18.0°C).

ion $CeOH^{3+}$ displaces 2, 3, or 4 protons from the ligand molecule in complexation with, respectively, lactic, malic, and tartaric acids. In this case, similarly to that of interaction of oxyacids with the cations Sc^{3+}, Ga^{3+}, In^{3+}, and Th^{4+} [18], protons of the oxy groups of oxyacids are displaced because of the high coordination numbers of rare-earth elements and the effective negative charge on electron-donor oxygen atoms.

Consequently, the complexation pre-equilibrium in oxidation of the acids under consideration by cerium(IV) can be represented as

$$CeOH^{3+} + L^{x-} \overset{\beta_1}{\rightleftarrows} [(CeOH)L]^{3-x} \qquad (5)$$

or, which is equivalent in terms of the theory of ionic equilibria,

$$CeOH^{3+} + L^{x-} \overset{\beta_1}{\rightleftarrows} [(CeO)HL]^{3-x}, \qquad (6)$$

where x = 2, 3, and 4 for, respectively, H_2Lact, H_3Malt, and H_4Tart.

It is noteworthy that, in a sulfate medium, the formula $[CeOHL]^{3-x}$ should be only regarded as an abbreviated designation of all the possible substances with variable number of ions of the ionic background $\Sigma_y\Sigma_z[(NH_4)_yCeOHL(SO_4)_z]^{3-x+y-z}$, where y and z can be estimated by the inequalities $y \geq 0$, $0 \leq z \leq 3$ [19].

For the complexation equilibrium (5), the equilibrium constant β_1:

$$\beta_1 = \frac{[CeOHL]}{[CeOH][L]} \qquad (7)$$

(charges are omitted) was calculated from the data of the series D^0–pH and the ascending portion of the saturation curve by the formula

$$\beta_1 = \frac{c^0_K}{(c_M - c^0_K)(c_L - c^0_K)} f = \beta_{1eff} f, \qquad (8)$$

$$f = 1 + \sum_{i=1}^{m} B_i [H]^i$$

for each point of the dependence

$$\log \beta_1 = \log \beta_{1eff} + \log f \qquad (9)$$

with the subsequent averaging of the log β_1 values obtained (Tables 1–4).

The agreement between the results obtained by different methods (D–pH, molar ratios) in determining the stability constants for, e.g., the malate complex of cerium(IV) (log β_1 = 18.39, log β_1 = 18.45, Tables 2 and 4) indicates that the basic equilibria in solution are taken into account correctly. The $\log \beta_1$ value for the complex $[\mathrm{CeOHL}]^{3-x}$ (x = 2, 3, 4), found in a sulfate medium by averaging data of two to four series for each of the systems, grows in order H_2Lact < H_3Malt < H_4Tart with increasing ligand denticity from $\log \beta_1 = 14.97 \pm 0.18$ for H_2Lact to $\log \beta_1 = 27.83 \pm 0.23$ for H_4Tart.

The kinetics and mechanism of the redox process observed in the system was studied by analyzing the dependence of its initial rate $-\dot{D}^0$ on the equilibrium concentration of hydrogen ions at the initial concentration of the organic ligand in terms of the generalizations of the D^0–pH and D^0–c_L/c_M methods to the case $\dot{D}^0 \neq 0$ (see below), which can be named the D^0, $\dot{D}^0$–pH and D^0, $\dot{D}^0$–c_L/c_M methods, respectively.

The rate constants of the redox decomposition of $[\mathrm{CeOHL}]^{3-x}$ complexes were calculated from the data of series D^0–pH, D^0–c_L/c_M (supplemented with the dependences $\dot{D}^0$–pH, $\dot{D}^0$–c_L/c_M) with the use of the equilibrium concentrations of the complex, calculated from the series D^0–pH, D^0–c_L/c_M (Tables 1–4):

$$c_K^0 = \begin{cases} \dfrac{D^0 - D_M}{D_\infty^0 - D_M} c_M, & c_M < c_L; \\ \dfrac{D^0 - D_M}{D_\infty^0 - D_M} c_L, & c_L < c_M, \end{cases} \tag{10}$$

where c_M and c_L are the initial concentrations of the metal ion and ligand, D_M the optical density of the metal ion solution, and D_∞^0 the light absorption by the reaction mixture at the instant of time $\tau = 0$, corresponding to a yield of the complex equal to unity.

The analysis of nonlinear dependences $\dot{D}^0$–pH (Fig. 4) and $\dot{D}^0$–c_L/c_M (Fig. 2) within the series D^0, $\dot{D}^0$–pH, D^0, $\dot{D}^0$–c_L/c_M was supplemented with analysis of linear dependences $\dot{D}^0$–c_K^0 (Fig. 5):

$$-\dot{D}^0 = A + k_{\mathrm{app}} c_K^0, \tag{11}$$

allowing, in particular, graphical evaluation of the rate constants of the intramolecular redox decomposition.

An analytical calculation of the logarithm of the apparent rate constant of intramolecular redox decomposition was carried out for each point of the dependence

$$\log k_{\mathrm{app}} = \log \dot{D}^0 - \log c_K^0 \tag{12}$$

with the subsequent averaging of the $\log k_{\mathrm{app}}$ values obtained.

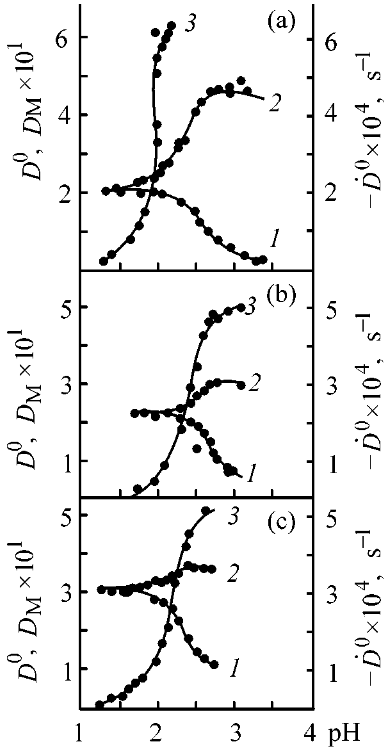


Fig. 4. (*1*) D^0–pH, (*2*) D_M–pH, and (*3*) $-\dot{D}^0$–pH diagrams. System: (a) Ce^{4+}–$SO_4{}^{2-}$–H_4Tart ($c_M = c_L = 2.14 \times 10^{-3}$ M, I = 2, T = 28.0°C, λ = 400 nm), (b) Ce^{4+}–SO_4^{2-}–H_3Malt ($c_M = 2.14 \times 10^{-3}$, $c_L = 2.00 \times 10^{-3}$ M; I = 2; T = 17.7°C; λ = 400 nm), (c) Ce^{4+}–$SO_4{}^{2-}$–H_2Lact ($c_M = 6.0 \times 10^{-3}$, $c_L = 3.0 \times 10^{-2}$ M; I = 2; T = 18.0°C; λ = 400 nm).

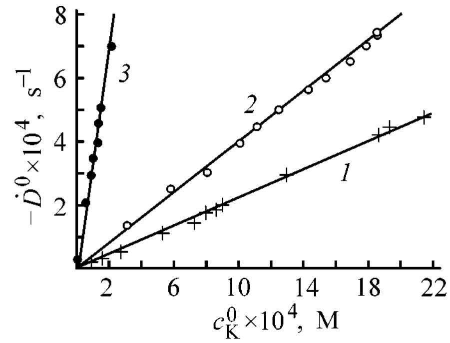


Fig. 5. $-\dot{D}^0$–c_K^0 diagrams. System: (*1*) Ce^{4+}–SO_4^{2-}–H_2Lact ($c_M = 6.0 \times 10^{-3}$, $c_L = 3.0 \times 10^{-2}$ M; I = 2; T = 18.0°C; λ = 400 nm); (*2*) Ce^{4+}–SO_4^{2-}–H_3Malt ($c_M = 1.88 \times 10^{-3}$, $c_L = 3.00 \times 10^{-3}$–$2.11 \times 10^{-2}$ M; pH 2.70; I = 2; T = 18.0°C; λ = 400 nm); (*3*) Ce^{4+}–SO_4^{2-}–H_4Tart ($c_M = c_L = 2.14 \times 10^{-3}$ M; I = 2, T = 28.0°C, λ = 400 nm).

Since the apparent rate constants of redox decomposition of the complexes, k_{app} (l mol^{-1} s^{-1}) depend on their extinction coefficients:

$$k_{\mathrm{app}} = \varepsilon_K l / k_2 \tag{13}$$

(l is the thickness of the absorbing layer of the solution), logarithms of the true rate constants k_2 (s^{-1}) of the intramolecular redox decomposition were also calculated (Tables 1–4):

$$\log k_2 = \log k_{app} - \log \varepsilon_K l. \qquad (14)$$

The calculated k_2 values were used to evaluate, in accordance with the formula

$$E = 2.303R \frac{\log k_{2\,T_2} - \log k_{2\,T_1}}{\Delta T} T_1 T_2 \qquad (15)$$

[$R = 8.314$ J K^{-1} mol^{-1} is the gas constant, T the absolute temperature (K); $\Delta T = T_2 - T_1$, $T_2 > T_1$], the activation energy of redox decomposition of the complexes (Table 2).

The fact that the dependence $\dot{D}^0 = f(c_K^0)$ remains linear in the concentration ranges under study (Fig. 5) and the constancy of the calculated $\log k_{app}$ value within the series D^0, $\dot{D}^0$–pH, D^0, $\dot{D}^0$–c_L/c_M (Tables 1–4) indicate that a single kinetically active complex is predominant in the systems; and the equality to zero of its free term A (Fig. 5) points to the absence of any contribution from the bimolecular pathway to the process within the concentration ranges studied. Thus, we have an intermediate mechanism of oxidation of the organic ligand by cerium(IV).

In this case the initial rate of the redox process, found using generalized methods of isomolar series and molar ratios, depends on the yield of the complex

$$-\dot{D}^0 = k_{app} c_K^0 = \begin{cases} k_{app}\alpha_K^0 c_M, & c_M < c_L; \\ k_{app}\alpha_K^0 c_L, & c_L < c_M; \end{cases} \qquad (16)$$

[$\alpha_K^0 = (D^0 - D_M)/(D_\infty^0 - D_M)$ is the yield of the complex at instant of time $\tau = 0$] and reaches a maximum simultaneously with its maximum yield—at the stoichiometric ratio of the components. In the case in question, this indicates that an intermediate complex of composition 1 : 1 is formed in the system (Figs. 1c and 1e; Fig. 2, curve *2*).

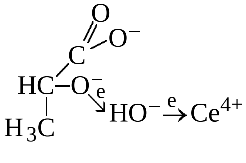
The logarithm of the apparent rate constant of redox decomposition of the complexes, $\log k_{app}$ (12), grows in the order lactic < malic < tartaric acid from $\bar{1}.39 \pm 0.06$ to 0.11 ± 0.04 (18°C). However, the logarithms of true rate constants, $\log k_2$, calculated using expression (14), are constant and equal to $\bar{3}.40 \pm 0.05$ for all the complexes (18°C). The activation energy of intramolecular decomposition also takes a constant, within experimental error, value $E = 132.71 \pm 1.40$ kJ mol^{-1} for H_2Lact, H_3Malt, and H_4Tart.

The rate constants and activation energy of intramolecular redox decomposition, obtained in the present study, are in agreement with the corresponding rate constants and activation energy ($\log k_2 = \bar{3}.36 \pm 0.06$, recalculated to 18°C) and activation energy ($E = 131.8 \pm 1.2$ kJ mol^{-1}) for cerium tartrate $[(CeOH)_2Tart]^{2+}$ [20] and quinate complexes of cerium(IV) $CeOHL]^+$ [21].

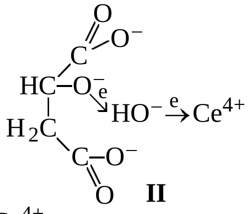
The rise in the rate pseudoconstants, observed in going from H_2Lact to H_3Malt [12] and from H_2Malt to H_4Tart [3, 19], is, thus, only apparent and reflects the increase in the extinction coefficients of the complexes in the series in question. Not only the composition of the intermediate complex [5], but also its reactivity are found to be independent, in the given series, of the denticity of the organic ligand. The rise in the stability of the complexes $[CeOHL]^{3-x}$ (x = 2, 3, 4) with increasing ligand denticity is not accompanied by stabilization of cerium(IV) in this series of oxyacids.

The independence of the true rate constants k_2 and the activation energy E of intramolecular redox decomposition from the denticity of oxyacids can be accounted for (as is done in [20]) by the common (single-electron) mechanism of electron transfer via one and the same bridge group in the complexes $[CeOHL]^{3-x}$ (x = 2–4). According to the assumption made in [13], this group is the oxo group of the ceryl ion, which can form a hydrogen bond with the alcohol hydroxyl of tartaric acid. In terms of the theory of ionic equilibria this is equivalent to the formation of a hydrogen bond between a deprotonated alcohol hydroxyl of anions of oxyacids and the hydroxy group of monohydroxo ion of cerium(IV) [Eqs. (5) and (6)].

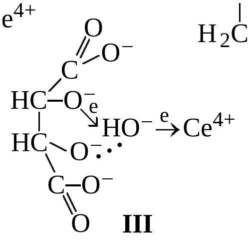
Thus, the following structure of the intermediate complexes formed in oxidation by cerium(IV) of the ligand series under consideration—H_2Lact (**I**), H_3Malt (**II**), and H_4Tart (**III**), can be suggested:



I



II



III

The equation for the initial rate of the redox process occurring in the systems can be represented, with account of expressions (3), (7), and (12), as

$$-\frac{dc_M}{dt} = k_2R_1[CeOH^{3+}][H_mL][H^+]^{-x}$$

$$= k_2\beta_1[CeOH^{3+}][H_{m-x}L^{x-}] \quad (x = m = 2, 3, 4). \qquad (17)$$

This equation establishes the type of the functional dependence of the rate on the equilibrium concentration of hydrogen ions in solution and indicates that oxyacids are involved in the redox process not as molecules, contrary to the previous assumption, but as L^{x-} anions, where $x = 2, 3, 4$.

To conclude, it should be mentioned that the redox reactions analyzed in the present study can be, apparently, regarded as indicator reactions [22] for the corresponding complexation pre-equilibria and used not only to solve the inverse problem of determining the rate constants of intramolecular redox decomposition, but also to tackle with the direct problem of finding the equilibrium concentrations of the complexes (and, as a consequence, of their stability constants) by kinetic methods.

EXPERIMENTAL

Twice recrystallized lactic H_2Lact, malic H_3Malt, and tartaric H_4Tart acids, oxycarboxylic acid of chemically pure grade, and cerium(IV) sulfate $Ce(SO_4)_2 \cdot 4H_2O$ of analytically pure grade were used in the study. The required ionic strength of solution, $I = 2$, was created with ammonium sulfate of analytically pure grade. The initial solutions wee prepared from precisely weighed portions. The concentration of organic acid solutions was refined by pH-metric titration with a NaOH solution containing no CO_3^{2-} ions. The content of cerium (IV) in the salt and a freshly prepared solution were determined by back titration with Mohr's salt in the presence of ferroin [23] before and after an experiment.

The optical density of the solutions was recorded with a Specord UV VIS recording spectrophotometer and a KF-5 photoelectrocolorimeter with MEA-4 recording unit, mainly at a wavelength of 400 nm. As the time of reaction onset was taken the instant at which the mixing vessel, in which the starting components were placed, was turned upside-down. The initial optical density of the reaction mixture of the metal and the ligand D^0 was found by linear extrapolation of the kinetic curves plotted in semilogarithmic coordinates to the instant of time $\tau = 0$. The solutions were thermostated using a Wobser thermostat.

The pH value was measured in a mixture of components, after the recording of the optical density ($\tau \approx 1$ min and also $\tau \approx 10$ min), and in cerium(IV) sulfate solutions with a pH-673 precision pH meter.

The step constant of protonation of the carboxy group in the lactic acid anion was also determined at an ionic strength $I = 2$

$$æ_2 = \frac{[H_2L]}{[HL][H]}. \qquad (18)$$

The value $\log æ_2 = 3.72 \pm 0.02$, obtained for H_2Lact, is in agreement with $\log æ_2 = 3.69$ ($I = 2$) [7]. The logarithms of step constants of protonation of carboxy groups in the malic acid anion ($\log æ_1 = 3.22$, $\log æ_2 = 4.71$) were taken from [24], and those for the tartaric acid anion ($\log æ_1 = 2.95$, $\log æ_2 = 4.11$), from [25].

Since, according to the dissociation constants of oxy groups, oxyacids are weak acids, the following value of the logarithm of the dissociation constant of the oxy group was used in calculations for all oxyacids: $\log B_1 = 14.6$ (obtained by averaging the data of [16, 25]; in [25], the value of $\log B_1$ was determined by mathematical modeling). The logarithms of the total protonation constants $B_i = [H_iL] / [L][H]^i$, $i > 1$, were taken to be as follows: $\log B_2 = 18.31$ for H_2Lact; $\log B_2 = 19.31$, $\log B_3 = 22.53$ for H_3Malt; and $\log B_2 = 25.90$, $\log B_3 = 30.01$, and $\log B_4 = 32.96$ for H_4Tart.

CONCLUSIONS

(1) A generalization of the methods used to study complexation (D–pH method and methods of molar ratios and isomolar series) to the case on nonzero rate of redox decomposition of complexes was proposed.

(2) The above methods were used to determine the composition, stability constants, true rate constants, and activation energies of intramolecular redox decomposition of hydroxo complexes of cerium(IV) with a number of organic ligands; the law governing the rate of the redox process occurring in the systems and its intermediate mechanism was established.

(3) The absence of stabilization of cerium(IV), with the stability of its complexes increasing in the series of the α oxycarboxylic acids considered, and the independence of the reactivity of these complexes from the denticity of an organic ligand were demonstrated.

(4) The independence of the rate constants and activation energy of redox decomposition of complexes from the denticity of oxyacids was interpreted in

terms of the bridge mechanism of redox decomposition as transfer of an electron via one and the same bridge group in the complexes $[CeOHL]^{3-m}$ (m = 2, 3, 4).

(5) A conclusion was made that the redox reactions considered in the present study can be used as indicator reactions in investigating the corresponding complexation equilibria by kinetic methods.

REFERENCES

1. Kiselev, Yu.M., *Zh. Neorg. Khim.*, 1999, vol. 44, no. 5, pp. 711–717.
2. Kiselev, Yu.M., *Zh. Neorg. Khim.*, 1998, vol. 43, no. 5, pp. 759–767.
3. *Koordinatsionnaya khimiya redkozemel'nykh elementov* (Coordination Chemistry of Rare-Earth Elements), Spitsyn, V.I. and Martynenko, L.I., Eds., Moscow: Mos. Gos. Univ., 1974.
4. Kiselev, Yu.M., *Vestn. Mos. Gos. Univ.*, 1998, vol. 38, no. 1, pp. 3–10.
5. Sarana, N.V., in *Trudy Leningradskogo tekhnologicheskogo instituta tsellyulozno-bumazhnoi promyshlennosti* (Coll. of Sci. Works of Leningrad Technol. Inst. of Pulp and Paper Industry), 1969, no. 24, pp. 56–59.
6. Dolgoplosk, B.A. and Tinyakova, E.I., *Okislitel'no-vosstanovitel'nye sistemy kak istochnik svobodnykh radikalov* (Redox Systems as a Source of Free Radicals), Moscow: Nauka, 1972.
7. Inczedi, J., *Analytical Application of Complex Equilibria*, Translation Editor J.Tyson, Budapest: Academia Kiado, Coll House: Ellis Horwood, 1976.
8. Duka, G.G., Batyr, D.G., Romanchuk, L.S., and Sychev, A.Ya., *Koord. Khim.*, 1990, vol. 16, no. 1, pp. 93–106.
9. Rao, B.M., Sastrys, T.P., and Parekh, T., *Z. phys. Chem.*, 1983, vol. 264, no. 5, pp. 906–920.
10. Krishna, B. and Tewari, K.C., *J. Chem. Soc.*, 1961, no. 25, pp. 3097–3102.
11. Mehrotra, R.N. and Chosh, S., *Z. phys. Chem. (DDR)*, 1965, vol. 230, no. 3/4, pp. 231–239.
12. Lahid, A. and Alexander, A., *J. Chem. Soc. Dalton Trans.*, 1974, no. 23, pp. 2521–2530.
13. Luzan, A.A. and Yatsimirskii, K.B., *Zh. Neorg. Khim.*, 1968, vol. 13, no. 12, pp. 3216–3221.
14. Vakhramova, G.P., Pechurova, N.I., and Spitsyn, V.I., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, no. 10, pp. 2361–2366.
15. Vakhramova, G.P., Pechurova, N.I., and Spitsyn, V.I., *Zh. Neorg. Khim.*, 1974, vol. 19, no. 10, pp. 2722–2725.
16. Kostromina, N.A., Kumok, V.N., and Skorik, N.A., *Khimiya koordinatsionnykh soedinenii* (Chemistry of Coordination Compounds), Moscow: Vysshaya Shkola, 1990.
17. Trubacheva, L.V. and Pechurova, N.I., *Zh. Neorg. Khim.*, 1981, vol. 26, no. 12, pp. 3254–3258.
18. Skorik, N.A. and Artish, A.S., *Zh. Neorg. Khim.*, 1985, vol. 30, no. 8, pp. 1994–1997.
19. Bachmann, K. and Lieser, K.H., *Ber. Bunsgesell. Phys. Chem.*, 1963, vol. 67, no. 8, pp. 810–816.
20. Voskresenskaya, O.O. and Skorik, N.A., *Zh. Neorg. Khim.*, 2000, vol. 45, no. 12, pp. 2090–2098.
21. Voskresenskaya, O.O. and Skorik, N.A., *Zh. Neorg. Khim.*, 2000, vol. 45, no. 4, pp. 719–726.
22. Yatsimirskii, K.B., *Kinetic Methods of Analysis*, Oxford: Pergamon, 1966.
23. Kolthoff, I.M., Belcher, R, Stenger, V. A., and Matsuyama, G., *Volumetric Analysis*, vol. III, *Titration Methods: Oxidation–Reduction Reactions*, New York: Interscience, 1957.
24. Sillen, L.G. and Martell, A.E., Stability Constants of Metal–Ion Complexes: *Special publication no. 17*, London: Chemical Soc., 1964.
25. Dobrynina, N.A. and Martynenko, L.I., *Problemy sovremennoi khimii koordinatsionnykh soedinenii* (Problems of Modern Chemistry of Coordination Compounds), Burkov, K.A., Ed., Leningrad: Len. Gos. Univ., 1989, p. 98.