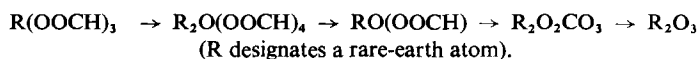# A Structural and Thermogravimetric Investigation of the Rare-Earth Formates

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Anhydrous rare-earth triformates (Sc, Y, La–Tm) and triformate dihydrates (Ho–Lu) have been prepared by direct reaction of the sesquioxides with aqueous formic acid. The thermal decomposition of anhydrous and thermally dehydrated formates, which have been investigated by TGA and high temperature X-ray diffraction techniques, and by mass spectrometric gas analysis is consistent with the following scheme:

$$R(OOCH)_3 \rightarrow R_2O(OOCH)_4 \rightarrow RO(OOCH) \rightarrow R_2O_2CO_3 \rightarrow R_2O_3$$
(R designates a rare-earth atom).

The monoxytetraformate appears to exist as an amorphous intermediate only for the lighter elements (La, Pr); the other intermediates are observed across the series except for ytterbium and lutetium, which exhibit more complex decomposition paths involving the pentoxymonocarbonate, $R_4O_5CO_3$. Lattice parameters obtained from powder and single crystal X-ray diffraction data for rhombohedral $R(OOCH)_3$ (Y, La–Tm), hexagonal LaO(OOCH), orthorhombic (*Pmma*) $R(OOCH)_3 \cdot 2H_2O$ (Y, Ho, Er), triclinic $R(OOCH)_3 \cdot 2H_2O$ (Yb, Lu), and monoclinic ($P2_1/c$) Sc(OOCH)$_3$ and linear thermal expansion data for Pr(OOCH)$_3$ are presented. The preparative results, decomposition schemes, and structural data are discussed and compared with those of previous reports.

Introduction

Some comprehensive reports on the rare-earth formates have been made by Shklover and co-workers (*1–5*) whose investigations have included the use of TGA, DTA, X-ray, and ir techniques. Other thermal studies have been described by Sahoo et al. (*6*) on lanthanum formate and by Head and Holley (*7*) on scandium formate. The only detailed X-ray investigations have been the single crystal studies on anhydrous gadolinium formate by Pabst (*8*) who classified the structure as rhombohedral ($a = 6.17$ Å, $\alpha = 115.5°$) with space group $R3m$, and on anhydrous scandium formate by Guseinova et al. (*9*) who reported a monoclinic structure ($a = 10.316$ Å, $b = 6.622$ Å, $c = 8.940$ Å, $V = 605$ Å^3) with space group $P2_1/c$. Mayer et al. (*10*) have indicated that the hydrated compounds $R(OOCH)_3 \cdot 0.2H_2O$ (Ce, Pr, Nd, and Sm) are isostructural with the anhydrous gadolinium formate. Plyushchev et al. (*4*) have

grouped the anhydrous and hydrated rare-earth formates into four series of isostructural phases as follows: (1) $R(OOCH)_3 \cdot nH_2O$ (La–Er, $0 \leqslant n \leqslant 0.5$) rhombohedral, isostructural with Gd(OOCH)$_3$; (2) $R(OOCH)_3 \cdot 2H_2O$ (Ho, Y, Er) structure unknown; (3) $R(OOCH)_3 \cdot 2H_2O$ (Tm, Yb, Lu) α-modification, structure unknown; (4) $R(OOCH)_3$ (Tm–Lu), β-modification, structure unknown.

Experimental Part

The rare-earth formates were prepared by direct reaction of formic acid with the sesquioxides. Small samples of oxide (99.9% with respect to rare-earth content) were calcined at 1000°C and combined with a large excess of reagent grade formic acid held at a temperature just below its boiling point. The mixture was heated and stirred until the oxide had dissolved or until 48 hr had elapsed. The anhydrous formates were prepared in both 50 and 95% acid, but di-hydrated products were obtained only in the dilute solution. Single crystals were obtained by slow evaporation of the solutions. After evaporation of

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the solvents the products were washed with acetone and dried in air.

The thermal decomposition data for the formates were obtained with a Cahn RG–10 microbalance. The 0.3 g samples were placed in a platinum bucket which was suspended from the beam by a meter-long platinum wire. The heated region of the quartz hang-down tube was surrounded by an Inconel block which contained a well for the accommodation of a Pt–Pt (10% Rh) thermocouple. The thermocouple was positioned approximately 6 mm from the sample, which was heated under 730 Torr CO_2 by means of a well-insulated, resistance furnace. A Data Track FGE 5110 programmer provided a linear heating rate ($\frac{1}{2}$ deg/min) up to 850°C.

Phase changes and decompositions were examined by X-ray powder diffraction using a high temperature diffractometer (11) with either a vacuum or a 730 Torr CO_2 atmosphere. Room temperature data were taken on a Guinier camera using Cu K_α radiation ($\lambda = 1.54184$ Å) with ThO_2 ($a_0 = 5.59625$ Å) as an internal standard. Single crystal X-ray diffraction data were obtained by oscillation and equiinclination Weissenberg techniques. The refined lattice parameters were obtained from the Guinier data with a least-squares regression program on a CDC 3400 computer; the program of Appleman et al (12) was employed in the indexing of some data.

The gaseous decomposition products were analyzed qualitatively with a Consolidated Electrodynamics Corporation Model 21-130 mass spectrometer. A sample of $La(OOCH)_3$ (~0.2 g), which was contained in an alumina boat, was pyrolyzed in an evacuable tube furnace system connected to the bleed inlet of the mass spectrometer. The sample and quartz reaction system were vacuum degassed at 175° to a residual pressure of 10^{-4}–10^{-5} Torr, and the background spectrum (20 eV ionizing electrons) was obtained for the isolated system. The sample temperature, which was measured with a cromel-alumel thermocouple, was increased slowly (~3°C/min) to 600°C, and the intensities of masses 18^+ (H_2O), 28^+ (CO, N_2), and 44^+ (CO_2) of the pyrolysis products were obtained at 20°C temperature intervals.

The gaseous decomposition products were analyzed gravimetrically for H_2O, CO_2, H_2, and CO in a modified carbon–hydrogen analysis train. Samples (0.5 g) of the anhydrous formates of La and Yb were pyrolyzed in a tube furnace under a flow of inert gas (Ar or N_2) which carried the gaseous products through H_2O and CO_2 collection tubes (magnesium perchlorate and Ascarite, respectively), through a one-way valve, and into a second portion of the

apparatus where oxygen was combined with the carrier gas before it passed over a cupric oxide-ceria catalyst at 650°C and again through collection tubes for H_2O and CO_2. Both alumina and platinum sample containers were employed; samples were heated to constant weight at selected temperatures which were chosen by reference to the TGA data.

Results and Discussion

Although many of the preparative reactions went to completion, the oxides of the cerium subgroup never dissolved completely in formic acid; the granular starting materials gradually changed into finely divided, gummy products. As might be expected, long exposures on the Guinier camera revealed minor traces of oxide (<1%) in some preparations. Thermogravimetric analysis indicated that in all cases, the ratio (OOCH):R was three. The H_2O:R ratios which were determined for some products by drying in air at 125–150°C follow: Sc, 0.10; Y, 0.058 (95%); La, 0.030; Pr, 0.024; Nd, 0.003; Sm, 0.012; Dy, 0.016; Ho, 2.008 (50%); Er, 0.086 (95%); Tm, 0.001 (95%); Yb, 2.014 (50%); and Lu, 2.014 (50%). The percentages appearing after some of the ratios indicate the acid concentration of the reaction solvent. It should be noted that the extent of hydration observed for most of the compounds is a factor of ten lower than that reported by others (2, 10). It seems probable that although the formates may retain some moisture, the compounds are best represented by the formula $R(OOCH)_3$. It also seems clear that the formates of the smaller rare-earths form hydrates of the formula $R(OOCH)_3 \cdot 2H_2O$.

It is convenient to discuss the thermogravimetric and X-ray results in terms of the isostructural reaction products, viz. (A) the anhydrous rhombohedral formates, (B) and (C) the two types of dihydrated formates, and (D) scandium formate.

A. The Anhydrous Rhombohedral Formates (La–Tm)

Thermogravimetric Analysis. In the TGA experiments no evidence was found for the existence of the partially hydrated formates $R(OOCH)_3 \cdot nH_2O$ ($n = 0.2$–0.5) reported previously (1–5). We can only conclude that the earlier preparations contained water which can be reduced by a factor of ten by air drying (i.e., Arizona air), and which can be removed completely by heating to ~150°C. The TGA data (Fig. 1) for the anhydrous formates show an interesting trend with increasing atomic number and are much less complex than those of the dihydrated
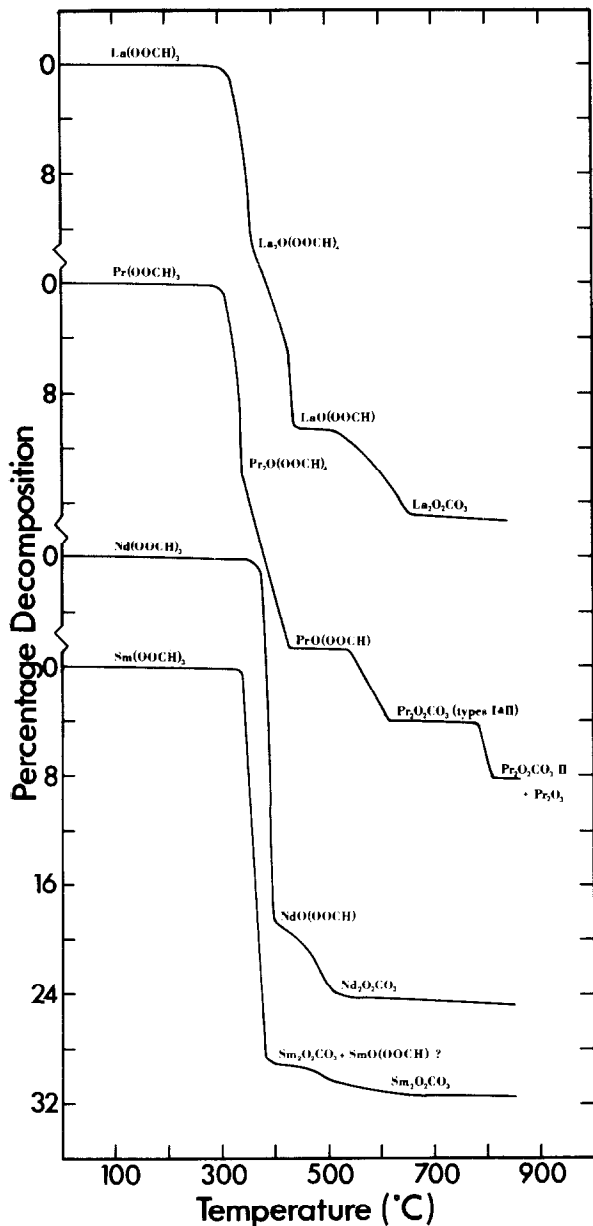
FIG. 1. Thermograms for the anhydrous formates in one atmosphere of carbon dioxide.
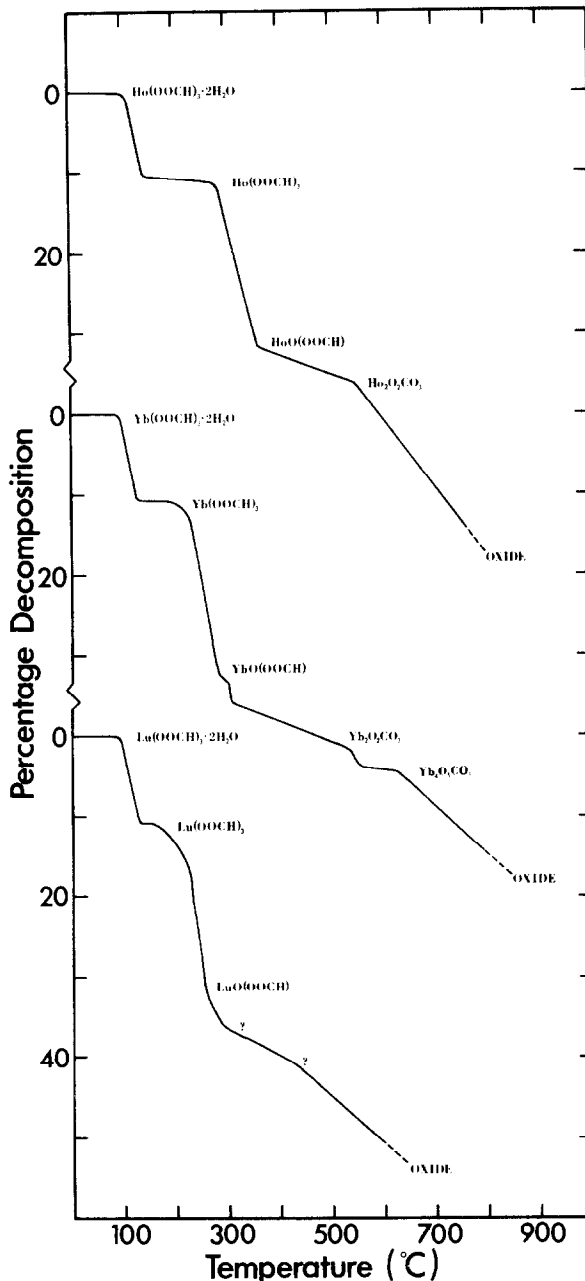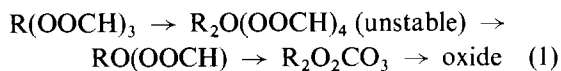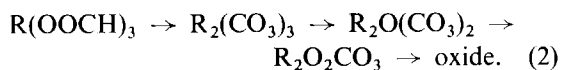

FIG. 2. Thermograms for the formate dihydrates in one atmosphere of carbon dioxide.

formates (Fig. 2). Two possible decomposition schemes for the TGA data follow:

$$R(OOCH)_3 \rightarrow R_2O(OOCH)_4 \text{ (unstable)} \rightarrow$$
$$RO(OOCH) \rightarrow R_2O_2CO_3 \rightarrow \text{oxide} \quad (1)$$

and

$$R(OOCH)_3 \rightarrow R_2(CO_3)_3 \rightarrow R_2O(CO_3)_2 \rightarrow$$
$$R_2O_2CO_3 \rightarrow \text{oxide}. \quad (2)$$

Scheme (1) gives an excellent fit of the observed plateaus, but (2) also shows some correspondence of plateaus and formulae. A third decomposition path involving the formation of $R_2(C_2O_4)$ as the first intermediate is possible, but the poor correspondence of this scheme did not merit it further consideration. Despite the unusual formula of

$R_2O(OOCH)_4$, which corresponds to the loss of one formate group per mole, scheme (1) fits the data better than (2). The tricarbonate has been shown by Head and Holley (7) to be stable up to 500°C, but if the tricarbonate is formed, scheme (2) requires that the carbonate decompose below 400°C. Furthermore, the monoxydicarbonate was not observed during the thermal decomposition of the rare-earth oxalates by Turcotte et al. (13). Therefore, the decomposition of the anhydrous formates is described according to scheme (1) as follows.

Lanthanum Formate. The anhydrous formate is stable up to 300°C. A slight plateau at 340°C indicates the formation of a compound which can be assigned the formula $La_2O(OOCH)_4$. It is unstable and decomposes almost immediately to give the monoxymonoformate, LaO(OOCH), which exists up to 500°C. At this point, the weight loss is 27.02% of the initial weight. This oxyformate slowly decomposes until at about 600°C a plateau (32.49 wt% loss) corresponding to the previously characterized dioxymonocarbonate ($La_2O_2CO_3$) (13) is reached. The oxycarbonate is stable up to 820°C.

It is interesting to compare these results with those reported by Plyushchev et al. (1) whose measurements were made in air at a much faster heating rate (17–20°C/min). They observed only the dioxymonocarbonate and the sesquioxide; however, their DTA data obtained using a platinum sample container showed two exothermic peaks (427 and 510°C) which could possibly be due to the formation of the oxyformates and the oxycarbonate. The percentage weight loss and temperature of formation of the dioxymonocarbonate agree well with the present work if allowance is made for the difference in heating rates and the presence of a Co_2 atmosphere.

Praseodymium Formate. Decomposition of the anhydrous formate begins at 320°C. A plateau at 13.41wt% loss indicates that $Pr_2O(OOCH)_4$ forms and then decomposes immediately to give the monoxymonoformate at 430°C with a total weight loss of 26.82%. At 550°C the sample decays to a mixture of types I and II dioxymonocarbonate. The sharp weight loss at 780°C corresponds to the reaction of type I + (type II) → (type II) + oxide.

Neodymium Formate. The TGA analysis shows that $Nd(OOCH)_3$ is stable up to 380°C. Unlike the La and Pr formates, the Nd phase apparently does not form $Nd_2O(OOCH)_4$, but decays directly to the monoxymonoformate plus carbon at 26.50 wt% loss. A third plateau at 480° (31.87 wt% loss) corresponds to the dioxymonocarbonate which remains up to 820°C.

Samarium Formate. The samarium phase begins to decompose at 380°C, the same temperature observed for $Nd(OOCH)_3$. Unlike the previous decompositions, there is no evidence for the formation of any oxyformate. This behavior may be due to a catalytic effect of a trace of oxide initially present in the sample. At 390°C, there is a plateau (31.19 wt% loss) corresponding to oxycarbonate plus carbon, which oxidizes slowly up to 700°C. The remaining $Sm_2O_2CO_3$ is stable up to 820°C.

X-Ray Analysis. The lattice constants, which are given for the anhydrous formates as a function of cation radius in Fig. 3, are in good agreement with values reported previously (2). If the parameters reported by Pabst (8) are correct, a noticeable cusp appears at Gd as a result of the f shell being half filled. The more interesting result is the increase in the rhombohedral angle with decreasing cell edge. A consideration of the structure (8) indicates that the formate oxygens designated O(II) are very close together. If the C–O bond angle is quite rigidly constrained to ~121°C, the observed change in the rhombohedral angle is understandable because it must increase with decreasing cell edge in order to accommodate the formate groups. The inability of the structure to withstand a distortion greater than
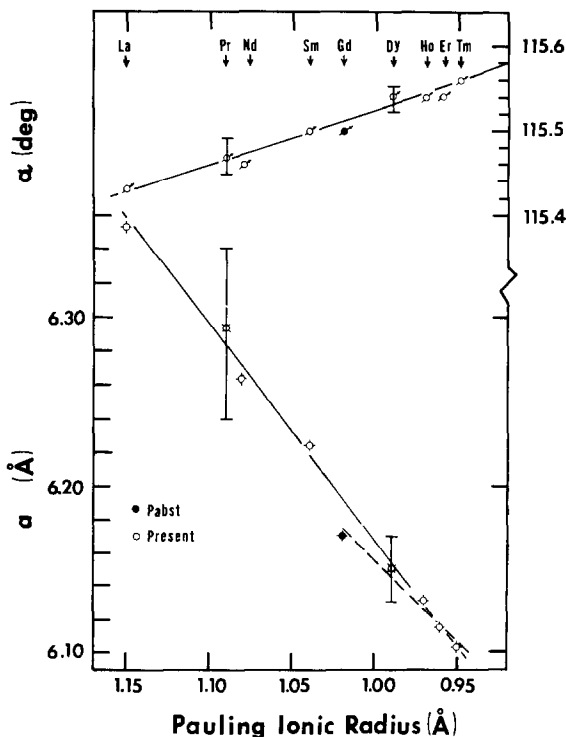

Fig. 3. Lattice parameters for the anhydrous formates.

the 115.55°C found for thulium formate may be the cause for the different structure observed for the anhydrous ytterbium and lutetium compounds. No obvious difference in the quality of the diffraction patterns was observed across the series; however, the probable error limits, approaching ±0.01 Å for the lighter members, are noticeably higher than those of the heavier elements. Although this might suggest a distortion of the true rhombohedral symmetry, no extra lines or splittings were observed.

Detailed high temperature diffraction data were collected for representative members (La, Pr, and Tm) of this structure type. Lanthanum formate decomposed at $380°C < t < 413°C$. A very poor pattern corresponding to monoxymonoformate indicated by the TGA study was observed at 413°C. The most intense oxyformate reflection ($2\theta = 28.5°$), which was scanned as the temperature increased, remained (although broad and weak) until at least 520°C. At 575°C, a pattern of type I $La_2O_2CO_3$ was obtained. Subsequent phase transitions were identical with those described previously (13).

The phase transitions observed for praseodymium formate were analogous to those of lanthanum, i.e., the decomposition of the formate beginning at 320°C, an indication of a poorly crystallized phase at 419°C, and the slow conversion of type I $Pr_2O_2CO_3$ to type II.

A value for the thermal expansion coefficient of the formates was obtained from the lattice parameter of the praseodymium compound at 26, 74, 170, 220, and 282°C. Within limits of error (±0.01 Å), the expansion is linear with $\alpha = 5 \times 10^{-5}/deg$ ($\alpha = [(a_t - a_0)/a_0]/[T - T_0]$). No change in the rhombohedral angle was detected.

X-Ray evidence was found for all intermediates detected in the thermograms except the very unstable $R_2O(OOCH)_4$, which was apparently amorphous. Attempts to prepare samples of RO(OOCH) (La and Pr) by annealing in CO_2 at 400–450°C gave praseodymium samples which were either amorphous or of type I $Pr_2O_2CO_3$. The diffraction pattern for LaO(OOCH) was weak and diffuse, but satisfactory indexing was obtained on a hexagonal unit cell with $a = 7.28 \pm 0.02$ Å and $c = 9.94 \pm 0.03$ Å. The calculated and observed data are presented in Table I.

Mass Spectrometric Analysis. The onset of La(OOCH)$_3$ pyrolysis was evidenced by a pressure increase beginning at 250–275°C. Large increases in the 18^+ and 44^+ intensities and a slight increase in 28^+ intensity indicated that large quantities of H_2O and CO_2 were produced along with a small amount of CO. The pressure continued to rise, and at 325–350°C a large pressure increase began. This increase

TABLE I

X-RAY DATA FOR LaO(OOCH)[a]

I	h k l	d spacing (Å)
s	1 0 0	10.63
s	0 0 2	8.34
s	1 0 2	6.54
m	1 1 0	6.12
m–s	2 0 0	5.30
w	1 1 2	4.93
w–m	0 0 4	4.15
w–m	3 0 0	3.516
vw	1 1 4	3.454
m	3 0 2	3.257

[a] Cu K$_\alpha$, hexagonal cell, $a = 7.28$, $c = 9.94$.

in the partial pressures of H_2O and CO_2 was accompanied by a sizeable increase in that of CO; however, estimation of the actual change in carbon monoxide concentration was complicated by the N_2 background. A sharp pressure rise corresponding to the third weight loss (Fig. 1) was not discernable.

Gas Train Analysis. The pyrolysis products of La(OOCH)$_3$ contained H_2O CO_2, H_2, and CO. At 340–350°C, a weight loss of 25.5 ± 1.0 wt% was observed. During this decomposition, which is in good agreement with the theoretical weight loss to LaO(OOCH) (27.02%), H_2O was collected in essentially equimolar (±1%) quantities in the two collection tubes and accounted for two-thirds of the total hydrogen of the sample. At 440–450°C the remaining one-third of the hydrogen was collected as equimolar quantities of H_2O with an accompanying weight loss which was consistent with the formation of $La_2O_2CO_3$ (32.5 ± 0.5% obsd, 32.49% theor). Although no differences were observed with Al_2O_3 and Pt crucibles, the ratio of H_2O in the first tube to that in the second was slightly higher for the N_2 carrier than for Ar; a slight O_2 contamination was subsequently found to be present in the N_2. The ratio of CO_2 collected in the first and second tubes varied 0.6–0.8 at the lower temperatures and 1.5–2.0 at the higher temperatures. Total hydrogen and oxygen contents were completely accounted for by the collection analysis, but the collected carbon was less than the theoretical quantity for conversion to the dioxymonocarbonate. After heating at 340–350°C, the solid residue was ivory-colored and amorphous to X-ray powder diffraction analysis, but the product obtained at the higher temperature was black. Treatment of this solid with dilute acid produced rapid evolution of carbon dioxide and an

insoluble black residue which appeared to be amorphous carbon.

The weight loss and analytical data eliminate the possibility of either $La_2(CO_3)_3$ or $La_2(C_2O_4)_3$ as a decomposition intermediate. The loss of one-third of the theoretical hydrogen in the second pyrolysis step reconfirms the decomposition path involving the LaO(OOCH) intermediate.

B. The Formate Dihydrates of Yttrium, Holmium, and Erbium

Thermogravimetric Analysis. The TGA data for three dihydrates are shown in Fig. 2. The decomposition pattern of each is unique and is much more complex than those of the anhydrous formates.

Holmium Formate. The thermogravimetric data for holmium is typical of this dihydrate type. The results appear to be much less complex than those of the ytterbium and lutetium dihydrates. A loss of two moles of water (10.72%) occurs at 120°C to give the anhydrous formate which is stable up to 280°C. At the $\frac{1}{2}$ deg/min heating rate, there is no evidence for intermediate hydrates. Between 280 and 360°C there is a steady weight loss of 32.75%. The compound formed at 360°C corresponds to the monoxymonoformate, which slowly converts to the dioxycarbonate at $t < 580$°C with a 36.01 wt% loss. The decomposition to the oxide was not complete at 820°.

X-Ray Analysis. Although direct attempts to index the powder diffraction data for these triformates were unsuccessful, the symmetry and space group were obtained from oscillation and equiinclination Weissenberg data. Single crystals of both the yttrium and holmium phases were examined and found to be orthorhombic. The systematic extinctions, which were observed for $hk0$ with $h = 2n + 1$ absent, are consistent (14) with space group $Pmma$ (No. 51). Refinement of the indexed powder data gave the following lattice parameters for the triformate dihydrates:

$$Ho, \quad a = 12.286 \pm 0.006 \text{ Å};$$
$$b = 8.364 \pm 0.004 \text{ Å};$$
$$c = 7.498 \pm 0.004 \text{ Å};$$
$$Y, \quad a = 12.270 \pm 0.009 \text{ Å};$$
$$b = 8.353 \pm 0.008 \text{ Å};$$
$$c = 7.480 \pm 0.007 \text{ Å};$$
$$Er, \quad a = 12.240 \pm 0.009 \text{ Å};$$
$$b = 8.328 \pm 0.006 \text{ Å};$$
$$c = 7.473 \pm 0.005 \text{ Å}.$$

The indicated errors are at the 95% confidence level.

Dehydration of the yttrium compound in vacuum was followed by continuously scanning several low angle peaks as the temperature was increased up to

90°C. The data suggested that extreme structural changes occur during dehydration. Drastic changes in peak intensities and the appearance of new peaks were observed. It is not known whether a complete series of related structures can be had by changing the degree of hydration or whether there are discrete intermediate phases of fixed hydration number. These results are different from the sharp dehydration observed with a static CO_2 atmosphere. After dehydration, the material was completely amorphous up to 200°C, where it crystallized in the rhombohedral structure common to the lighter rare earths. The dihydrates of holmium and erbium behaved similarly. At ~300°C, the anhydrous rhombohedral formates of these elements decomposed to a second amorphous material which remained until ~550°C where weak, broad, C-form sesquioxide lines appeared.

C. The Formate Dihydrates of Ytterbium and Lutetium

Thermogravimetric Analysis. As was noted in the preceding discussion, the decompositions of the ytterbium and lutetium formate dihydrates (Fig. 2) are different from those of the other dihydrates. Many plateaus cannot be assigned a rational formula.

Ytterbium Formate. The dihydrate of ytterbium is considerably less stable than the previous hydrates and begins to decompose at 90°C. The conversion to anhydrous form is complete by 130°C with a weight loss of 10.46%. Again there is no evidence of intermediate hydrates. The anhydrous formate is stable up to 220°C. At 295°C a slight inflection indicates the formation of the monoxymonoformate plus carbon with a weight loss of 31.97%. During the course of one decomposition run, the sample was removed from the bucket after having been heated to 350°C and was found to be black with the original external form still intact. It is possible that due to the increasing instability with increasing atomic weight, the decomposition route oxyformate → oxycarbonate → oxide cannot be distinguished. The plateau at 520°C can be assigned the formula $Yb_4O_5CO_3$, which was also characterized by chemical analysis. Decomposition to the oxide begins at 640°C.

Lutetium Formate. Two moles of water are removed beginning below 90°C (10.40 wt% loss), and the anhydrous formate begins to decompose at ~170°C. There is a slight indication for the formation of the monoxymonoformate at ~260°C. Although further assignment is not possible, the dioxycarbonate probably decomposes to the oxide as it is formed.

X-Ray Analysis. The ytterbium and lutetium triformate dihydrates give diffraction patterns which are very different from those of the orthorhombic dihydrates. These products, in contrast to the other dihydrates, were poorly crystallized, exhibited few sharp faces, and appeared to grow in masses of randomly oriented fragments or in layered material. Several ytterbium crystals and one lutetium crystal were aligned on optical extinction axes and examined by oscillation and equiinclination Weissenberg techniques. The data collected about three extinction axes of one ytterbium crystal were consistent with those of lutetium and indicated triclinic symmetry. The lattice constants refined from the indexed Guinier data for ytterbium and lutetium triformate dihydrates are $a = 6.46 \pm 0.02$ Å, $b = 9.70 \pm 0.03$ Å, $c = 6.78 \pm 0.02$ Å, $\alpha = 111.0 \pm 0.2°$, $\beta = 83.1 \pm 0.1°$, $\gamma = 90.7 \pm 0.1°$, and $a = 6.46 \pm 0.02$ Å, $b = 9.66 \pm 0.03$ Å, $c = 6.78 \pm 0.02$ Å, $\alpha = 110.6 \pm 0.2°$, $\beta = 82.7 \pm 0.1°$, $\gamma = 90.6 \pm 0.1°$, respectively. The powder diffraction data, which differ noticeably from those reported previously (4), are presented in Table II. Interpretation of the single crystal data was, however, somewhat difficult. A pseudomirror, which appears in the more intense reflections and is almost perpendicular to the c axis, introduces a false symmetry and suggests that the metal sublattice is nearly monoclinic. In addition, twinned and layered crystals were encountered. Twinning, which was observed in the $hk0$ Weissenberg layer, arises from right and left orientations of the crystal lattice about the a axis, and crystals, which otherwise appear single, exist as fragments layered along the a axis. The preparation of single crystals by concentration of the aqueous solutions is further complicated by the formation of highly supersaturated media, which in some instances evaporated to dryness without nucleation.

The X-ray decomposition studies also showed that these dihydrates are different from the yttrium-type and different from each other. The $Yb(OOCH)_3 \cdot 2H_2O$ dehydrated at 82°C with diffraction peaks of the anhydrous material growing in at this temperature. In contrast to the yttrium-type dihydrates, there was no amorphous period following dehydration. This result may suggest that the metal and formate positions in the anhydrous and hydrated phases are similar. Just how closely the two structures are related (the Russian workers have thought them equivalent) became very apparent after several attempts to prepare anhydrous samples for the Guinier camera. Patterns of dehydrated material were consistently the same for ytterbium and lutetium, but different from those taken on the dif-

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TABLE II

X-Ray Data for the Ytterbium and Lutetium Triformate Dihydrates

		d spacing (Å)	
I	$h\,k\,l$	Yb	Lu
s	0 0 1	6.150	6.134
m–s	1 1 0	5.311	5.304
m	$\bar{1}$ 1 0	5.174	5.173
m	1 0 1, 1 $\bar{1}$ 1	4.760	4.747
vs	0 $\bar{2}$ 1, 0 2 0	4.535	4.531
m	$\bar{1}$ 0 1	4.244	4.243
w–m	1 $\bar{2}$ 1	3.817	3.803
w	$\bar{1}$ 1 1	3.463	3.468
w	2 0 0	3.209	3.209
s	0 0 2	3.141	3.121
vw	1 $\bar{1}$ 2	3.104	---
vw	2 1 0	3.075	---
w	2 $\bar{1}$ 1, 1 0 2	3.003	3.000
vw	1 2 1	2.930	---
vw	$\bar{1}$ $\bar{3}$ 1	2.835	---
vw	1 3 0, $\bar{1}$ 2 1	2.762	---
w–m	$\bar{1}$ 0 2, $\bar{1}$ 3 0	2.712	2.705
w	2 2 0	2.654	2.651
w	1 1 2	2.594	2.592
w–m	$\bar{2}$ 2 0	2.577	2.577
w	$\bar{2}$ $\bar{2}$ 1	2.542	2.521
w–m	$\bar{1}$ $\bar{3}$ 2	2.441	2.433
w	0 $\bar{4}$ 1, 2 0 2	2.427	2.418
w	2 2 1	2.376	2.378
w–m	2 $\bar{3}$ 1	2.291	2.284
m–s	1 $\bar{4}$ 1	2.270	2.262
w–m	$\bar{2}$ $\bar{1}$ 2	2.194	2.190
w	2 1 2	2.160	---
w	$\bar{2}$ $\bar{2}$ 2	2.148	---
w	3 0 0	2.129	---
w–m	3 1 0	2.097	2.095
w	1 $\bar{3}$ 3	2.074	---

fractometer after in situ dehydration. Immediately after preparation in the diffractometer an ytterbium sample gave a pattern (Table III, column II) which was similar to that of samples prepared in air at 150°C (column III), but markedly different from that obtained a few hours earlier on the diffractometer (column I). After a few minutes exposure of the anhydrous formate to water vapor, a pattern (column IV) much like that of the dihydrate (column V) was obtained. These results suggest that the anhydrous formate undergoes a structural change between room temperature and 165°C, and that it is very hydroscopic. All the patterns of anhydrous material were examined for lines indicating formation

TABLE III

A COMPARISON OF RELATIVE INTENSITIES AND d SPACINGS OF YTTERBIUM FORMATES

I[a]		II[b]		III[c]		IV[d]		V[e]	
Int.	d (Å)	Int.	d (Å)	Int.	d (Å)	Int.	d (Å)	Int.	d (Å)
—	—	s	6.563	w	6.534	—	—	—	—
3	6.19	vs	6.075	m	6.053	s	6.137	s	6.150
—	5.94	—	—	—	—	—	—	—	—
50	5.602	m	5.616	s	5.601	—	—	—	—
100	5.526	w–m	5.515	m	5.511	—	—	—	—
—	—	m	5.271	m	5.250	m–s	5.314	m–s	5.311
—	—	—	—	—	—	w	5.179	m	5.174
—	—	—	—	—	—	w	4.972	—	—
—	—	m	4.866	vw	4.858	—	—	—	—
10	4.714	m	4.733	m	4.726	vw	4.783	m	4.760
30	4.683	s	4.676	m–s	4.676	—	—	—	—
20	4.430	m	4.432	m–s	4.426	diffuse		vs	4.535
5(b)	4.11	—	—	—	—	diffuse		m	4.244
10	3.486	—	—	—	—	diffuse		m	3.817
30	3.453	—	—	—	—	diffuse		w–m	3.463

[a] Diffractometer data for Yb(OOCH)$_3$ prepared in situ by vacuum dehydration at 165°C.

[b] Guinier data (in air) of Yb(OOCH)$_3$ prepared in air or CO$_2$ at 150°.

[c] Guinier data (in air) of sample I.

[d] Guinier data for sample II after exposure to water vapor.

[e] Guinier data for Yb(OOCH)$_3 \cdot 2H_2O$.

of the rhombohedral structure common to the other rare earth formates, but no assignments could be made.

Gas Train Analysis. Analysis of the products from thermally dehydrated Yb(OOCH)$_3$ indicated pyrolysis to H$_2$O, CO$_2$, H$_2$, and CO and reconfirmed the complex decomposition observed by TGA. A constant weight plateau which corresponded with that of the oxyformate was not observed, but at 290–300°C the weight loss data were consistent with the Yb$_2$O$_2$CO$_3$ composition (28.6 ± 0.4 wt% loss, 28.89% theoretical weight loss for anhydrous Yb(OOCH)$_3$). The collection data indicated the production of H$_2$O and H$_2$ in a ratio of approximately 2:1 and a CO$_2$:CO ratio of approximately 0.5. However, heating at a higher temperature (440–450°C) apparently resulted in the evolution of additional H$_2$O; the combined H$_2$O and H$_2$ analysis gave a hydrogen content which was 15–25% in excess of the theoretical quantity. The origin of this discrepancy is not understood, but during the course of these analyses the magnesium perchlorate in the first collection tube acquired a waxy appearance similar to that produced when formic acid was combined with the perchlorate. Although ir absorp-

tion spectra of the perchlorate were unsuccessful in the identification of formic acid as a collected species, its evolution cannot be excluded. The collection of even a small fraction of HCOOH would give rise to an increased H$_2$O:H$_2$ ratio and to a larger apparent hydrogen content. At 440–450°C, the total weight loss of the residue (32.0 ± 0.3 wt%) agrees with the TGA plateau at 520°C and with the theoretical weight loss to Yb$_4$O$_5$CO$_3$ (33.81 wt%). X-Ray analysis of the graphite-coated product indicated that it was amorphous. Subsequent heating at 700° produced the sesquioxide (36.0 ± 0.1 wt% obsd, 36.01 wt% theor) and CO$_2$ as the only decomposition products. On the basis of metal and carbon dioxide analyses, the composition of this oxycarbonate is YbO$_{1.24}$(CO$_3$)$_{0.26 \pm 0.02}$, or nominally Yb$_4$O$_5$CO$_3$. The identical composition has been reported by Head and Holley (15) as the first decomposition intermediate in the pyrolysis of Yb$_2$(CO$_3$)$_3$.

D. Scandium Formate

X-Ray Analysis. Anhydrous scandium formate was of particular interest because of the possibility that it is isostructural with one of the anhydrous

ytterbium formates. Oscillation and equiinclination Weissenberg data collected for the phase indicated monoclinic symmetry with space group $P2_1/c$ (No. 14) (systematic extinctions: $h0l$, $l = 2n + 1$ absent and $0k0$, $k = 2n + 1$ absent) (14). These results agree with those reported recently (9), but the lattice constants ($a = 10.322 \pm 0.009$ Å, $b = 6.617 \pm 0.003$ Å, $c = 9.033 \pm 0.007$ Å, and $\beta = 98.02 \pm 0.09°$) differ slightly. An attempt to correlate this structure with that of either anhydrous ytterbium phase was unsuccessful.

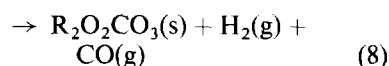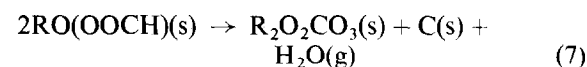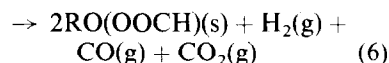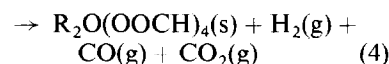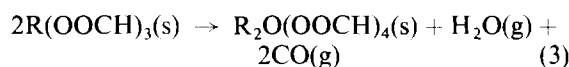## Conclusions

A combination of X-ray and TGA data are summarized in Table IV. In addition to the sesquioxide, nine structurally different phases have been observed in the course of the preparative and decomposition studies. As indicated in Table IV, the rhombohedral $R(OOCH)_3$ (Y, La–Tm) is the most frequently occurring phase. The previously unreported oxyformate, $R_2O(OOCH)_4$ (La, Pr), is proposed as a decomposition intermediate only for the lighter rhombohedral formates, while the monoxymonoformate intermediate, $RO(OOCH)$, is observed for all the rare earths investigated with the possible exceptions of samarium and thulium. The dioxycarbonate intermediate, $R_2O_2CO_3$, is discernible for yttrium and all the rare earths except lutetium. Although the anhydrous rhombohedral formates of Y, Ho, and Er may be prepared by reaction of the oxides with 95% formic acid solution, they are also obtained by thermal decomposition of the dihydrates, $R(OOCH)_3 \cdot 2H_2O$, which are obtained in

TABLE IV

Structural Classification of Rare-Earth Formates

Compound	Rare earth	Structure
1. $R(OOCH)_3$	Y, La → Tm	Rhombohedral
2. $R_2O(OOCH)_4$	La, Pr	Unknown
3. $RO(OOCH)$	La, Pr, Nd	Hexagonal
4. $R_2O_2CO_3$	all (?)	Tetragonal, monoclinic, hexagonal forms see Ref. (13)
5. $R(OOCH)_3 \cdot 2H_2O$	Ho, Er, Y	Orthorhombic
6. $R(OOCH)_3 \cdot 2H_2O$	Yb, Lu [Tm, Ref. (4)]	Triclinic
7. $R(OOCH)_3$	Yb, Lu [Tm, Ref. (4)]	Unknown
8. $R(OOCH)_3$	Sc	Monoclinic

more dilute acid solution. For Yb and Lu, only the triformate dihydrate has been attained in the preparative procedures. The anhydrous triformates, which are obtained for these elements by decomposition of the dihydrates, are structurally different from those of the other rare earths. The tricarbonate, which was suggested (1) as an intermediate in the decomposition of $La(OOCH)_3$, is not observed.

The decompositions are sharp for the light rare earths, but those of the heavier members are essentially continuous over wide temperature ranges. The decomposition of the triformates and the formation of the oxides both begin at lower temperatures for the heavier elements than for the lighter ones. This thermal instability is consistent with trends in the enthalpies of formation of both the sesquioxides (16) and those estimated for the triformate (2). While ΔH^0_{f298} of the sesquioxides become increasingly more negative from lanthanum to lutetium (−428 to −449 kcal/mole), those of the formates become more positive from lanthanum to holmium (−479 to −447 kcal/mole). The increasing stability of the oxides with increasing molecular weight is a possible cause for the more rapid and unresolvable decompositions of the heavier rare earths.

The analytical data for the gaseous decomposition products reconfirms decay scheme (1) and permits the proposal of reactions (3)–(8) for the formation of the intermediate phases.

$$2R(OOCH)_3(s) \rightarrow R_2O(OOCH)_4(s) + H_2O(g) + 2CO(g) \quad (3)$$

$$\rightarrow R_2O(OOCH)_4(s) + H_2(g) + CO(g) + CO_2(g) \quad (4)$$

$$R_2O(OOCH)_4(s) \rightarrow 2RO(OOCH)(s) + H_2O(g) + 2CO(g) \quad (5)$$

$$\rightarrow 2RO(OOCH)(s) + H_2(g) + CO(g) + CO_2(g) \quad (6)$$

$$2RO(OOCH)(s) \rightarrow R_2O_2CO_3(s) + C(s) + H_2O(g) \quad (7)$$

$$\rightarrow R_2O_2CO_3(s) + H_2(g) + CO(g) \quad (8)$$

For each intermediate phase, two decomposition paths are necessary to account for the simultaneous production of both water and hydrogen. Although the formation of monoxytetraformate by only one reaction and the formation of monoxymonoformate by the other would account for the observed 1:1 H_2O to H_2 ratio, the mass spectrometric data indicate that H_2O is produced continuously during both steps. Unfortunately, the dissociation of CO into CO_2 and carbon limits the usefulness of the data

for these products; however, the low $CO_2:CO$ ratio is consistent with the evolution of the large quantities of CO predicted by Eqs. (3)–(6). Another observation which tends to substantiate these reactions is the darkening of the lanthanum sample by carbon at temperatures above 350°C. This result, which was also reported by Plyushchev et al. (*1*), is readily accounted for by Eq. (7). The data for ytterbium and lutetium formates are not entirely consistent with decay scheme (1) for the lighter rare earths; the same decomposition reactions possibly occur at different extents, but evidence for a more complex pyrolysis was observed. Although the simultaneous decomposition of a formate by two different reactions is unusual, sodium and potassium formates have recently been shown (*17*) simultaneously to produce the oxalate plus hydrogen by one reaction and the carbonate plus hydrogen and carbon monoxide by a second. The extent of these reactions was found to vary markedly as a function of oxygen pressure, but no such effects were evident in the present investigation. For lanthanum formate, the more curious occurrence is that the alternate reactions appear to proceed at equal extents. The decomposition reactions may be controlled mechanistically by the structural relationships of the formate groups in the solids, but no obvious explanation for Eqs. (3) and (4) is afforded by the structural data for the triformate (*8*).

The combined TGA, analytical, and X-ray data have provided a more detailed description of the decomposition behavior and the structural properties of the rare-earth formates than has previously been reported. These results should broaden the current knowledge of carbonylic acid salts of the rare-earth elements.

Acknowledgments

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