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An Investigation on the Effect of Structural Variation on Thermal Decomposition of Rare Earth Chromates(V)

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Synopsis. Non-isothermal decomposition kinetics of $LaCrO_4$, $PrCrO_4$, and $NdCrO_4$ have been investigated. In each case, first order decomposition takes place. The energy of activation, E_a^* has been evaluated by applying five different computational procedures based on the data of TG, DTA, and DTG. These values are fairly in good agreement with each other and the average activation energies per mole of the compounds are : $LaCrO_4$: 240 kcal, $PrCrO_4$: 180 kcal and $NdCrO_4$: 170 kcal. The above trend in E_a^* has been rationalized by taking into consideration the packing of atoms in rare earth chromates(V).

In previous publications[1-3] we have shown that rare earth (Ln) trisoxalato complexes, $LnM(C_2O_4)_3 \cdot nH_2O$ (M=Fe(III), Co(III), and Cr(III)) serve as excellent precursors for the corresponding rare earth perovskites, $LnMO_3$. Rare earth trisoxalatochromates(III) are additionally interesting because not only the rare earth orthochromites but also the rare earth chromates(V), $LnCrO_4$ can be obtained from them.[3] An important feature of the rare earth chromates(V) is the variation of structure in the series. While $LaCrO_4$ is monoclinic and $NdCrO_4$ and other higher members are tetragonal, $PrCrO_4$ is dimorphic.[4] We have been intrigued therefore, to see how variation on structure of these compounds influence the activation energies of their thermal decomposition. While the present work was in progress Doyle and Pryde have reported[5] isothermal decomposition kinetics of several rare earth chromates(V). The present study intends to report the activation energies for the decomposition of $LaCrO_4$, $PrCrO_4$, and $NdCrO_4$ from TG, DTA, and DTG under nonisothermal condition by applying several computational procedures. The results obtained here are significantly at variance with those reported by Doyle and Pryde.

Experimental

$LnCrO_4$ were prepared[3] by heating $LnCr(C_2O_4)_3 \cdot nH_2O$ at 520 °C for 2 h. The purity of the products were checked by chemical analysis and from their X-ray powder patterns.[4] Thermal analysis were carried out in a MOM Derivatograph. The sample size was *ca.* 750 mg and the particle size was *ca.* 200 mesh. The samples were heated in air and the heating rate was maintained to 6 °C/min. The enthalpy change was evaluated in a way described earlier.[6]

Results and Discussion

The sole feature of the decomposition reaction

$$LnCrO_4 \longrightarrow LnCrO_2 + 1/2O_2$$

is the endothermic evolution of oxygen in the temperature range 700—800 °C. The observed weight losses are in good agreement with the expected values showing the purity of the compounds. The first order decomposition behavior of these compounds has been established by applying five different computational procedures.[7-11] Table 1 summarizes the E_a^* values for each of the compounds obtained from these methods. The results show that for each compounds, the E_a^* values are fairly in good agreement, the variation is within 10%. The average values of E_a^* for these compounds are: $LaCrO_4$, 240 kcal; $PrCrO_4$, 180 kcal; $NdCrO_4$, 170 kcal. In Table 1 the values reported by Doyle and Pryde[5] are also shown for comparison. It may be noted that activation energies reported by Doyle and Pryde are quite low compared to our values. While the present study shows that the decreasing order of the activation energies are $LaCrO_4 > PrCrO_4 > NdCrO_4$, the trend observed by Doyle and Pryde is $PrCrO_4 > LaCrO_4 > NdCrO_4$.

The trend in E_a^* observed by us can be rationalized if the structures of rare earth chromates are taken into consideration. It may be pointed out that $LaCrO_4$ is isostructural to the monoclinic modification of $CePO_4$ whose crystal structure has been determined.[12] $CePO_4$ structure may be described by a space-filling network in which the cation has an irregular coordination of eight oxygen. For each Ce atom, four short bonds, given as 2.37 Å extend to the corner of four different phosphate groups. Four longer bonds 2.66 Å, connect to the edges of two additional tetrahedra. On the other hand, $NdCrO_4$ is isostructural to zircon, $ZrSiO_4$. In zircon, Si–O bond length is 1.62 Å within the SiO_4 tetrahedra and Zr–O distance is 2.05 Å within the longer ZrO_4 tetrahedra.[13] Buisson *et al.*[14] have shown that in $YCrO_4$, the shortest Cr–O distance is 1.66 Å and the shortest Y–O bond length is 2.44 Å. The stereoscopic models of $CePO_4$ and $ZrSiO_4$ reveal that $CePO_4$ is having a much more close packed structure than $ZrSiO_4$.

Inasmuch as the thermal energy required to activate

Table 1. Activation energies of $LnCrO_4$

Method used	E_a^* (kcal/mol)		
	$NdCrO_4$	$PrCrO_4$	$LaCrO_4$
Freeman-Carroll[a]	167	169	220
Horowitz-Metzger[a]	170	181	244
Coats-Redfern[a]	157	165	225
Borchardt-Daniel[b]	171	177	261
Dave-Chopra[c]	170	202	251
Average E_a^*	170	180	240
Doyle-Pryde[d]	59	84	73
ΔH	4.1	3.9	3.9

a) From TG. b) From DTA. c) From DTG.
d) The values reported in Ref. 5.

a compound having tight packing of atoms will be more than a compound having less packed structure, the activation energy for $LaCrO_4$, therefore, is expected to be greater than $NdCrO_4$. Although $PrCrO_4$ is dimorphic, powder diffraction pattern reveals that the lines due to the tetragonal phase are much abundant. It is reasonable therefore to expect that the activation energy for $PrCrO_4$ will be closer to $NdCrO_4$ rather than $LaCrO_4$. Table 1 shows such is actually the case.

The enthalpy change involved in the decomposition of the rare earth chromates are almost same for each of the compounds and is about 4 kcal/mol.

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