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INVESTIGATIONS ON THE FORMATION OF RUBIDIUM DIMOLYBDATE VIA THERMAL DECOMPOSITION OF RUBIDIUM OXOMOLYBDENUM(VI) OXALATE

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The complex $Rb_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ (RMO) was prepared and characterized by means of chemical analysis and IR spectral studies. Its thermal decomposition was studied by using TG and DTA techniques. RMO loses its water between 160 and 200°C, this immediately being followed by the decomposition of anhydrous RMO, which takes place in three stages. The first two stages occur in the temperature ranges 200–220 and 220–255°, to give intermediates with tentative compositions $Rb_8[Mo_8O_{22}(C_2O_4)_6]$ and $Rb_8[Mo_8O_{26}(C_2O_4)(CO_3)]$, respectively, the latter then decomposing in the third stage between 255 and 340° to give the end-product, rubidium dimolybdate ($Rb_2Mo_2O_7$). The *d* spacings for $Rb_2Mo_2O_7$ are given for 2θ values between 10 and 70°.

The mixed metal oxalates have been extensively used for the preparation of important materials such as $BaTiO_3$ [1] and $ZnZrO_3$ [2]. Molybdenum(VI) also forms a number of oxalato complexes [3]. A literature survey reveals that, although the complex $Rb_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ (RMO) has been prepared and its vibrational spectra studied [4], the mechanism of its thermal decomposition, which forms the subject of this paper, is still unknown. As in our recent attempts to prepare the dimolybdates of lithium [5], sodium [6] and potassium [7] by the thermal decomposition of different molybdenum(VI) oxalato complexes, RMO is found to give $Rb_2Mo_2O_7$ as the end-product. The *d* spacings for $Rb_2Mo_2O_7$ 2θ values between 10 and 70° are also given.

Experimental

Baker analysed ammonium para-molybdate and Analar grade oxalic acid and rubidium chloride were used to prepare RMO as follows: To a hot solution of 1.2605 g of oxalic acid in about 200 ml of distilled water, 1.4395 g of MoO_3

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(prepared by heating ammonium para-molybdate at about 400° for 2 hr) was added in small lots and the solution was filtered to remove any unreacted MoO_3. A solution containing 1.2096 g of rubidium chloride in a small amount of water was then added and the solution was concentrated to about 40 ml to obtain crystals of RMO, which were washed with water and air-dried in a desiccator.

Molybdenum in RMO was determined gravimetrically as molybdenyl oxinate, and oxalate was determined by $KMnO_4$ oxidation. Rubidium was estimated by atomic absorption spectroscopy. The chemical analysis of RMO gave Rb^+, 26.02; Mo, 29.29 and $C_2O_4^{-2}$, 26.89%, the calculated values for $Rb_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ being Rb^+, 26.10; Mo, 29.30 and $C_2O_4^{-2}$, 26.87%. These data show that there is no noticeable deviation of RMO from the composition $Rb_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$.

Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out on a Stanton Red-Croft TG 770 thermobalance and a DTA 673-4 instrument, respectively. 5–10 mg samples were used for TG and the heating rate was 3° deg min^{-1}. For DTA, about 20 mg samples were used and the rate of heating was 10° deg min^{-1}. Both studies were carried out in an atmosphere of static air. The IR spectra were recorded in a KBr matrix on a Beckman IR–20 double beam instrument in the range 250–4000 cm^{-1}. The X-ray diffraction patterns were taken on a Philips diffractometer using CuKα radiation. The magnetic measurements were made on a vibrating sample magnetometer, model VSM–155, at room temperature (23°).

Results and discussion

RMO is a white crystalline compound with a low symmetry class. The magnetic measurements indicate it to be diamagnetic, suggesting that it is a molybdenum(VI) complex. The IR spectrum of RMO (Fig. 1A), in addition to the bands characteristic of the coordinated oxalato group [8, 9], shows two strong bands at 960 and 920 cm^{-1}, which indicate the presence of metal-oxygen double bonds and may be assigned to the asymmetric and symmetric $Mo{=}O$ stretches, respectively, while the band at 790 cm^{-1} probably results from the $Mo{-}O{-}Mo$ stretch [10–12]. In addition to these, three weak bands have also been observed at 900, 770 and 670 cm^{-1}, which are probably due to the rocking, wagging and metal-oxygen stretching vibrations, respectively, of the coordinated water [13].

Figure 2 gives the DTA, TG and differential thermogravimetric (DTG) curves for RMO in an atmosphere of static air. The thermogram shows that the dehydration of RMO takes place in a single step and is immediately followed by the decomposition of anhydrous RMO, which is a multistep process. The various stages are discussed in detail below.

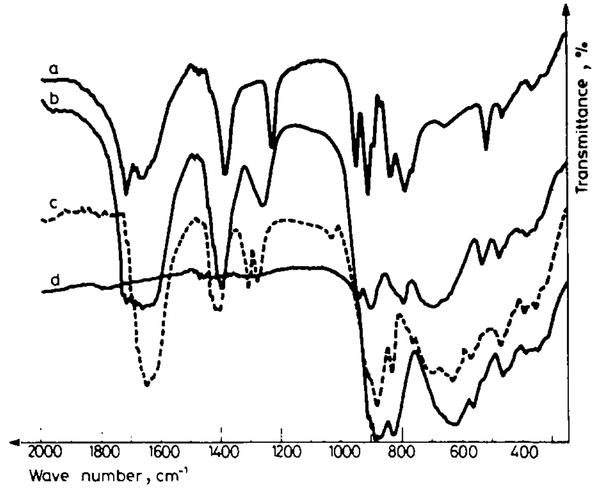

Fig. 1 IR spectra of RMO (a), RMO heated to 220 °C (b), 255 °C (c) and 350 °C (d)

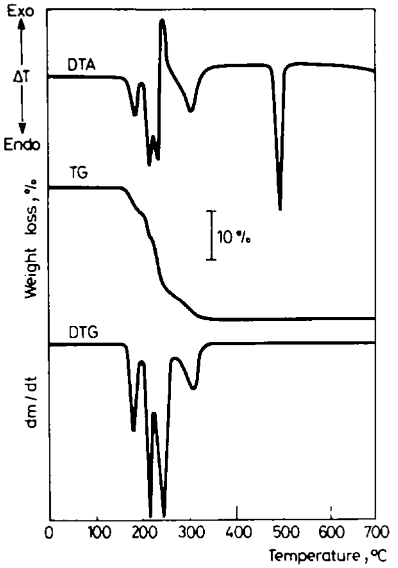

Fig. 2 DTA, TG and DTG curves of RMO in air

Dehydration

RMO is stable up to 160° and then loses its 2 mol of water in a single step between 160 and 200°. This is observed as DTA and DTG peaks at 185 and 180°, respectively. The observed weight loss is 5.49%, the calculated value being the same. The loss of water at such a high temperature indicates that it is probably coordinated to the metal.

Decomposition of oxalate

As seen from the TG, the dehydration of RMO is immediately followed by the decomposition of oxalate, which occurs in three stages between 200 and 340°. The first stage extends up to 220° and corresponds to the loss of 2 mol of carbon monoxide and 2 mol of carbon dioxide per 4 mol of RMO, to give an intermediate compound with tentative composition $Rb_8[Mo_8O_{22}(C_2O_4)_6]$, both DTA and DTG showing peaks at 215°. The observed weight loss is 5.49%, against the calculated value of 5.50%. The second stage occurs between 220 and 255° and involves a further loss of 5 mol of carbon monoxide and 4 mol of carbon dioxide to give an oxalate-carbonate intermediate having the tentative composition $Rb_8[Mo_8O_{26}(C_2O_4)(CO_3)]$. This reaction is observed in DTG as a peak at 245°. However, in DTA, an endothermic peak at 235° is followed by an exothermic peak at about 245°, which may be due to the predominance of oxidation of carbon monoxide to carbon dioxide. The observed weight loss is 12.09%, while the calculated value is 12.06%. The third and last stage occurs between 255 and 340° and involves the decomposition of $Rb_8[Mo_8O_{26}(C_2O_4)(CO_3)]$ to give the end-product $Rb_2Mo_2O_7$. This is observed in DTA as an endotherm at 305°, while DTG shows a peak at 310°. The observed weight loss is 4.45%, the calculated value being 4.43%.

The compositions of the intermediates are well supported by the IR spectra of the samples obtained by heating RMO isothermally at 220° (Fig. 1B) and at 255° (Fig. 1C), the former showing only the bands of the coordinated oxalato group, and the latter indicating the presence of both oxalate and carbonate.

Melting

DTA reveals an additional endothermic peak at 495°, corresponding to which no weight change is observed in the TG curve. This has been attributed to the melting of the end-product, the reported melting point of $Rb_2Mo_2O_7$ being 490° [14]. On the isothermal heating of RMO at $500 \pm 5°$, a molten product is obtained, which immediately solidifies to a white crystalline compound, thereby confirming that the peak at 495° is due to melting.

The end-product was obtained by heating RMO isothermally at 350 as well as at 500°. The two samples gave identical chemical analyses, IR spectra (Fig. 1D), and X-ray diffraction patterns. The IR spectrum is comparable to those of $Na_2Mo_2O_7$ [6, 15] and $K_2Mo_2O_7$ [7]. However, in addition to the peaks reported for $Rb_2Mo_2O_7$ by Salmon et al. [14], the observed X-ray diffraction pattern contains

Table 1 *d* spacings (Å) for $Rb_2Mo_2O_7$ ($\lambda = 1.5405$ Å)

Reported	Observed			
	d spacing	Relative intensity I/I_1	*d* spacing	Relative intensity I/I_1
3.31	7.9641	15	2.0011*	10
3.20	6.6265	3	1.9969	6
2.96	6.3884	3	1.9856	5
2.55	5.9305	6	1.9394*	10
2.37	5.3040	3	1.9345	6
2.17	5.1214	10	1.9124	2
2.00	4.7599	5	1.8717*	15
1.939	4.3601	3	1.8681	8
1.872	3.9919	5	1.8609*	10
1.862	3.8717	20	1.8485	5
1.776	3.7903	6	1.7850	2
1.658	3.7431	3	1.7745*	15
1.636	3.6782	2	1.7697	10
1.584	3.5552	3	1.6973	2
1.562	3.4733	3	1.6723	3
1.484	3.4111	2	1.6597*	10
1.458	3.3115*	100	1.6556	5
1.411	3.2006*	20	1.6420	10
1.394	3.1727	10	1.6379*	10
1.348	3.1025	4	1.6001	5
1.285	3.0608	6	1.5898*	10
	2.9663*	40	1.5862	5
	2.8845	12	1.5696	5
	2.8158	5	1.5660*	5
	2.7859	5	1.4858	4
	2.6439	2	1.4810*	4
	2.5597*	18	1.4589*	4
	2.4925	4	1.4113*	5
	2.4710	2	1.4099	5
	2.3748*	10	1.3983*	5
	2.2780	4	1.3483*	10
	2.2058	6	1.3454	5
	2.1778*	15	1.2850*	10
	2.0212	3	1.2821	5

* *d* spacings matching closely with the reported data.

many additional peaks which could not be assigned to any of the mixed or simple oxides of rubidium and/or molybdenum reported in the literature. This leaves us with the only conclusion that probably all the peaks belong to a single crystal system of $Rb_2Mo_2O_7$. Most of the additional peaks are found to be of low intensity. A comparison of the reported and observed *d* spacings, along with the relative peak intensities (calculated on the basis of peak heights), is given in Table 1. Our recent studies on the preparation of $Cs_2Mo_2O_7$ by the thermal decomposition of precursor oxalato complexes [16] revealed that the X-ray diffraction pattern of $Cs_2Mo_2O_7$ too has many peaks additional to those reported for $Cs_2Mo_2O_7$ by Salmon et al. [14]. These additional peaks have also been attributed to the $Cs_2Mo_2O_7$ phase. It appears that, similar to the orthorhombic structure of $Na_2Mo_2O_7$ [17], $Rb_2Mo_2O_7$ probably has a low symmetry class and the *d* spacings reported by Salmon et al. are incomplete. However, like Salmon et al., we could not index the pattern.

As a result of all these studies, the following scheme can be proposed for the thermal decomposition of RMO in air:

$$Rb_2[Mo_2O_5(C_2O_4)_2(H_2O)_2] \xrightarrow{160\text{–}200^\circ} Rb_2[Mo_2O_5(C_2O_4)_2] + 2H_2O \quad (1)$$

$$4Rb_2[Mo_2O_5(C_2O_4)_2] \xrightarrow{200\text{–}220^\circ} Rb_8[Mo_8O_{22}(C_2O_4)_6] + 2CO + 2CO_2 \quad (2)$$

$$Rb_8[Mo_8O_{22}(C_2O_4)_6] \xrightarrow{220\text{–}255^\circ} Rb_8[Mo_8O_{26}(C_2O_4)(CO_3)] + 5CO + 4CO_2 \quad (3)$$

$$Rb_8[Mo_8O_{26}(C_2O_4)(CO_3)] \xrightarrow{255\text{–}340^\circ} 4Rb_2Mo_2O_7 + CO + 2CO_2 \quad (4)$$

Equation (1) represents the dehydration of RMO, while Eqs (2), (3) and (4) represents the three different stages of decomposition of anhydrous RMO to give the end-product. The mechanism proposed here is a tentative one based on the results obtained from dynamic thermogravimetry and isothermal studies.

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Zusammenfassung — Der Komplex $Rb_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ (RMO) wurde dargestellt und durch chemische Analyse und IR-Spektroskopie charakterisiert. Die thermische Zersetzung wurde mittels TG und DTA untersucht. RMO verliert das Wasser zwischen 160 und 200 °C, worauf unmittelbar die in drei Schritten verlaufende Zersetzung des wasserfreien RMO folgt. Die ersten beiden Schritte verlaufen in den Temperaturbereichen 200–220 °C und 220–255 °C und ergeben Zwischenprodukte mit der möglichen Zusammensetzung $Rb_8[Mo_8O_{22}(C_2O_4)_6]$ bzw. $Rb_8[Mo_8O_{26}(C_2O_4)(CO_3)]$. Das letztere wird in einem Schritt zwischen 255 und 340 °C zum Endprodukt Rubidium-molybdat ($Rb_2Mo_2O_7$) zersetzt. Die *d*-Werte der in den Bereich $2\theta = 10$–$70°$ fallenden Reflexionen von $Rb_2Mo_2O_7$ sind angegeben.

Резюме — Синтезированный комплекс $Rb_2[Mo_2O_5(C_2O_4)(H_2O)_2]$ был охарактеризован химическим анализом и ИК спектроскопией, а методом ТГ и ДТА изучено его термическое разложение. В интервале температур 160–200° комплекс теряет воду, после чего немедленно начинается разложение безводного соединения, протекающее в три стадии. Первые две стадии протекают в интервале температур 200–220 и 220–255°, давая промежуточные продукты состава $Rb_8[Mo_8O_{22}(C_2O_4)_6]$ и $Rb_8[Mo_8O_{26}(C_2O_4)(Co_3)]$. Последнее соединение затем разлагается на третьей стадии в интервале 255–340°, давая конечный продукт димолибдат рубидия. Для этого соединения приведены *d* постоянные для 2θ значений между 10 и 70°.