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THE MODES OF DECOMPOSITION OF SOME RARE-EARTH-METAL TROPOLONATES AND ACTIVATION ENERGIES OF DECOMPOSITION

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The modes of decomposition of some rare-earth-metal tropolonates were studied by the use of DT, TG and DTG techniques. The volatile products and residues were identified. The activation energies of decompositions were calculated.

The rare-earth-metal tropolonates decompose in two steps: the first yielding a basic tropolonate and the second a basic carbonate for Sm and Eu tropolonates and the normal trioxides for La, Nd, Er, Tm and Yb tropolonates. The activation energies of decomposition of these tropolonates vary from 21.0 to 96.5 kcals/mole and is environment-sensitive.

Considerable interest exists in the study of changes which occur in solid inorganic compounds, as they are uniformly heated. By studying such changes much information can be gained concerning the mode of decomposition, phase changes, energies of transition, heats of decomposition, and similar properties. Also one often discovers novel methods of preparing compounds.

In this study we have examined thermal analysis of rare-earth-metal tropolonates by differential thermal and thermogravimetric techniques.

Experimental

Starting materials

The source of lanthanide materials was lanthanide metal oxides, 99.9% pure. They were purchased either from Research Chemicals, Inc., Burbank, California, or Lindsay Chemical Division, West Chicago, Illinois. Tropolone was purchased from Aldrich Chemical Company Inc., Milwaukee, Wisconsin.

Preparation and properties

All the tropolonates were prepared by the method described by Wright and Muetterties [1]. Their purity was verified by carbon and hydrogen analysis the results of which are given in Table 1. For all compounds the experimental results agree fairly well with the calculated values. In the case of Er, Tm and Yb tropolonates, the stoichiometric percentages were obtained only after the compounds

were heated to constant weight at 250°. The percentages for the unheated compounds are shown in parenthesis.

All the tropolonates were yellow solids whose depth of color increase with increasing molecular weight of the rare earth metal. This uniformity of color was unexpected, since most rare-earth-metal compounds exhibit colors characteristic of the metal. The close similarity in color raised the question of whether some similarity of electronic configuration had been induced. We decided to test this possibility by measuring the magnetic susceptibility and electronic spectra of the tropolonates. Also the approximate solubilities of the tropolonates in chloroform were measured at room temperature. The results of these measurements are discussed under Results and Discussion.

Table 1

Carbon and hydrogen analysis of rare-earth-metal tropolonates

Compound	% Carbon		% Hydrogen	
	found	calc.	found	calc.
La tropolonate	49.27	50.03	3.08	3.02
Nd tropolonate	49.10	49.70	3.20	2.96
Sm tropolonate	48.90	49.10	3.18	2.92
Eu tropolonate	48.41	48.80	3.18	2.95
Er tropolonate	47.43	47.50	2.84	2.83
	(50.57)		(4.30)	
Tm tropolonate	47.70	47.30	2.98	2.82
	(48.86)		(3.18)	
Yb tropolonate	46.93	46.75	2.88	2.80
	(53.91)		(5.82)	

Apparatus and procedure

Thermoanalytical measurements were made with the Dupont 900 differential thermal analyser (DTA) and the 951 thermogravimetric analyzer (TG) provided with derivative (DTG) capability. The infrared 621 Perkin Elmer Spectrophotometer was used for obtaining I. R. spectra of residues and volatile products. A Coleman 33 carbon-hydrogen analyzer was used to analyze the percent carbon and hydrogen of the tropolonates.

Magnetic susceptibilities were measured by the Guoy method [2]. The magnet was a Varian Associate, Model V-4004, with four-inch-pole pieces, the balance was a Mettler, type H-16, modified to permit the suspension of the weighing tube from one of its arms. The reference substance was mercuric tetrathiocyanocobaltate (II). Corrections were made for diamagnetic contributions. Ultra-violet data were measured with a Cary-14 spectrophotometer.

Differential thermal studies were performed by placing about 3.0 mg of the

sample in a quartz tube (4.0 mm deep). Alumina was used as the reference. In all cases the thermocouples were immersed inside the sample and reference.

Thermogravimetric analysis was performed on 5.0 – 20.0-mg samples in various atmospheres, usually at a heating rate of 20°/min. The thermogravimetric results were plotted as weight lost against temperature. Derivative thermogravimetric curves were obtained as the rate of weight lost against temperature. The sample holder was a small platinum boat (about 0.5 cm deep), attached to a quartz rod. The thermocouple was adjacent to the boat but not touching it. The samples were loaded by means of a micro spatula.

Results and conclusions

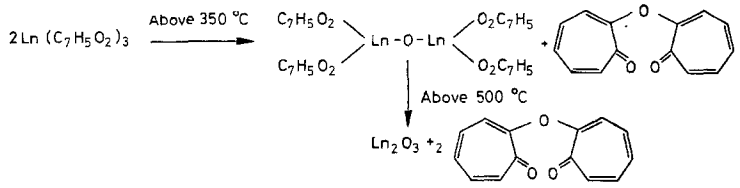
Differential thermal analysis

Differential thermal analytical data were obtained for the tropolonates of La, Nd, Sm, Eu, Er, Tm and Yb. The data are summarized in Table 2. Based on DTA data, the tropolonates fall in two groups: a light group La, Nd, Sm and Eu and a heavy group Er, Tm and Yb. Each member of the light group exhibited three distinct exothermic peaks. The first peaks all occurred at about the same temperature, whereas the second and third peaks occurred at temperatures which decreased, as the molecular weight of the tropolonate increased.

All members of the second group exhibited a low-temperature endothermic peak which is associated with the loss of unreacted tropolone. They also exhibited two distinct higher-temperature exothermic peaks which occurred at temperatures decreasing with increasing molecular weight. $Er(TP)_3$ also exhibited two lower-temperature endothermic peaks which appeared to be irreversible transitions.

Thermogravimetric analysis

All thermogravimetric analyses of these tropolonates were done in air and in vacuum, except $Nd(TP)_3$, which was also studied in CO_2. In general, the thermal decomposition of rare-earth-metal tropolonates may be expressed as follows:



The volatile residue, assumed to be a decomposition product of 2,2'-ditroponyl ether, had the odour of phenol, yielded an I.R. spectrum similar to that of phenol, and exhibited a transition temperature of 185°C in the DTA cell. Phenol boils at

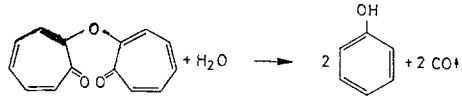
Table 2

Data for the differential thermal analysis of rare-earth-metal tropolonates in air (temp., °C)

$La(TP)_3$	$Nd(TP)_3$	$Sm(TP)_3$	$Eu(TP)_3$	$Er(TP)_3$	$Tm(TP)_3$	$Yb(TP)_3$
—	—	—	—	235 (endo, s, Sp)	165 (endo, m)	125 (endo, m, Sp)
—	—	—	—	—	—	—
—	—	—	—	375 (endo, s, Sp)	—	—
435 (exo, w)	440 (exo, w)	440 (exo, b)	430 (exo, Sp)	405 (endo, s, Sp)	—	—
480 (exo, s, Sp)	470 (exo, s, Sp)	465 (exo, s, Sp)	465 (exo, s, Sp)	480 (exo, m, Sp)	480 (exo, m, Sp)	470 (exo, s, Sp)
670 (exo, b)	660 (exo, b)	535 (exo, w)	540 (exo, w)	700 (exo, b)	630 (exo, b)	530 (exo, b, w)

m = medium, s = strong, Sp = sharp, w = weak

182°. Phenol could arise by the high-temperature decomposition of 2,2'-ditroponyl ether in presence of traces of water in accordance with the equation:



The mechanism proposed for the decomposition of the rare-earth-metal tropolonates is supported by the data given in Tables 3 and 4.* Carbon and hydrogen analysis on the first decomposition product of neodymium tropolonate are given in Table 3. Table 4 contains stoichiometric data for the decomposition product

Table 3

Carbonhydrogen analysis for the first residue of $Nd(TP)_3$

Compound	%C		%H	
	found	calc.	found	calc.
$C_7H_5O_2$, $C_7H_5O_2$, Nd—O—Nd, $C_7H_5O_2$, $C_7H_5O_2$	43.2	42.6	2.69	2.54

Note: In most cases the rare-earth-metal tropolonates decomposed directly to the oxide. However, in air the tropolonates of lanthanum and neodymium decomposed first to the oxycarbonate $Ln_2O_2CO_3$, and then to the oxide.

Table 4

Data for the composition of the decomposition product of rare-earth-metal tropolonates

Compound	Weight in mg	M. moles of reactants	Mole weight of 1st residue $(C_7H_5O_2)—Ln—O—Ln—(C_7H_5O_2)_2$		Mole weight of 2nd residue Ln_2O_3	
			found	calc.	found	calc.
$La(TP)_3$	6.50	0.0129	388	389	163	163
$Nd(TP)_3$	22.40	0.0442	395	396	160	168
$Sm(TP)_3$	3.22	0.0062	397	400	199	196 $Sm_2O_2CO_3$
$Eu(TP)_3$	12.20	0.0237	398	402	192	198 $Eu_2O_2CO_3$
$Er(TP)_3$	19.00	0.0356	416	417	189	191
$Tm(TP)_3$	5.60	0.0105	421	418	199	195
$Yb(TP)_3$	6.4	0.0119	424	423	204	197

of the rare-earth-metal tropolonates. One sees that there is quite good agreement between the found and calculated weights.

In the TG studies of the tropolonates of Br, Tm and Yb the first volatile product given off around 200° condensed to yellow needles. This compound exhibited a transition at 51° in the DSC cell. Tropolone melts at 51°. The carbonhydrogen analysis of these three compounds, Table 1, also indicates the presence of adhered tropolone.

Table 5

Procedural decomposition temperatures for rare-earth-metal tropolonates (Temp., °C)

Compound	1st Stage			2nd Stage		
	Ti	Ts	Tf	Ti	Ts	Tf
$La(C_7H_5O_2)_3$						
Vacuum	370	440	470	495	535	730
Air	360	400	430	450	480	550
	710	750	800 (third stage)			
$Nd(C_7H_5O_2)_3$						
Vacuum	390	440, 455,*	470	485	530	650
Air	370	410,* 440,	465	465	490	600
	760	790	820 (third stage)			
$Sm(C_7H_5O_2)_3$						
Vacuum	360	455	490	490	550	630
Air	360	410	430	465	490	630
$Eu(C_7H_5O_2)_3$						
Vacuum	350	410, 455,*	485	485	530	610
Air	360	400, 450,*	470	470	490	640
$Er(C_7H_5O_2)_3$						
Vacuum	400	465	500	500	550	650
Air	370	460	480	480	510	630
$Tm(C_7H_5O_2)_3$						
Vacuum	390	460	500	510	555	720
Air	390	450	485	490	520	630
$Yb(C_7H_5O_2)_3$						
Vacuum	410	460	500	505	540	660
Air	360	450	480	480	520	590

* Doublet Ts peaks — major peaks indicated by an asterisk.

The procedural decomposition temperatures in vacuum and air are given in Table 5. Tropolonates of Nd, Sm and Eu exhibited doublet Ts peaks; the major peak is indicated by an asterisk. The procedural decomposition temperatures appeared to be the same for all compounds.

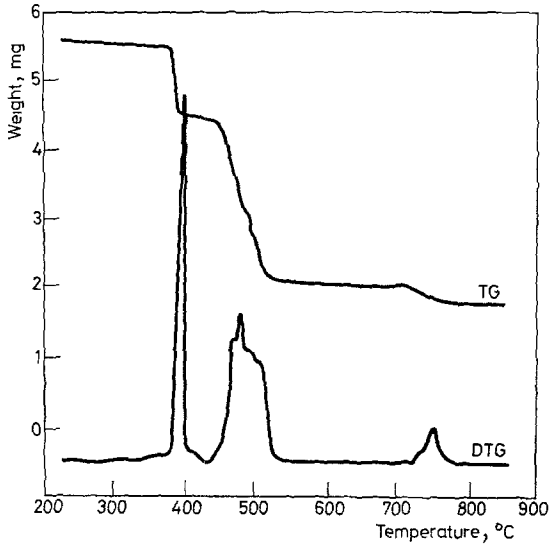


Fig. 1. TG and DTG curves of $La(T_p)_3$ in air

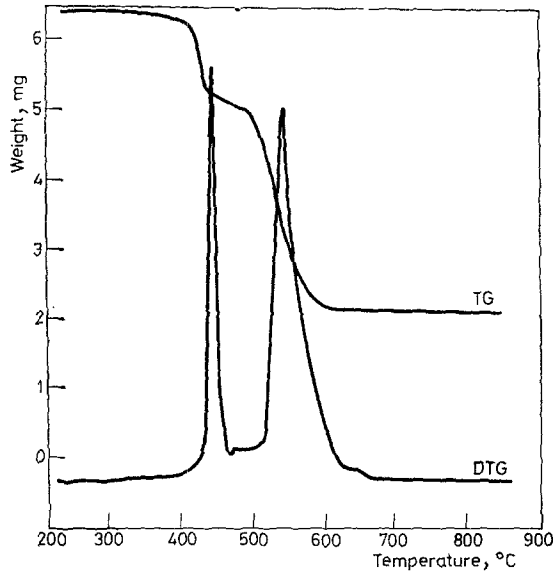


Fig. 2. TG and DTG curves of $La(T_p)_3$ in vacuum

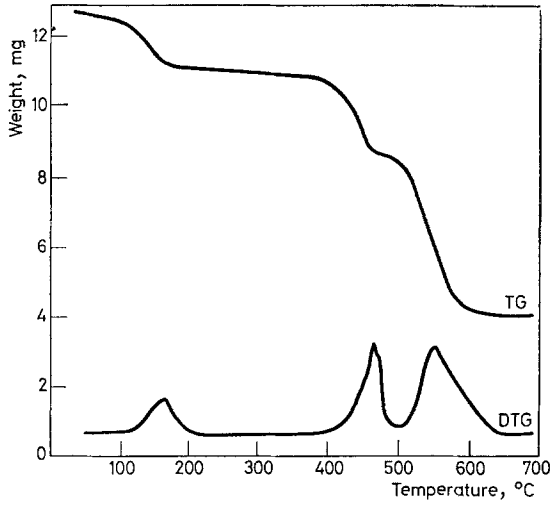


Fig. 3. TG and DTG curves of $Er(T_p)_3$ in vacuum

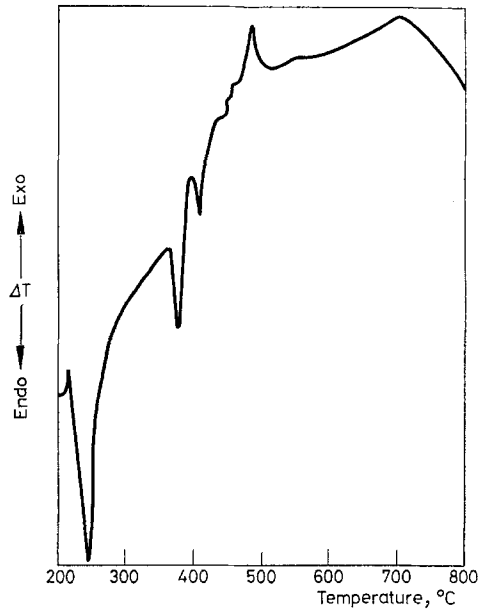


Fig. 4. DTA curve of $Er(T_p)_3$ in air

Some typical thermograms for the decomposition of the rare-earth-metal tropolonates are given in Figures 1, 2, 3 and 4.

Activation energies

The activation energies for these decompositions were calculated by the method of Horowitz and Metzger [3], with the modification given by Dharwadkar and Karkhanavala [4]. The equation used for calculation is

$$E_a = \text{Slope} \frac{T_f - T_i}{100} RT_i^2 \ (T\text{K}).$$

A typical slope obtained by plotting $\ln \ln \frac{W - W_f^t}{W_0 - W_f^t}$ vs. θ is given in Fig. 5. Here θ is $T - T_s$, W = weight remaining at a given temperature, W_0 = initial weight and W_f^t is the final weight for that particular decomposition step.

Table 6 gives the activation energies calculated for the two-step decompositions in vacuum and air. Obtaining the slope by actually plotting the data proved rather tedious. It was more conveniently obtained with the use of a computer programme written with the help of Professor E. Price of our Chemistry Department and Mr. C. Moore of the Computer Center. Generally, the activation energies of decompositions in vacuum appear to decrease, as the atomic number increases. This is also the case for four lighter-group elements in air, but the heavier group elements follow a slightly different pattern with Tm exhibiting the highest activation energy. The magnitude of activation energy of decomposition is always higher in vacuum than in air. It is also higher for the second step than for the first step.

Table 6

Activation energies of decompositions of rare-earth-metal tropolonates (kcals/mole)

Compound	Vacuum		Air	
	1st step	2nd step	1st step	2nd step
$La(C_7H_5O_2)_3$	41.4	96.5	49.5	60.9
$Nd(C_7H_5O_2)_3$	44.8	60.1	27.2	59.4
$Sm(C_7H_5O_2)_3$	40.9	92.0	22.7	37.3
$Eu(C_7H_5O_2)_3$	37.5	75.4	21.1	24.7
$Er(C_7H_5O_2)_3$	33.2	75.3	37.7	48.5
$Tm(C_7H_5O_2)_3$	31.2	72.8	38.2	67.6
$Yb(C_7H_5O_2)_3$	30.7	71.5	31.4	65.1

Solubilities of rare-earth-metal tropolonates

The rare-earth-metal tropolonates were found to be essentially insoluble in the following solvents: water, methanol, ether, dioxane, n-hexane and nitromethane. However, they were found to dissolve to a small extent in chloroform. Thus solubility measurements were made in this solvent. The approximate solubilities

are reported in Table 7. One observes that the compounds fall essentially in two groups: one containing tropolonates of La, Nd, Sm and Eu which are practically insoluble and the other containing the tropolonates of Er, Tm and Yb which are slightly soluble. Also the solubilities of Er and Yb tropolonates which contains bound tropolone are greater than those of the pure tropolonates of Er and Yb.

Table 7

Solubility data for rare-earth-metal tropolonates in chloroform

Compound	Grams of tropolonate suspended in 50 ml of $CHCl_3$ 25°C	[1]Gram of tropolonate per 100 ml $CHCl_3$ 25°C	[2]Gram of tropolonate per 100 ml $CHCl_3$ 25°C
$La(C_7H_5O_2)_3$	0.00555	—	—
$Nd(C_7H_5O_2)_3$	0.00572	—	—
$Sm(C_7H_5O_2)_3$	0.00550	—	—
$Eu(C_7H_5O_2)_3$	0.00551	—	—
$Er(C_7H_5O_2)_3$	0.13855	0.22020	0.04032
$Tm(C_7H_5O_2)_3$	0.11641	0.21240	—
$Yb(C_7H_5O_2)_3$	0.21075	0.40750	0.08428

[1] Contains attached tropolone
[2] Free of attached tropolone

Magnetic susceptibilities

Magnetic susceptibility measurements for the rare-earth-metal tropolonates were obtained for the purpose of ascertaining if they possessed magnetic properties different from those of other rare earth compounds. A difference was suspected

Table 8

Magnetic susceptibilities and magnetic moments of the rare-earth-metal tropolonates

Compound	Magnetic susceptibility xm (corrected) $\times 10^{-6}$	Magnetic moments experimental	Reported [5]
$La(C_7H_5O_2)_3$	0	0	0
$Nd(C_7H_5O_2)_3$	3 868.59	3.07	3.62
$Sm(C_7H_5O_2)_3$	1 183.07	1.69	1.65
$Eu(C_7H_5O_2)_3$	3 762.45	3.03	3.12
$Er(C_7H_5O_2)_3$	41 547.47	10.06	9.6
$Tm(C_7H_5O_2)_3$	34 284.77	9.10	7.6
$Yb(C_7H_5O_2)_3$	7 995.01	4.41	4.5

because of the similarity in color of the tropolonates. The results of the approximate measurements are given in Table 8. One sees that there are no appreciable differences. Apparently, the color of the tropolonates is determined largely by the polarizability of the large anion.

Electronic spectra of the rare-earth-metal tropolonates

As a further test of whether tropolone affected the electronic structure of the rare-earth-metal ions, electronic spectra for tropolonates of Er, Tm and Yb were measured over the frequency range 600–220 mμ. Measurements could not be obtained for the other tropolonates, since they were insoluble in chloroform. The spectra obtained for the three compounds were essentially identical.

The concentrations of the rare-earth-metal tropolonates used to measure the electronic spectra were of the order of 10^{-4} mole per liter. The concentrations of the rare-earth-metal chloride used to obtain their spectra were of the order of 10^{-2} mole per liter. At concentrations of 10^{-3} mole per liter the rare-earth-metal chlorides exhibited no absorption. It appears that what is being obtained is the spectrum of the tropolonate ion.

Table 9

Electronic spectra of tropolone, rare-earth-metal tropolonates, and rare-earth chlorides

Compound	Medium	Frequencies, (mμ)
Tropolone	Chloroform	240–280
$Er(C_7H_5O_2)_3$	Chloroform	370, 320–340, 260
$Tm(C_7H_5O_2)_3$	Chloroform	390, 350, 270
$Yb(C_7H_5O_2)_3$	Chloroform	390, 340, 260
$ErCl_3$	Water	205, 230, 245
		259, 278, 359
		368, 382, 430
		445, 450, 490
		495, 525, 545
$TmCl_3$	Water	203, 218, 230, 267
		269, 271, 282, 315
		355, 359, 463
$YbCl_3$	Water	233, 236

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RÉSUMÉ — On a étudié par ATD, TG et TGD le mécanisme de la décomposition des tropolonates de quelques terres rares. On a identifié les produits volatils, ainsi que les résidus. On a calculé les énergies d'activation.

Les tropolonates de terres rares se décomposent en deux étapes: la première fournit un tropolonate basique et la seconde un carbonate basique dans le cas des tropolonates de Sm et d'Eu et les sesquioxydes correspondants pour La, Nd, Er, Tm et Yb. Les énergies d'activation de la décomposition de ces tropolonates varient de 21.0 à 96.5 kcal/mol et dépendent du milieu environnant.

ZUSAMMENFASSUNG — Die Zersetzungsarten der Tropolonate einiger Seltener Erden wurden an Hand von DTA-, TG- und DTG-Techniken untersucht und die flüchtigen Produkte und Rückstände identifiziert. Die Aktivierungsenergien der Zersetzungsvorgänge wurden errechnet.

Die Tropolonate der Seltenen Erden werden in zwei Stufen zersetzt: die erste ergibt ein basisches Tropolonat und die zweite ein basisches Carbonat für Sm- und Eu-Tropolonate und die normalen Trioxide für La, Nd, Sr, Ta und Yb-Tropolonate. Die Aktivierungsenergien der Zersetzungsreaktion dieser Tropolonate variieren zwischen 21.0 und 96.5 kcal/mol und sind umgebungsempfindlich.

Резюме — Изучен распад трополонатов некоторых редкоземельных металлов с использованием ДТА, ТГ и ДТГ. Идентифицированы летучие продукты и остаток. Рассчитана энергия активации распада. Трополонаты редкоземельных металлов распадаются в две ступени: сначала образуется щелочной трополонат, а затем в случае трополонатов Sm и Eu, — щелочной карбонат, и в случае трополонатов La, Nd, Er, Tm и Yb — нормальные триокиси. Энергии активации распада этих трополонатов находятся в пределах 21,0—96,5 ккал/мол.