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PREPARATION OF SODIUM TETRAMOLYBDATE BY THE THERMAL DECOMPOSITION OF A NEW SODIUM OXOMOLYBDENUM(VI)-FORMATO COMPLEX

S.P. GOEL, G.R. VERMA and SANJIVE KUMAR

Department of Chemistry, S.D. Post Graduate College, Muzaffarnagar (U.P.) 251001 (India)

P.N. MEHROTRA

Department of Chemistry, University of Roorkee, Roorkee 247667 (India)

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ABSTRACT

A new molybdenum(VI)-formato complex $Na_2[Mo_4O_{12}(HCOO)_2]$ (SMF) was prepared and characterized by chemical analysis and IR spectral studies. Thermal decomposition studies were made using TG, DTA and DTG techniques. The compound is anhydrous and is stable up to 200 ° C and then decomposes in two stages. The first stage, which occurs between 200 and 210 ° C, corresponds to the loss of 1 mol of hydrogen per mol of SMF to give an intermediate compound having the tentative composition $Na_2[Mo_4O_{12}(C_2O_4)]$. The second stage starts from 225 ° C and corresponds to the decomposition of $Na_2[Mo_4O_{12}(C_2O_4)]$ to give the end product sodium tetramolybdate ($Na_2Mo_4O_{13}$) at 305 ° C. The tetramolybdate melts at 520 ° C and decomposes into the dimolybdate and molybdenum trioxide. Both the products obtained before and after melting were characterized by chemical analysis, IR spectral and X-ray studies.

INTRODUCTION

Although some oxalato [1,2] and other oxomolybdenum(VI) [3] complexes have been prepared and studied, a survey of the literature reveals that no such formato complex has been synthesized. The present work deals with the preparation, characterization and thermal decomposition of a new oxomolybdenum(VI)-formato complex $Na_2[Mo_4O_{12}(HCOO)_2]$ (SMF) which gives sodium tetramolybdate, $Na_2Mo_4O_{13}$ at 305 ° C and sodium dimolybdate, $Na_2Mo_2O_7$ at 830 ° C.

EXPERIMENTAL

Baker analysed ammonium paramolybdate and AnalaR grade sodium formate were employed in the preparation of SMF. Molybdenum trioxide (prepared by heating ammonium *para*-molybdate at about 400 °C for 2 h) was added in small amounts to a hot solution containing sodium formate in about 250 ml of double distilled water until it became saturated. The solution was filtered to remove any unreacted molybdenum trioxide and the clear solution was concentrated to about 30 ml to obtain the crystals of SMF. The crystals were washed with water and then air-dried in a desiccator.

The molybdenum content in the compound was determined gravimetrically as molybdenyl oxinate and the formate was determined by titrating with potassium permanganate solution [4]. Sodium was estimated by flame photometry. Analysis of the sample gave Na^+, 6.44%; Mo, 53.98% and $HCOO^-$, 12.61%, whereas calculated values for $Na_2(Mo_4O_{12}(HCOO)_2]$ are Na^+, 6.46%, Mo, 53.92% and $HCOO^-$, 12.65%. These data confirm that the composition of SMF is $Na_2[Mo_4O_{12}(HCOO)_2]$.

TG, DTA and DTG were carried out on a Stanton Redcroft STA-780 series model using 10–20 mg samples in platinum crucibles. For DTA, ignited alumina was used as the reference material. The heating rate was 10 °C min^{-1}. IR spectra were recorded on a Beckman IR-20 double beam instrument in the range 250–4000 cm^{-1} with samples in the form of potassium bromide pellets. X-ray diffraction patterns were recorded on a Philips diffractometer using Cu $K\alpha$ radiation.

RESULTS AND DISCUSSION

As revealed by its X-ray diffraction pattern, the white powder of SMF is found to be a crystalline compound probably with a low symmetry. The results of IR studies of SMF (Fig. 1(A)) are summarized in Table 1. The normal bands for the formato group have been assigned on the basis of existing data in the literature [5]. Besides these, the two strong bands at 950 and 915 cm^{-1} suggest the presence of metal–oxygen double bonds, and the bands at 880 and 600 cm^{-1} can be assigned to the asymmetric and symmetric Mo–O stretches respectively [6–8].

As seen on the TG curve (Fig. 2), SMF is an anhydrous compound and is stable up to 200 °C; thereafter there is a slight change on the TG curve which probably corresponds to the loss of 1 mol of hydrogen per mol of SMF. This occurs up to 210 °C to give an intermediate compound having the tentative composition $Na_2[Mo_4O_{12}(C_2O_4)]$. This is observed in DTA and DTG as small peaks at 210 and 205 °C, respectively. The observed weight loss is 0.26% as compared to the calculated value of 0.28%. $Na_2[Mo_4O_{12}(C_2O_4)]$ is stable up to 255 °C and then loses one mole each of carbon monoxide and carbon dioxide in a single step to give sodium tetramolybdate, $Na_2Mo_4O_{13}$ as the end product at 305 °C. The peaks at 300 °C in DTA and 295 °C in DTG correspond to this reaction. The

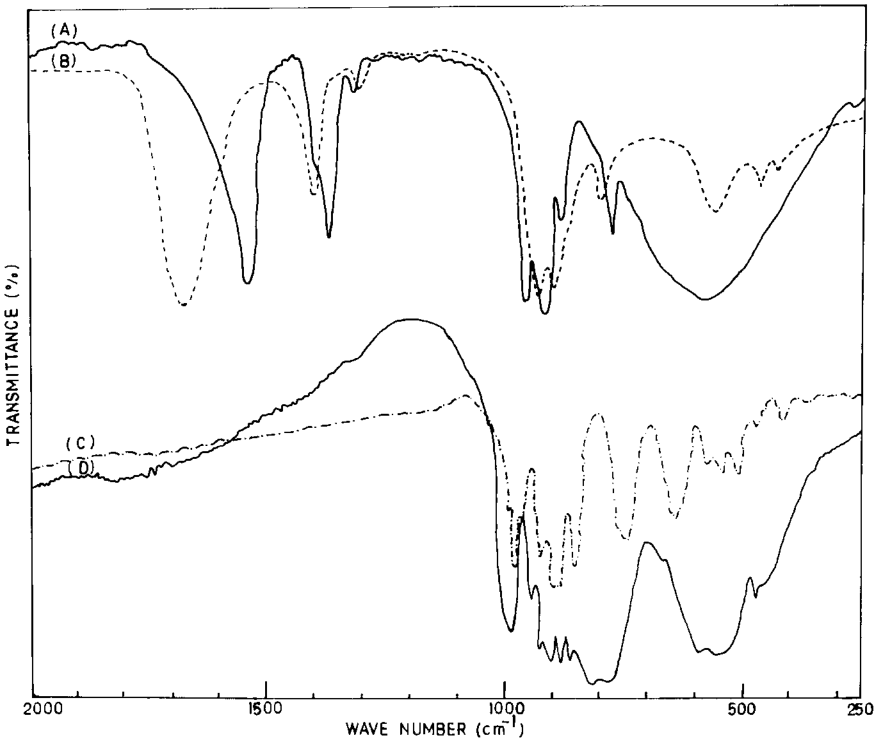

Fig. 1. IR spectra of (A), SMF; (B), SMF heated at 215 °C; (C), 310 °C; (D), 525 °C.

observed weight loss is 10.13% as compared to the calculated value of 10.11%.

The tentative composition assigned to the intermediate compound formed at 210 °C is well supported by the IR spectra data and by the chemical

TABLE 1

IR absorption bands of SMF and their probable assignments

Band position		Probable assignment
Frequency (cm^{-1})		
2800	s	ν(CH)
1560	vs	ν(COO)
1370	s	δ(CH)
1320	w	ν(COO)
950	s	ν_{as}Mo=O
915	s	ν_{sym}Mo=O
880	w	ν(O–Mo–O)
770	m	δ(OCO)
600	vs,br	ν(O–Mo–O)

vs = very strong, s = strong, m = medium, w = weak, br = broad, as = asymmetric, sym = symmetric.

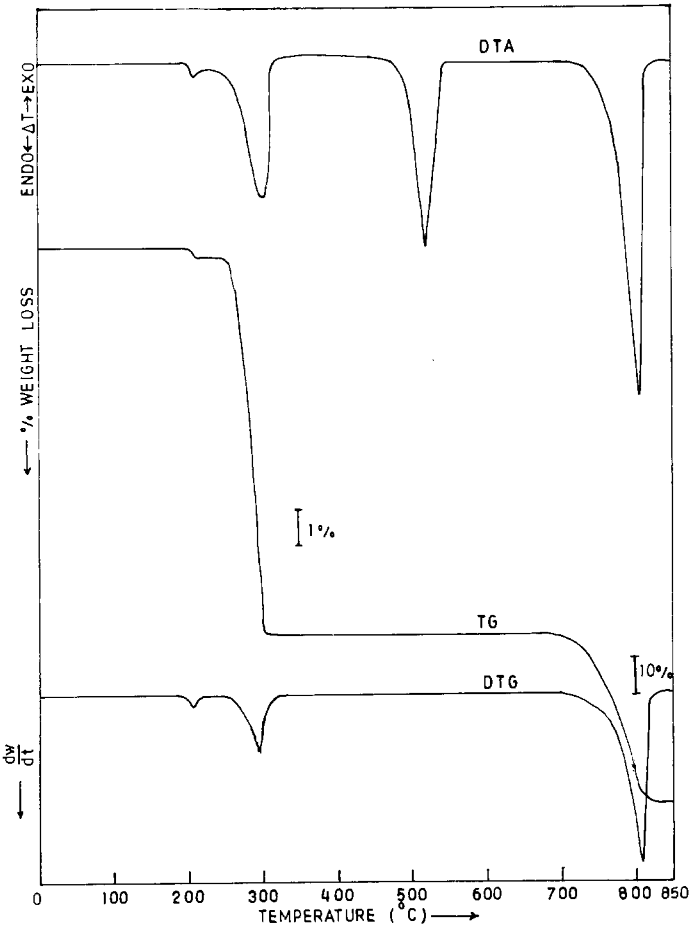

Fig. 2. DTA, TG and DTG curves of SMF in air.

analysis of the sample obtained by heating SMF isothermally at 215 ± 5 °C. The IR spectra (Fig. 1(B)) show no indication of the presence of formate but show bands characteristic of the oxalate group [9]. The chemical analysis of such a sample also confirms its composition to be $Na_2[Mo_4O_{12}(C_2O_4)]$.

An additional endothermic peak is observed in DTA at 520 °C and is attributed to the melting of sodium tetramolybdate, the reported melting point being the same [10]. This was further confirmed by heating SMF isothermally at 530 ± 5 °C where a partly molten product was obtained which immediately solidified. The TG curve shows a further weight loss of 40.48% between 700 and 825 °C which corresponds to the loss of two moles of molybdenum trioxide per mole of sodium tetramolybdate, the calculated value being 40.44%. This is seen in DTA and DTG as peaks at 805 and 810 °C respectively. This is attributed to the sublimation accompanied by the melting (the melting point of molybdenum trioxide being 795 °C) of molybdenum trioxide. Thus the total weight loss for the process

$$Na_2[Mo_4O_{12}(HCOO)_2] \rightarrow Na_2Mo_2O_7 + 2MoO_3 + H_2 + CO + CO_2$$

was found to be 50.87%, compared with the calculated value of 50.83%.

SMF samples were heated isothermally at 310 ± 5, 525 ± 5 and 830 ± 5 °C to obtain products (1), (2) and (3) respectively. All these samples were studied using chemical analysis, IR spectroscopy and X-ray diffraction. Sample (1) was found to be a white crystalline compound; chemical analysis suggests that its composition is $Na_2Mo_4O_{13}$. The IR spectrum (Fig. 1(C)) is also almost identical to that of $K_2Mo_4O_{13}$ as reported in the literature [11]. From its X-ray diffraction pattern, the *d* values closely match the data reported earlier for $Na_2Mo_4O_{13}$ [12]. Sample (2) was found to be a partly molten product which immediately solidified on cooling. Its chemical analysis suggests that the composition is $Na_2Mo_4O_{13}$ but the IR spectrum (Fig. 1(D)) shows bands for $Na_2Mo_2O_7$ [2] and molybdenum trioxide [13], which indicates that, as also reported earlier [10], $Na_2Mo_4O_{13}$ decomposes into $Na_2Mo_2O_7$ and MoO_3 after melting. The *d* values calculated from the observed X-ray pattern closely match the data reported earlier for $Na_2Mo_2O_7$ [14] and MoO_3 [15]. This was further confirmed by taking a thermogram of sample (2), in which no change was observed on the TG and the DTG curve, but a sharp peak was obtained on the DTA curve at 620 °C which was attributed to the melting of $Na_2Mo_2O_7$, the earlier reported value being 615 °C [10]. Sample (3) was a molten product, which on cooling solidified to a white crystalline compound. Its chemical analysis confirms that the composition is $Na_2Mo_2O_7$. The IR spectrum also only shows bands of $Na_2Mo_2O_7$. In the X-ray pattern, only the peaks corresponding to $Na_2Mo_2O_7$ were obtained. On the basis of all these studies, the following scheme can be proposed for the decomposition of SMF in air.

$$Na_2[Mo_4O_{12}(HCOO)_2] \xrightarrow{200-210\,^\circ C} Na_2[Mo_4O_{12}(C_2O_4)] + H_2 \tag{1}$$

$$Na_2[Mo_4O_{12}(C_2O_4)] \xrightarrow{255-305\,^\circ C} Na_2Mo_4O_{13} + CO + CO_2 \tag{2}$$

$$Na_2Mo_4O_{13} \xrightarrow{520\,^\circ C} Na_2Mo_2O_7 + 2MoO_3 \tag{3}$$

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