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Some Observations Regarding Rare-Earth Lactates¹

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Abstract

Lactates of all the rare earths except lanthanum, cerium, and praseodymium were prepared and studied. In the case of lanthanum, cerium, and praseodymium the lactates are apparently so soluble that they cannot be crystallized directly from aqueous solution. Products obtained by addition of anhydrous ethanol to sirupy solutions of the light-rare-earth lactates were not well characterized and were deliquescent. Neodymium lactate trihydrate was prepared only by the addition of alcohol to a sirupy solution. Since it was not as deliquescent as the lactates of lanthanum, cerium, and praseodymium, some of its properties could be studied. The lactates of all the other rare earths, samarium through lutetium, as well as the lactate of yttrium, separated readily from aqueous media as trihydrates--the solubility of the hydrated lactate decreasing as the atomic number of the rare earth increased. Thermal decomposition of the crystalline lactates, except those of neodymium and samarium, proceeded through dihydrated and anhydrous states to a composition corresponding roughly to $\text{Ln}(\text{lacCO}_3)$ at a temperature of about 290-300°C.

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$\text{Ln}_2(\text{CO}_3)_3$ or $\text{Ln}_2\text{O}(\text{CO}_3)_2$ were observed. In order to make a comparison, thermal decomposition of the rare-earth glycolates was studied also. Solubilities in water at both 20 and 60°C have been tabulated.

Introduction

Ammonium lactate has been used rather extensively in the separation of micro-amounts of rare earths by ion-exchange elution chromatography.²⁻⁹ Consequently, it is desirable to establish a clear picture of the chemistry of rare-earth lactates.

Recent work in this laboratory by Karraker¹⁰ has provided much information regarding the stabilities of individual $\text{Ln}(\text{lac})^{++}$, $\text{Ln}(\text{lac})_2^+$, and $\text{Ln}(\text{lac})_3$ species in water and has established a firm basis for explaining the elution orders observed when rare earths are eluted from cation-exchange columns with ammonium lactate buffer solutions. The general application of the lactate process to the separation of macro-amounts of rare earths, however, is dependent to a large degree on the intrinsic solubility of the various hydrated trilactate species in water. For this reason a program was initiated which involved the preparation and study of the individual rare-earth trilactates.

Preparation

The general method chosen for preparation of yttrium lactate and the rare-earth lactates was the addition of the individual rare-earth chloride to an amount of ammonium lactate slightly in excess of the

trilactate stoichiometry in sufficient water to dissolve the product. After filtering, each solution was allowed to stand in a rapid current of dry air until the volume was reduced sufficiently to permit crystallization of most of the rare-earth lactate present. Lactates of the rare earths from samarium through lutetium were readily prepared in this manner, but solutions of lanthanum, cerium, praseodymium, and neodymium lactates failed to yield crystalline products, apparently due to the high solubility of these compounds in water and their deliquescent nature. Solutions of the lactates of lanthanum, neodymium, samarium, europium, and gadolinium were also prepared by direct combination of the individual rare-earth sesquioxide with an amount of lactic acid slightly in excess of the trilactate stoichiometry in sufficient water to dissolve the product. Crystalline lactates of samarium, europium, and gadolinium were obtained readily from such solutions after filtration and concentration.

Some material which corresponded closely to the composition $\text{Nd}(\text{lac})_3 \cdot 3\text{H}_2\text{O}$ was obtained from a sirupy solution by the addition of anhydrous alcohol; but, in general, the light-rare-earth lactates precipitated by the addition of alcohol were not well characterized.

The crystalline products obtained were collected by filtration, washed with distilled water, dried in air at room temperature, and assayed for rare-earth content by igniting a weighed specimen of each to the corresponding oxide in a tared porcelain crucible at 800-900°C. The hydration numbers were then estimated from the respective weights of

the samples and the oxide residues, assuming a proportionality of rare earth; lactate:water equal to 1:3:n. In every case, n corresponded almost exactly to 3. This was a little surprising, since the glycolates of the rare earths, lanthanum through europium, were previously observed to separate in anhydrous form and the glycolates of the elements, gadolinium through lutetium, and yttrium glycolate were obtained as dihydrates under identical conditions.¹¹

Thermal Decomposition of Hydrated Rare-Earth

Lactates and Glycolates

Samples weighing approximately 0.3 g each were weighed into a small platinum-foil dish on the pan of the thermobalance (the essentials of the balance have been described previously¹² and will not be described here) and heated in a slow current of dry nitrogen while the temperature of the furnace was increased from room temperature to 465°C at a rate of about 45° per hr. The loss in weight was sensed by the displacement of the core of a linear variable differential transformer (Schaevitz Engineering type 200 SS-L) which was incorporated into the balance mechanism. The outputs of the transformer and a chromel-alumel thermocouple, located in the furnace just above the sample, were recorded by means of a Brown Electronik Recorder. Weight variations as small as 0.2 mg and temperature variations of approximately 1° could be detected by the system. Results obtained with lactates and glycolates are summarized in Tables I and II, respectively.

Trihydrated neodymium and samarium lactates apparently decompose directly to anhydrous form, but with the other hydrated rare-earth lactates

Table I

LEVELS OBSERVED DURING THERMAL DECOMPOSITION OF RARE-EARTH LACTATES

original composition	Ln ₃ lac ₃ ·3H ₂ O (mol. wt.) theor. obs. temp.	Ln ₃ lac ₃ (mol. wt.) theor. obs. temp.	Ln ₃ lacCO ₃ (mol. wt.) theor. obs. temp.
Ndlac ₃ ·3.11H ₂ O	level not observed	411.5 413 116	293.4 292 290
Smlac ₃ ·3.01H ₂ O	level not observed	417.6 413 134	299.4 292 288
Eulac ₃ ·2.91H ₂ O	455.3 454 98	419.2 416 147	301.1 not observed
Gdlac ₃ ·3.01H ₂ O	460.5 457 107	424.5 421 156	306.3 302 290
Tblac ₃ ·3.08H ₂ O	462.2 462 98	426.1 425 153	308.0 302 290
Dylac ₃ ·2.98H ₂ O	465.8 465 96	429.7 428 149	311.6 306 291
Holac ₃ ·2.99H ₂ O	468.2 467 101	432.2 431 155	314.0 306 294
Erlac ₃ ·2.99H ₂ O	470.5 469 103	434.5 434 160	316.3 311 291
Tmlac ₃ ·2.95H ₂ O	472.2 469 105	436.2 434 163	318.0 312 293
Yblac ₃ ·2.98H ₂ O	476.3 476 110	440.3 440 167	322.1 315 295
Lulac ₃ ·2.97H ₂ O	478.2 476 105	442.2 440 164	324.1 316 293
Ylac ₃ ·2.99H ₂ O	392.2 387 100	356.2 352 154	238.0 227 289

Table II

LEVELS OBSERVED DURING THERMAL DECOMPOSITION OF RARE-EARTH GLYCOLATES

original composition	anhydrous level (mol. wt.)			Ln glyCO ₃ (mol. wt.)		
	theor.	obs.	temp.	theor.	obs.	temp.
Lagly ₃ ·0.00H ₂ O	364.1	364	25	not well-defined		
Cegly ₃ ·0.24H ₂ O	365.3	370	25	rapid decomp. to CeO ₂		
Prgly ₃ ·0.00H ₂ O	366.1	366	25	not well-defined		
Ndgly ₃ ·0.14H ₂ O	369.4	372	25	not well-defined		
Smgly ₃ ·0.13H ₂ O	375.5	378	25	285.4	259	367
Eugly ₃ ·0.06H ₂ O	377.1	378	25	287.1	284	314
Gdgly ₃ ·0.06H ₂ O	382.4	383	25	292.3	272	355
Gdgly ₃ ·2.07H ₂ O	382.4	383	175	292.3	297	349
Tbgly ₃ ·2.09H ₂ O	384.1	384	181	294.0	315	314
Dygly ₃ ·2.03H ₂ O	387.7	388	194	297.6	318	315
Hogly ₃ ·2.04H ₂ O	390.1	391	210	300.0	325	321
Ergly ₃ ·2.03H ₂ O	392.4	392	199	302.3	316	319
Tmgly ₃ ·2.10H ₂ O	394.1	393	199	304.0	314	321
Ybgly ₃ ·2.05H ₂ O	398.2	397	201	308.1	322	320
Lugly ₃ ·2.07H ₂ O	400.1	399	197	310.0	315	316
Ygly ₃ ·2.02H ₂ O	314.1	313	209	224.0	237	326

studied, a definite inflection in the weight vs. temperature plot confirmed the existence of dihydrated compounds as well as trihydrated and anhydrous forms. Agreement between the theoretical and observed molecular weights was in every case within a few units, so that it was concluded that very little hydrolysis or degradation of the parent chelate compound occurred below 150°C.

From 180 to about 290°C decomposition was quite marked, and an arrest between 290 and 320° in nearly every case suggests the formation of a compound of the type $\text{Ln}(\text{lacCO}_3)_3$. In the case of europium lactate no such inflection was noted. Instead, a very rapid weight loss occurred at about 240°, suggesting that the sample had ignited. When the rapid rate of decomposition subsided, the composition corresponded in one case to $\text{Eu}_2(\text{CO}_3)_3$ and in a second attempt closer to $\text{Eu}_2\text{O}(\text{CO}_3)_2$. Terbium exhibited the $\text{Tb}(\text{lacCO}_3)_3$ level, but a rapid weight loss then occurred at 305°C. When the rate of loss diminished, the composition corresponded roughly to $\text{Tb}_2\text{O}(\text{CO}_3)_3$. Beyond the temperature corresponding to the formation of $\text{Ln}(\text{lacCO}_3)_3$ all the other samples lost weight gradually and each gave a further inflection at a composition between $\text{Ln}_2\text{O}(\text{CO}_3)_2$ and $\text{Ln}_2(\text{CO}_3)_3$ before being converted to oxide form.

In general, the sesquioxide level (in the case of terbium the Tb_4O_7 level) was not reached at the upper limit of the thermobalance furnace, and it was necessary to ignite the residue at 800-900°C in another furnace in order to obtain a weighing form which could be used to compute the apparent composition of the compounds associated with the various arrests or inflections observed in the weight vs. temperature plot.

With the dihydrated rare-earth glycolates, decomposition to anhydrous form was observed to have been completed at a temperature ranging from 175 to 210°C, depending on the rare earth involved. Little hydrolysis or degradation was apparent up to 250°C, except in the case of cerium glycolate which apparently ignited at 225° and ended up as CeO_2 . Inflections due to the formation of Ln glyCO_3 were not well-defined in the case of lanthanum, praseodymium, and neodymium, but with the other rare earths a possible Ln glyCO_3 level was apparent between 310 and 360°C. Above 360°C additional degradation occurred and $\text{Ln}_2(\text{CO}_3)_3$ and/or $\text{Ln}_2\text{O}(\text{CO}_3)_2$ formation produced a further inflection. Since these upper inflections were not as well-defined as the others, the data have been omitted from Tables I and II.

Solubilities of the Trihydrated Rare-Earth Lactates

Samples of the individual $\text{Ln lac}_3 \cdot 3\text{H}_2\text{O}$ compounds in excess of the amount required for saturation were combined with distilled water in stoppered flasks and shaken mechanically in thermostated water baths in order to establish the intrinsic solubilities at 20 and 60°C. Samples were withdrawn after various time intervals and analyzed for rare earth. Since equilibrium was being approached from the undersaturated side, and it was observed that the apparent solubility was either constant or had actually begun to decline somewhat after seven days, we have chosen to include only the data obtained on the seventh day, the time at which the solutions were first sampled. To date, we have been unable to ascertain any definite reason for this anomalous decline in apparent solubility of the rare-earth lactates. The effect was noted in the case of samarium,

europium, and gadolinium lactates at 20°C and with nearly all of the rare-earth lactates studied at 60°. The greatest effect was noted with samarium lactate at the higher temperature. The solubility was observed to decrease from 1.87 g $\text{Sm}(\text{lac})_3 \cdot 3\text{H}_2\text{O}$ per 100 g H_2O on the seventh day to 1.41 g $\text{Sm}(\text{lac})_3 \cdot 3\text{H}_2\text{O}$ per 100 g H_2O on the fourteenth day. At 20°C the change observed for $\text{Sm}(\text{lac})_3 \cdot 3\text{H}_2\text{O}$ was from 1.25 to 1.19 g cmpd. per 100 g H_2O . An assay of the rare-earth content of the crystals in contact with the solution did not reveal any substantial difference in composition even after 133 days. Of course, both the original compounds and the residual crystals were assayed only after drying in air. It is possible, therefore, that $\text{Ln}(\text{lac})_3 \cdot 3\text{H}_2\text{O}$ does not truly represent the compound which is in stable equilibrium with the saturated solution. The crystals available were so fine that the excess water could not be eliminated satisfactorily except by allowing it to evaporate. Perhaps the crystals which originally separate from aqueous solution are more highly hydrated than is apparent from the composition of crystals which are dried in air, but when moist crystals were examined on the thermobalance no hydrate levels other than the trihydrate and dihydrate levels were noted. Due to our failure to resolve the difficulty we have rounded off all the data at two decimal places and report them with some reservations.

The trihydrated rare-earth lactates are about twice as soluble at 60 as at 20°C, and at both temperatures solubility decreases as the atomic number of the rare earth increases. Yttrium lactate has about the same solubility as holmium lactate. Lanthanum, cerium, praseodymium, and neodymium lactates are so soluble that they can not be prepared readily

Table III

THE SOLUBILITIES OF THE RARE-EARTH LACTATES IN WATER AT 20 AND 60°C

compound	solubility observed (g compd./100 g H ₂ O)	
	20°	60°
Smlac ₃ · 3H ₂ O	1.25	1.87
Eulac ₃ · 3H ₂ O	0.65	1.08
Gdlac ₃ · 3H ₂ O	0.41	0.75
Tblac ₃ · 3H ₂ O	0.24	0.59
Dylac ₃ · 3H ₂ O	0.17	0.36
Holac ₃ · 3H ₂ O	0.13	0.30
Erlac ₃ · 3H ₂ O	0.11	0.22
Tmlac ₃ · 3H ₂ O	0.09	0.19
Yblac ₃ · 3H ₂ O	0.07	0.15
Lulac ₃ · 3H ₂ O	0.06	0.13
Ylac ₃ · 3H ₂ O	0.13	0.27

from their solutions in water. In the case of the heavy rare earths, gadolinium through lutetium, it appears that the trihydrated lactates are about half as soluble as the corresponding dihydrated glycolates.

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