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V. E. Plyushchev, L. P. Shklover, L. M. Shkolnikova, G. P. Kuznetsova, G. V. Nadezhdina

Properties of the Formates of Rare-Earth Elements in the Lanthanum-Holmium Series

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The properties of the formates of rare-earth elements have been insufficiently studied. Compounds of Ho, Tu, and Lu have not previously been described at all. We synthesized the formates of Y, La, and all the lanthanoids of the Pr–Ho series (with the exception of Pm) by the interaction of freshly precipitated rare-earth hydroxides with HCOOH. Cerium(III) formate was obtained by dissolving the metal carbonate in HCOOH.

Table 1

Properties of rare-earth formates in the lanthanum–holmium series

Compound	Temperature of sample dehydration, °C, $Me(HCOO)_3 \cdot nH_2O$	ΔG^*, wt.%	Lattice parameters: a, Å	Lattice parameters: α	Pycnometric density d_{20}, g/cm^3	Solubility in water, wt.% Me_2O_3, at 25°	Solubility in water, wt.% Me_2O_3, at 40°	Solubility in water, wt.% Me_2O_3, at 50°	$-\Delta H°$, kcal/mol
$La(HCOO)_3$	230	0 (230)	6.36	115°25′	3.286	0.19	0.19	0.19	479.2
$Ce(HCOO)_3 \cdot 0.2H_2O$	230	23.54 (230)	6.29	115°26′	3.386	0.20	0.19	0.19	460.7
$Pr(HCOO)_3$	200	0 (200)	6.26	115°32′	3.447	0.24	0.26	0.26	458.7
$Nd(HCOO)_3$	230	0 (230)	6.23	115°29′	3.533	0.25	0.25	0.25	452.2
$Sm(HCOO)_3$	230	0 (230)	6.19	115°34′	3.707	0.47	0.49	0.48	450.4
$Eu(HCOO)_3$	200	0.37 (175)	6.18	115°34′	3.806	0.25	0.64	0.29	—

Compound	Temperature of sample dehydration, °C, $Me(HCOO)_3 \cdot nH_2O$	ΔG*, wt.%	Lattice parameters: a, Å	Lattice parameters: α	Pycnometric density d_{20}, g/cm^3	Solubility in water, wt.% Me_2O_3, at 25°	Solubility in water, wt.% Me_2O_3, at 40°	Solubility in water, wt.% Me_2O_3, at 50°	$-\Delta H°$, kcal/mol
$Gd(HCOO)_3$	20	0.30 (175)	6.17	115°35′	3.894	1.58	1.64	0.76	449.7
$Tb(HCOO)_3$	60	0 (230)	6.16	115°34′	3.950	2.58	2.79	1.91	447.6
$Dy(HCOO)_3$	80	0.79 (175)	6.14	115°25′	4.041	4.83	4.91	4.43	448.2
$Ho(HCOO)_3$	80	0.73 (175)	6.13	115°30′	4.110	10.39	11.52	8.20	447.5

* ΔG is the excess metal content in rare-earth formates, dried at the temperature (°C) indicated in parentheses, relative to the corresponding anhydrous compound.

The starting rare-earth oxides contained, as impurities, 0.05–1.5 wt.% of other rare-earth elements (the content of rare-earth impurities in the oxides of terbium and dysprosium was 2.9 and 2.3%, respectively). Solutions of the nitrates of Y, La, and the elements of the Pr–Dy series were subsequently treated with H_2O_2 in order to remove the cerium impurity. The purified HCOOH had $n_D^{20} = 1.3712$. Elemental analysis of the rare-earth formates dried to constant weight at room temperature makes it possible to represent the composition of the compounds by the formula $Me(HCOO)_3 \cdot nH_2O$, where the value of n in the series of formates from La to Ho varies within the range 0–0.5*.

X-ray study of polycrystalline samples (RKU-86 camera, copper radiation) confirmed the data of [1] on the isomorphism of the formates of Ce, Pr, Nd, Sm, and Gd and revealed isomorphism of all element formates in the La–Ho series. Across the series of rare-earth formates studied, a regular decrease is observed in the constant a of the rhombohedral lattice of the compounds (Fig. 1, Table 1), which is probably connected with lanthanoid contraction. In agreement with the work of Mayer et al. [1], a small amount (up to 0.5 mol) of water indeed does not affect the character of the crystal lattice of rare-earth formates. The choice of the series of compounds considered in the present communication was determined by the desire to reveal the relationship between the structure and properties of rare-earth formates.

* For europium and gadolinium formates, $n = 0$.

Fig. 1. Properties of formates of elements in the lanthanum–holmium series as a function of the rare-earth atomic number: 1 –change in the lattice constant a°; 2 –change in density d_{20}; 3 –change in the temperature of the most intense endothermic effect on DTA curves (heating in open Stepanov vessels); 4 – change in the value of the standard heat of formation (ΔH^0 $Me(HCCO)_3$), kcal/mol

Figure 1: Fig. 1. Properties of formates of elements in the lanthanum–holmium series as a function of the rare-earth atomic number: 1 –change in the lattice constant a°; 2 –change in density d_{20}; 3 –change in the temperature of the most intense endothermic effect on DTA curves (heating in open Stepanov vessels); 4 –change in the value of the standard heat of formation (ΔH^0 $Me(HCCO)_3$), kcal/mol

Isothermal drying in the interval 20-230° showed the possibility of complete dehydration without decomposition for all rare-earth formates (except cerium formate). The dehydration temperature is given in Table 1. According to our data, above 200° there occurs destruction of cerium formate that has not yet been completely dehydrated, accompanied by oxidation of Ce(III) to Ce(IV). The Debyegram of cerium formate dried to constant weight at 230° confirms the results of the chemical analysis (Table 1).

As can be seen from the data of Table 1, the formates of Eu, Gd, Dy, and Ho, when the drying temperature is increased to 175°, undergo comparatively slight destruction. Thus, we did not confirm the data ([2]) on the decomposition of La and Ce formates as a result of drying them above 90°.

Very little has been published on the density and solubility of rare-earth formates ([3-6]); we determined their density in benzene by the pycnometric method at $20 \pm 0.1^\circ$ (n_D^{20} 1.5015; d_4^{20} 0.8792). The root-mean-square error of the density determination was usually within ±1-3%. The results are given in Table 1 and in Fig. 1.

Fig. 1. Properties of formates of elements in the lanthanum–holmium series as a function of the rare-earth atomic number: **1** –change in the lattice constant a° of the rhombohedral lattice, **2** –change in density d_{20}, **3** –change in the temperature of the most intense endothermic effect on DTA curves (heating in open Stepanov vessels), **4** –change in the value of the standard heat of formation ($\Delta H^0 Me(HCCO)_3$), kcal/mol

Solubility was studied by the isothermal method at 25, 40, and 50°. The temperature was maintained with an accuracy of $\pm 0.1^\circ$. It was found that equilibrium in all cases was established within 7 days. Samples were taken according to the generally accepted procedure. The content of rare-earth elements in samples of La, Ce, Nd, and Sm formates was determined gravimetrically in the form of oxides; praseodymium was precipitated from solution as the oxalate and titrated from the residue with potassium permanganate. This route for de-

termining praseodymium is more reliable than the gravimetric method, owing to the inconstancy of the composition of praseodymium oxide. The content of rare-earth elements in samples of formates of the Eu–Ho series was determined complexometrically ([7]), which made it possible to work with microquantities of the substance analyzed. In view of the fact that at 50° hydrolysis of rare-earth formates in solution was already observed, it is more correct to express their solubility recalculated as wt.% Me_2O_3.

We paid special attention to the study of the thermal stability of rare-earth formates. Decomposition of the formates in air was carried out on an apparatus providing simultaneous photographic recording of thermogravimetric-analysis (TGA) and differential-thermal-analysis (DTA) curves upon heating a single sample of the compound weighing 40–50 mg. Heating was carried out at an average rate of 13–20 deg/min in the temperature interval from room temperature to 750–850°. On the basis of analysis of the TGA curves, the following dissociation schemes were proposed:

$$2Me(HCOO)_3 \rightarrow Me_2O_3 \cdot CO_2 \rightarrow Me_2O_3, \quad (1)$$

where $Me = La, Nd, Sm, Eu, Gd, Dy, Ho$.

$$Ce(HCOO)_3 \cdot 0.2H_2O \rightarrow CeO_2, \quad (2)$$

$$6Pr(HCOO)_3 \rightarrow 3(Pr_2O_3 \cdot CO_2) \rightarrow Pr_6O_{11}, \quad (3)$$

$$4Tb(HCOO)_3 \rightarrow 2(Tb_2O_3 \cdot CO_2) \rightarrow Tb_4O_7. \quad (4)$$

Common to schemes (1), (3), and (4) is the formation in the interval 390–480° of thermally ···

unstable (with the exception of the case of lanthanum formate) compounds $Me_2O_3 \cdot CO_2$, fairly close in composition to basic carbonates. Comparison of the results obtained by us with published data on the thermogravimetry of a series of rare-earth-element compounds shows that intermediate and basic carbonates dissociate in air and in an atmosphere of CO_2; lanthanum oxalate ([8–12]) and carbonate ([13]), the oxalates of Pr, Nd, Sm, Gd, Er, Lu ([11]), and yttrium ([14]). The decomposition products of the formates of Ca, Sr, and Ba are likewise ([15]) metal carbonates, $MeCO_3$. An exception among the rare-earth formates is cerium formate, which, like some other cerium(III) compounds—oxalate ([8,10,11,16]), acetate ([17]), carbonate ([13]), and citrate ([18])—is converted into CeO_2, bypassing the intermediate stage.

Fig. 2. Thermograms and thermogravimetric curves of $Ce(HCOO)_3 \cdot 0.2H_2O$, obtained on heating in a quartz (a) and platinum (b) crucible

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Figure 2: Fig. 2. Thermograms and thermogravimetric curves of Ce(HCOO)3 • 0.2H2O obtained on heating in quartz (a) and platinum (b) crucibles

At the same time, our results do not confirm the conclusions of the authors ([19]), who proposed for the intermediate decomposition products of lanthanum and cerium formates the formula $Me_2O_3 \cdot 6CO$ and established that the decomposition of the formates of La, Ce, Pr, Nd, and Sm ends with the formation of the corresponding oxide in the interval 445–520°, with the last three compounds dissociating directly to the oxide. According to the DTA data obtained by us, the temperature of formation of the indicated oxides (except CeO_2) proves to be considerably higher than was indicated in ([19]). Heating to 700–800° usually still does not lead to final decomposition to the oxides. The DTA results are confirmed by data from gravimetric determination of the metal content in the formates: ignition of weighed portions of the La, Pr, Nd, and Sm compounds of 0.2–0.3 g at 700–750° for three hours is insufficient for complete dissociation of the formates to oxides.

The decomposition of rare-earth formates to intermediate products in a quartz crucible is accompanied on the DTA curves by an endothermic effect with a minimum in the interval 360–448° and an exothermic effect* with a maximum at 420–465°. On the DTA curve of cerium formate, an intense exothermic effect is observed with a maximum at 390°, corresponding to decomposition to CeO_2.

We have found a dependence of the sign of the thermal effects on the DTA curves of the formates of La and the rare-earth elements in the Nd-Ho series on the material of the crucible in which the compound is heated. Thus, the DTA curves of the indicated formates heated in a platinum crucible differ by two exothermic effects in the region of decomposition to intermediate products (with maxima in the intervals 340–430° and 400–510°), although the nature of the decomposition remains unchanged. The reason for the reversal of the sign of the effects apparently lies in the catalytic influence of the platinum walls of the crucible on the pro-

* The latter is absent on the DTA curves of the formates of La, Nd, and Ho.

processes of oxidation and disproportionation of CO, the formation of which was observed during the decomposition of the formates of Mn, Fe, Co, and Ni (20) and of certain rare-earth elements (21). Disproportionation of CO by the reaction: $2CO \rightarrow C + CO_2$ was recorded in studies of the dissociation of rare-earth oxalates (9, 11, 12, 14); the appearance of carbon in solid intermediate products was found during the decomposition of La carbonate in vacuum (22) and of La, Pr, Nd, and Sm citrates (18) in air.

The degree of conversion of CO into CO_2 varies along the series of rare-earth oxalates (11). The absence of exothermic effects on the DTA curves of La, Nd,

and Ho formates heated in a quartz crucible is apparently connected with this phenomenon. The decomposition of Ce and Pr formates is accompanied by oxidation of Ce(III) and Pr(III), and the effect of the crucible material on the process of thermal dissociation is manifested here much more weakly. Figure 2 gives thermograms and thermogravigrams of cerium formate obtained using quartz (a) and platinum (b) crucibles.

Along the series of rare-earth formates from La to Ho, a decrease in thermal stability is observed, expressed, for example, by the temperature of the minimum of the most intense endothermic effect on the DTA curves of formates heated in open Stepanov quartz vessels * (Fig. 1).

It was of interest to compare the DTA data and the standard heat of formation (ΔH^0) of the rare-earth formates. We calculated $\Delta H^0_{\mathrm{Me(HCOO)3}}$ by the method (23, 24) from the value of the crystal-lattice energy (U) of the compounds. Using ΔH^0 of rare-earth oxides ** (25), we similarly (23, 24) obtained the values of the standard heats of formation of gaseous rare-earth ions needed for the calculation of $\Delta H^0_{\mathrm{Me(HCOO)3}}$. The value of ΔH^0 of the gaseous formate ion was taken as -110.1 kcal/g-ion (24, 26). The results are given in Table 1 and in Fig. 1. Despite the approximate nature of the calculation, Fig. 1 shows a decrease in ΔH^0 of the rare-earth formates along the series La–Ho.

It should be noted that it was not possible to confirm the presence of water in the rare-earth formates of the La–Ho series dried at room temperature by means of IR spectra. Thus, the question of the nature of water in the indicated compounds requires additional confirmation.

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* With this method of heating, because of the lack of oxygen at the surface of the dissociating compound, oxidation processes are hindered, and the DTA curves of all rare-earth formates are characterized only by endothermic effects. Under these conditions, in view of the uniformity of the DTA curves, comparison of thermal stability in this way is valid.

** Because of the absence of data for $\Delta H^0_{Eu_2O_3}$, it was not possible to calculate $\Delta H^0_{Eu(HCOO)3}$.

Note: Figure translations are in progress. See original paper for figures.

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