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# STUDIES ON DOUBLE MALONATES. III.* THERMAL DECOMPOSITION OF SODIUM LANTHANIDE MALONATES, $Na_5Ln(C_3H_2O_4)_4 . 7.5H_2O$, WHERE Ln = Gd, Tb or Ho

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The double malonates of gadolinium, terbium and holmium with sodium, of the type $Na_5Ln(C_3H_2O_4)_4 . 7.5H_2O$, have been studied by means of thermal analysis. A mechanism of thermal dehydration and decomposition has been proposed on the basis of the results obtained.

Thermal decomposition studies have been carried out on lanthanide malonates [1–4]. However, practically no attention has been paid to the double malonates of lanthanides with alkali metals, the only report available in the literature being on cerium(III) double malonates [5]. With such a background, it was thought worthwhile to study the double malonates of lanthanides and alkali metals from the thermal standpoint.

The present article, which is part of a systematic investigation of the double malonates and succinates of lanthanides with alkali and pseudoalkali metals [6, 7], describes the thermal decomposition of $Na_5Ln(C_3H_2O_4)_4 . 7.5H_2O$, where Ln = Gd, Tb or Ho.

## Experimental

The compounds were synthesized and their compositions fixed by the methods described previously [7]. The thermoanalytical curves were obtained on a Mettler Recording vacuum thermoanalyser (No. 84) in dry air, with a flow rate of 100 $cm^3$ $min^{-1}$. A Pt/Pt–Rh thermocouple was used for temperature detection. The samples were heated in a 0.5 $cm^3$ alumina crucible, at a rate of 10 K $min^{-1}$. The infrared spectra of some of the intermediates were scanned on a Beckman IR 4250 spectrophotometer, using the KBr disc technique.

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## Results and discussion

The thermoanalytical curves of gadolinium (excluding the DTA curve), terbium and holmium double malonates are reproduced in Figs 1, 2 and 3, respectively. The corresponding data and probable intermediates are given in Table 1. The general pattern of the curves is similar as far as the major decomposition reactions are concerned.

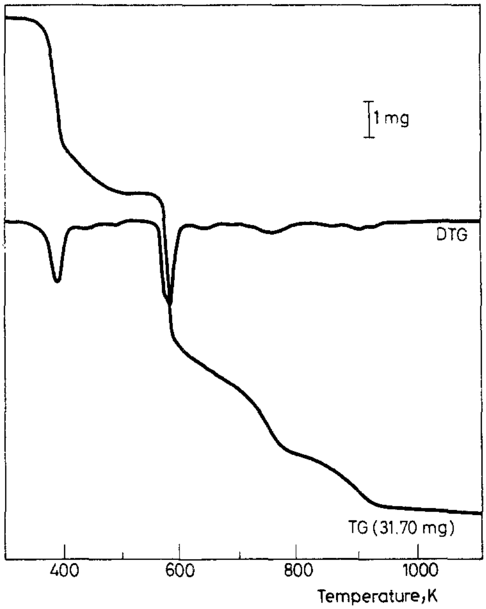

**Fig. 1** Thermal curves of $Na_5Gd(C_3H_2O_4)_4 \cdot 7.5H_2O$

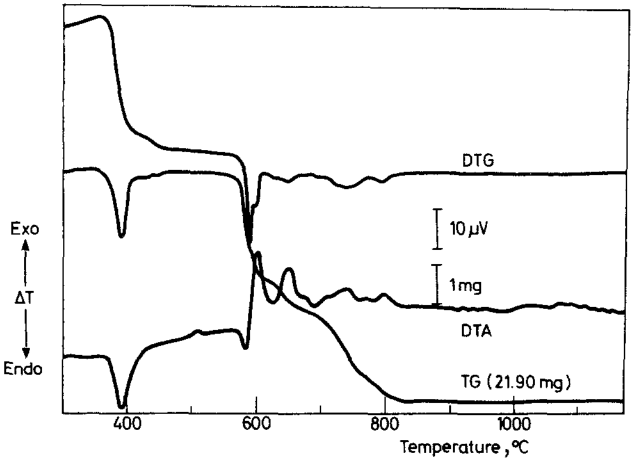

**Fig. 2** Thermal curves of $Na_5Tb(C_3H_2O_4)_4 \cdot 7.5H_2O$

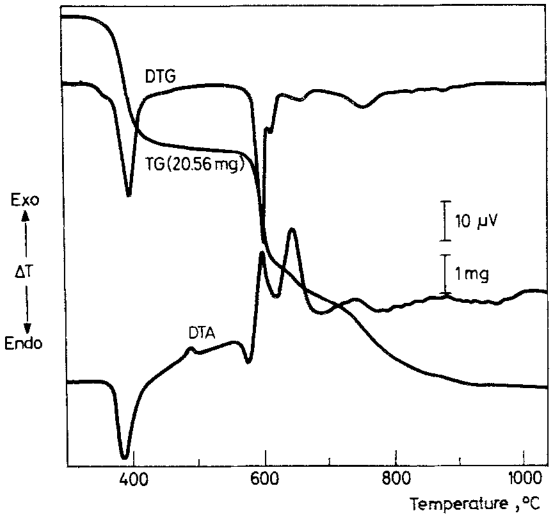

Fig. 3 Thermal curves of $Na_5Ho(C_3H_2O_4)_4 . 7.5H_2O$

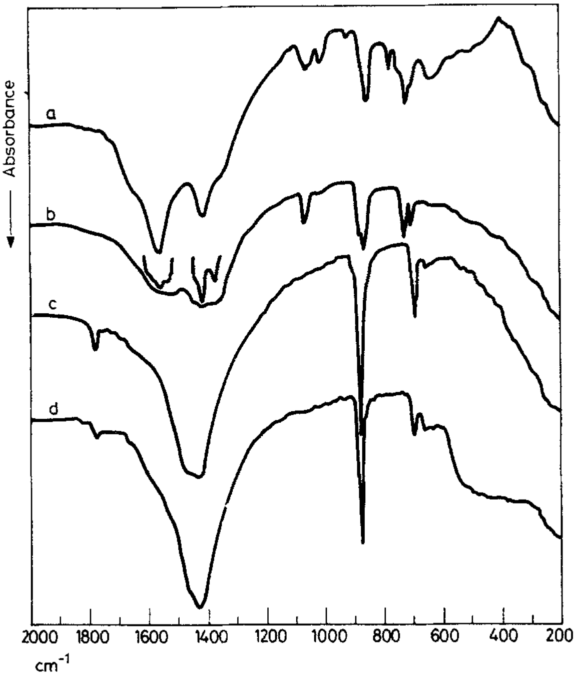

Fig. 4 Infrared absorption spectra of $Na_5Tb(C_3H_2O_4)_4 . 7.5H_2O$ heated at (a) 553 K, (b) 633 K and (d) 823 K, and (c) $Na_2CO_3$ heated at 553 K

**Table 1** Thermoanalytical results on $Na_5Ln(C_3H_2O_4)_4 . xH_2O$ ($x = 7.5$ for Ln = Gd and Ho and $x = 6.5$ for Ln = Tb)

| TG temp. range, K | DTG temp., K | % loss | | Interpretation |
|---|---|---|---|---|
| | | calcd. | obsd. | |
| Ln = Gd | | | | |
| | | | | $2Na_5Gd(C_3H_2O_4)_4 . 7.5H_2O$ |
| | | | | ↓ |
| 368–413 | 398 | 12.14 | 11.99 | $2Na_5Gd(C_3H_2O_4)_4 . 2H_2O$ |
| | | | | ↓ |
| 413–448 | 433 | 2.20 | 2.05 | $2Na_5Gd(C_3H_2O_4)_4 . 1H_2O$ |
| | | | | ↓ |
| 448–523 | 493 | 2.20 | 1.81 | $2Na_5Gd(C_3H_2O_4)_4$ |
| | | | | ↓ |
| 578–623 | 588<br>598 | 14.50 | 14.07 | $Na_{10}Gd_2O(CO_3)_{3.5}(OCOCHOCO)_{3.5}$ |
| | | | | ↓ |
| 623–683 | 663 | 2.70 | 2.30 | $Na_{10}Gd_2O_2(CO_3)_{2.5}(OCOCHOCO)_{3.5}$ |
| | | | | ↓ |
| 683–803 | 773 | 7.54 | 7.03 | $Na_{10}Gd_2O_2(CO_3)_{5.5}(OCOCHOCO)_{0.5}$ |
| | | | | ↓ |
| 803–888 | — | 1.23 | 1.90 | $2Na_5GdO(CO_3)_3$ |
| | | | | ↓ |
| 888–983 | 953 | 2.70 | 3.15 | $5Na_2CO_3 + Gd_2O_3$ |

| DTA temp., K | TG temp. range, K | DTG temp., K | % Loss | | Interpretation |
|---|---|---|---|---|---|
| | | | calcd. | obsd. | |
| Ln = Tb | | | | | |
| | | | | | $2Na_5Tb(C_3H_2O_4)_4 . 6.5H_2O$ |
| | | | | | ↓ |
| 398 (endo) | 378–428 | 398 | 12.40 | 12.56 | $2Na_5Tb(C_3H_2O_4)_4 . H_2O$ |
| | | | | | ↓ |
| — | 428–508 | 453 | 2.20 | 1.83 | $2Na_5Tb(C_3H_2O_4)_4$ |
| | | | | | ↓ |
| 508 (exo) | — | — | — | — | Structural rearrangement |
| | | | | | ↓ |
| 593 (endo)<br>608 (exo) | 583–628 | 588<br>608 | 14.80 | 14.57 | $Na_{10}Tb_2O(CO_3)_{3.5}(OCOCHOCO)_{3.5}$ |
| | | | | | ↓ |
| 653 (exo) | 628–673 | 643 | 4.04 | 3.93 | $Na_{10}Tb_2O_2(CO_3)_3(OCOCHOCO)_3$ |
| | | | | | ↓ |
| 763 (exo broad) | 673–773 | 763 | 7.70 | 7.94 | $2Na_5TbO(CO_3)_3$ |
| | | | | | ↓ |
| 803 (exo) | 774–833 | 798 | 2.25 | 2.74 | $5Na_2CO_3 + Tb_2O_{3.5}(Tb_4O_7)$ |

**Table** 1 (Contd.)

| DTA temp., K | TG temp. range, K | DTG temp., K | % Loss | | Interpretation |
|---|---|---|---|---|---|
| | | | calcd. | obsd. | |
| Ln = Ho | | | | | |
| | | | | | $2Na_5Ho(C_3H_2O_4)_4 . 7.5H_2O$ |
| | | | | | ↓ |
| 398 (endo) | 353–473 | 398 | 16.40 | 16.29 | $2Na_5Ho(C_3H_2O_4)_4$ |
| | | | | | ↓ |
| 503 (exo) | — | — | — | — | Structural rearrangement |
| | | | | | ↓ |
| 588 (endo)<br>603 (exo) | 568–608 | 598<br>608 | 14.40 | 14.59 | $Na_{10}Ho_2O(CO_3)_{3.5}(OCOCHOCO)_{3.5}$ |
| | | | | | ↓ |
| 663 (exo) | 613–668 | 658 | 3.92 | 3.21 | $Na_{10}Ho_2O_2(CO_3)_3(OCOCHOCO)_3$ |
| | | | | | ↓ |
| 753 (exo broad) | 668–873 | 753 | 10.15 | 11.92 | $5Na_2CO_3+Ho_2O_3$ |

Dehydration of the gadolinium double malonate takes place in three stages, as is evident from the DTG peaks at 398, 433 and 493 K, through the intermediates di- and monohydrates. The diffuse short inflexions on the TG curve, however, show their transient existence.

In the case of the terbium compound, one molecule of water is lost as soon as dry air is flushed through the sample chamber, prior to the heating, probably because it is loosely bound. Further dehydration occurs in two stages, the intermediate being the monohydrate. As against the two DTG peaks at 398 and 453 K, the DTA curve shows only a single endotherm, at 398 K. Dehydration of the monohydrate probably involves only a small energy change and hence the corresponding peak in the DTA curve is not discernible.

Interestingly, the holmium double malonate undergoes single-stage dehydration in the temperature range 353–453 K, as is observed from the TG and DTG curves.

The DTA curves of the terbium and holmium compounds show a small exotherm at 508 and 503 K, respectively, ascribable to some structural rearrangement of the anhydrous compounds, as this is not associated with any weight change

Decomposition of the anhydrous double malonates commences at ~570 K proceeds in two stages, as is evident from the DTG curves, to give an intermediate with probable composition $Na_{10}Ln_2O(CO_3)_{3.5}(OCOCHOCO)_{3.5}$ (I). The corresponding stage in the DTA curves is marked by endothermic activity, followed immediately by an exotherm for the terbium and holmium compounds. The formation of such an intermediate (I) has been reported in the thermal decomposition of lanthanum malonate pentahydrate [8].

(I) decomposes exothermally in the temperature range 613–673 K to give an intermediate of composition $Na_{10}Ln_2O_2(CO_3)_3(OCOCHOCO)_3$ (II–a) in the case of the terbium and holmium compounds. The composition of the intermediate formed in the temperature range 623–683 K for the gadolinium compound, however, is $Na_{10}Ln_2O_2(CO_3)_{3.5}(OCOCHOCO)_{3.5}$ (II–b).

The above intermediates (II–a and II–b) decompose to yield mixtures of sodium carbonate and the respective rare earth oxides directly (in a single stage) in the case of the holmium compound (temperature range 668–873 K), but via the formation of a double oxycarbonate of probable composition $Na_5LnO(CO_3)_3$ in the case of the gadolinium (temperature range 683–888 K) and terbium (temperature range 673–773 K) double malonates.

The terbium double malonate was heated isothermally at selected temperatures to obtain and characterise some of the intermediates.

The intermediate obtained by heating the parent compound at 553 K (29.7% loss) showed the presence of the carbonate group when tested qualitatively. The infrared spectrum (Fig. 4) of the intermediate reveals no bands due to the characteristic $CH_2$ wagging mode (1260 $cm^{-1}$) of the malonate group, suggesting the absence of the dicarboxylate ion. However, a very weak band was detected near 3000 $cm^{-1}$, which can be attributed to CH stretching vibrations in the (OCOCHOCO) grouping assumed to be present in the intermediate. The possibility of the formation of $Na_2CO_3$ is ruled out by comparison of the spectrum with that of pure $Na_2CO_3$ heated at 553 K. Moreover, the X-ray diffraction pattern of the intermediate shows. no reflexes due to $Na_2CO_3$. These observations support the conclusion that the intermediate is probably $Na_{10}Tb_2O(CO_3)_{3.5}(OCOCHOCO)_{3.5}$.

The spectrum of the intermediate obtained by heating the original sample at 633 K (39.0% loss) exhibits bands due to the internal vibrations of the carbonate group. The splitting of the band due to the $\nu_3$ vibration of the carbonate group in the region 1550–1390 $cm^{-1}$ is characteristic of the anhydrous double carbonates of the heavier rare earths [9].

Examination of the final product by means of X-ray powder diffractometry and infrared absorption spectroscopy reveals it to be a mixture of $Na_2CO_3$ and $Tb_4O_7$.

All the intermediates except the final product were contaminated with free carbon, probably formed in the disproportionation of CO, as has been suggested in an earlier study of lanthanum oxalate [10].

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**Zusammenfassung** — Doppelmalonate von Gadolinium, Terbium und Holmium mit Natrium des Typs $Na_5Ln(C_3H_2O_4)_4 . 7{,}5\,H_2O$ wurden mittels thermischer Analyse untersucht. Für die thermische Dehydratisierung und zersetzung wird ein auf den erhaltenen Ergebnissen basierender Mechanismus vorgeschlagen.

**Резюме** — Методом термического анализа изучены двойные соли малонатов гадолиния, тербия и гольмия с натрием общей формулы $Na_5Ln(C_3H_2O_4)_4 . 7.5H_2O$. На основе полученных результатов предложен механизм термической дегидратации и разложения.