Journal of Thermal Analysis, Vol. 36 (1990) 465-472

THERMAL DECOMPOSTION STUDIES ON NICKEL(II) BIS(OXALATO)NICKELATE(II) PENTAHYDRATE

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(Received June 11, 1988; in revised form March 15, 1989)

The paper describes the synthesis and thermal decomposition of nickel(II)bis(oxalato)nickelate(II)pentahydrate, $Ni[Ni(C_2O_4)_2].5H_2O$. The complex was characterized by elemental analysis, infrared, electronic, e.s.r., magnetic moment measurement and X-ray powder diffraction studies. The thermal decompostion of the complex led to NiO in air at about 338° and in nitrogen at about 720°. The activation energies (E^*) for the dehydration and decompostion reactions in air and nitrogen were evaluated. Tentative reaction mechanisms have been suggested for the termal decompostion of the complex in air and nitrogen.

Although the oxalato complexes of nickel and other transition and non-transiton metals of the type $MC_2O_4.xH_2O$ and $M^1[M^2(C_2O_4)_n]xH_2O$ (where M^1 = K, NH_4 and Na and M^2 = nickel and other metals) are well known [1-5], complexes of the type $M[M(C_2O_4)_n]xH_2O$ are relatively less known [6]. We have synthesized a series of oxalato complexes of the above type and their spectral and thermal studies were reported [7-10].

As an extension of our work reported earlier we are reporting here the synthesis, characterization and thermal decomposition of nickel(II)bis(oxalato)nickelate(II)pentahydrate, $Ni[Ni(C_2O_4)_2].5H_2O$.

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Experimental

Preparation of the complex

Nickel hydroxide, prepared from nickel chloride was made free from chloride. It was dissolved in glacial acetic acid and heated on a steam bath. The solution was filtered and a greenish blue compound was precipitated by dropwise addition of a hot saturated solution of oxalic acid in glacial acetic acid. The compound was filtered off and purified by standard procedure [6]. The water content of the compound was determined. The nickel content was estimated gravimetrically as bis(dimethylglyoximato)nickel(II). Carbon and hydrogen contents were estimated on a Thomas CH analyser. Analysis; Calculate for $Ni[Ni(C_2O_4)_2].5H_2O$, Ni, 30.61%; C, 12.53%; H, 2.63% H_2O, 23.49%; Found, Ni, 30.52%; C, 12.57%; H, 2.7%; H_2O, 23.43%.

Physical measurements

Infrared (4000-600 cm^{-1}), far infrared, diffuse reflectance, e.s.r. spectra at liquid nitrogen temperature, magnetic moment, X-ray powder diffraction photographs and thermal data (DTA, TG, DTG, and DSC) were recorded as described earlier [6-9].

Results and discussion

The greenish blue microcrystalline compound was insoluble in water or in common organic solvents. However, it decomposed in the presence of strong acid or alkali.

The low μ_{eff} value (0.92 BM) at room temperature and the presence of a weak signal in the e.s.r. spectra both at room and liquid nitrogen temperature indicated the compound to be weakly paramagnetic in nature. Furthermore, the electronic spectrum of the solid sample showed some complex multicomponent bands centered around 20200(15500, 20200, 25000sh and 27390 cm^{-1}). The complexity could be due to the presence of both distorted octahedral and square planar geometries around the two nickel atoms respectively. The band around 41320 cm^{-1} in the uv region was due to intraligand $\pi \rightarrow \pi^*$ transition [9]. Gravimetric analysis revealed the association of five molecules of water with each molecule of the compound. The infrared spectrum of the compound indicated the presence of coordinated oxalato groups [11-13]. The broad band in the region 3700-3000 cm^{-1} was due to the symmetric and asymmetric stretching frequencies of water [14] as well as due to hydrogen bonding. The sharp peak at 750 cm^{-1} and a small broad band around 600 cm^{-1} were due to the rocking mode [15] or to coordinated water and crystal water [11] respectively, whereas other prominent bands observed at lower frequencies might be due to the out-of-plane bending (π) motion of the oxalato group. The analytical results were consistent with the preposed formula of the complex to be $Ni[Ni(C_2O_4)_2].5\ H_2O$. The presence of a medium sharp band at 205 cm^{-1} in the far infrared spectrum of the complex is ascribed to the presence of a metal-metal bond [7, 9, 16]. The low μ_{eff} value and the insolubility of the compound could be due to the presence of a metal-metal bond.

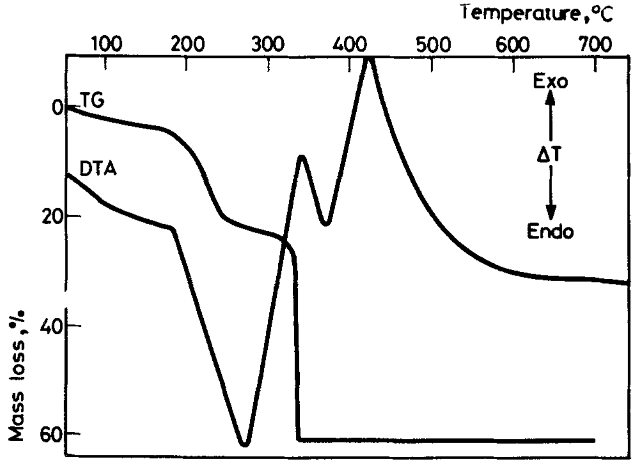

Fig. 1 DTA and TG curves in air medium

The water vapour, carbon monoxide and carbon dioxide evolved during decomposition were identified by i.r. spectroscopy [11].

The DTA curves (Fig. 1) recorded in air and nitrogen showed a sharp endothermic peak with ΔT_{min} of 270°. It was followed by a medium exothermic peak and an endothermic peak with ΔT_{max} of 340° in air and nitrogen, respectively. In air at 420° another large exothermic peak appeared while in nitrogen and endothermic peak at 358° followed by an exothermic change around 410° was seen.

The water loss started from 50° as indicated by the TG curve and the respective break around 172° and 180° in the TG and DTA curve in air indicated the loss of one molecule of water. This corresponded to the mass loss data (found 4.6%; calcd. 4.7%). In nitrogen the respective mass loss was (found 4.7%; calcd. 4.7%) observed around 175° in the TG curve. The endothermic peaks obtained around 270° in the DTA curve and the slope in the TG curve up to 248° and 253° in air and nitrogen, respectively, with a mass loss of 20% might be due to the evolution of four molecules of water. A broad peak observed between 175-253° in the DTG curve in nitrogen indicated the removal of three molecules of water simultaneously. The mass losses at 310° (in air) and 311° (in nitrogen) in the TG curves corresponded to the formation of anhydrous compound which decomposed immediately to further products.It was not possible to isolate the completely anhydrous form as the last traces of water got removed only during further decomposition of the compound [6]. The presence of a small band at 3400-3200 cm^{-1} in the i.r. spectrum of the compound preheated to 270° indicated the presence of trace amounts of water. The presence of the peaks indicated that the chelating character of the oxalato group was retained [17]. The faint green compound so produced absorbed moisture immediately [7, 9] on exposure to humid atmosphere resulting in the reformation of the original compound as evidenced by the reappearance of the broad band in the region of 3700-3000 cm^{-1}. The removal of water at high temperature supported the formation of metal-oxygen coordination bond with water as well as the presence of hydrogen bonding [18]. Similar observation was reported [4] with nickel oxalate dihydrate; however, the temperature of the removal of the last water molecule in the present complex was more than in the simple oxalate and it could be predicted that the water molecule might utilize the Ni^{2+} orbitals for bonding [2]. A broad endothermic peak observed between 164-280° with a ΔT_{min} of 245° (at 10 deg min^{-1}) and between 168-270° with a ΔT_{min} of 237° (at 5 deg min^{-1}) in air in the DSC scan. This must correspond to a dehydration process. The activation energies (E*) of this step were calculated from TG data by Freeman and Carroll's method [19] and were found to be 51 and 42.05 kJ mol^{-1} in air and nitrogen, respectively. The value derived from DSC data (5 deg min^{-1}) was 142.26 kJ mol^{-1}. The enthalpy change was (ΔH) 17.99x104 kJ mol^{-1}.

A greenish yellow compound was isolated around 330° (in air) as an intermediate. The mass loss was found to be 42% in the TG curve. The intermediate was assumed to be a mixture of NiO and NiC_2O_4. The constituents were separated by hot water. The greenish compound was identified to be NiO analytically (Ni, found 78.2%; calcd. 78.58%) and spectroscopically [20] with a broad band around 460 cm^{-1} in the i.r. spectrum. The i.r. spectrum of the greenish yellow compound was identical with that of the complex reported by Tanaka *et al.* [3] and the estimated nickel content (found 41%; calcd. 40.01%) confirmed the compound to be NiC_2O_4. However, TG traces did not indicate the presence of this intermediate because the heat produced caused NiC_2O_4 to decompose immediately, before its normal decomposition temperature was reached [5]. NiO may have an accelerating effect on the rapid decompostion of NiC_2O_4. The formation of a mixture of NiO and $Ni_2C_2O_4$ indicated that the outer nickel in the complex formed nickel oxide and the inner nickel formed NiC_2O_4 [6]. The steepness of the TG curve ended at 338° (in air) with a mass loss of 60.75% which might indicate the formation of a stable compound, NiO (calcd. weight loss is 61.04%) or a mixture of NiO and Ni_2O_3. The DTA peak around 340° corresponded to this overall decomposition step. The exotherm recorded at 420° without any mass change in the TG curve indicated the interaction or the solid-solid reaction of the products in addition to some partial oxidation [6] of NiO to Ni_2O_3 and Ni_3O_4. This might be ascribed to some phase transformation with the formation of a mixture of the oxides of nickel [21]. The black residue (Ni, 74.4%) was found to be paramagnetic in nature with g value of 1.35 in the e.s.r. spectrum and the i.r. spectrum showed a band at 465 cm^{-1}. The X-ray powder diffraction pattern of the residue was similar to that of NiO [22]. The results indicated that the residue could be a non-stoichiometric form of the oxides [7]. Corresponding to these decomposition stages an exothermic peak was obtained between 307-353° with a ΔT_{max} at 345° in the DSC curve (5 deg min^{-1}). The weight loss was 59.04%. The E^* of the overall decomposition stage was calculated to be 688.35 KJ mol^{-1} in contrast to the value, 394.17 KJ mol^{-1} determined by DSC (5 deg min^{-1}) along with the ΔH of 25.94 KJ mol^{-1}.

In nitrogen, the endothermic peak at 340° (DTA) corresponding to a mass loss of 24% in the TG curve indicated the removal of the last traces of water accompanied by some partial decomposition. A small endotherm at 358° with a mass loss in the TG curve of 30% indicated [23] the formation of $Ni[Ni(C_2O_4)_{1.5}]$. The continuous mass loss with slightly inclined slope up to 409° with a mass loss of 67.07% might be due to the formation of metallic nickel Ni (calcd. mass loss is 69.39%) or a mixture of Ni and NiO. The exothermic peak around 410° in DTA curve was due to this final decomposition. However, the compound thus formed gained mass of 6.07% up to 720° and beyond that the compound was stable. The overall mass loss of 61% indicated the final compound to be NiO. The gain in mass might be due to the disproportionation [24] of some CO(g) to CO_2(g) and carbon, due to the catalytic nature of Ni and NiO. Similar observation was made earlier [7, 8]. The E^* of this stage was evaluated to be 95.60 KJ mol^{-1}.

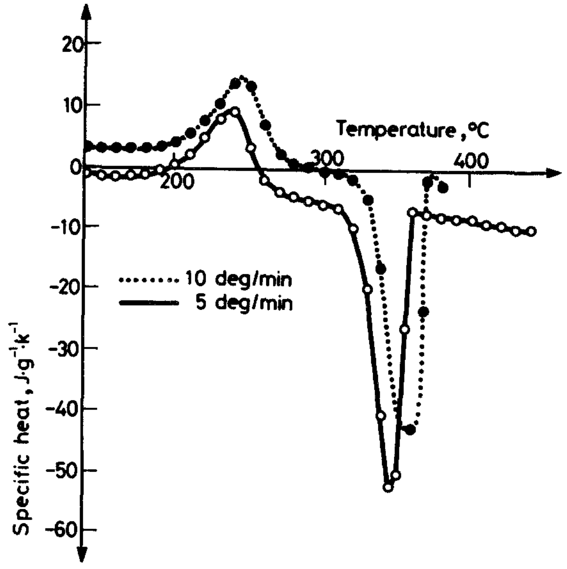

Fig. 2 Plot of specific heat values *vs*. temperature at heating rates of 5° and 10 deg min^{-1}

Plots of specific heat values *vs*. temperature (Fig. 2) recorded separately for heating rates of 10 and 5 deg min^{-1} indicated the transition in temperature ranges similar to the respective DSC traces [9]. Our results suggest the following reactions:

(i) In air

$$Ni[Ni(C_2O_4)_2].5H_2O \xrightarrow{50-172^\circ} Ni[Ni(C_2O_4)_2].4H_2O + H_2O(v) \xrightarrow{172-248^\circ}$$

$$Ni[Ni(C_2O_4)_2].H_2O + 3H_2O(v) \xrightarrow{\sim 330^\circ} NiO(s) + NiC_2O_4(s) + H_2O(v) +$$

$$CO(g) + CO_2(g) \xrightarrow{\sim 338^\circ + O_2} 2NiO \text{ or } (NiO + Ni_2O_3 + Ni_3O_4) + CO(g) +$$

$$CO_2(g).$$

(ii) In nitrogen atmosphere,

$$\mathrm{Ni[Ni(C_2O_4)_2].5H_2O} \xrightarrow{50-175^\circ} \mathrm{Ni[Ni(C_2O_4)_2].4H_2O} + \mathrm{H_2O(v)} \xrightarrow{175-253^\circ}$$

$$\mathrm{Ni[Ni(C_2O_4)_2].H_2O} + \mathrm{3H_2O(v)} \xrightarrow{\sim 340^\circ} \mathrm{Ni[Ni(C_2O_4)_2](s)} + \mathrm{H_2O(v)} \xrightarrow{\sim 358^\circ}$$

$$\mathrm{Ni[Ni(C_2O_4)_{1.5}](s)} + \mathrm{CO_2(g)} \xrightarrow{\text{above } 407^\circ} \mathrm{2Ni(s)} \text{ or } \mathrm{(Ni + NiO)(s)} +$$

$$m\mathrm{CO_2(g)} + n\mathrm{CO(g)} \xrightarrow{\sim 720^\circ} \mathrm{2NiO(s)} + \mathrm{pCO_2(g)}$$

* * *

The authors thank the RSIC, CDRI, Lucknow for microanalysis, RSIC, NEHU, Shillong for i.r. spectra, RSIC, IIT, Madras for far i.r. spectra, RSIC, Nagpur University for thermal analysis, Dr. S. K. Datta for Forensic Science Laboratory, Guwahati, Assam for DSC and Dr. K. L. Deori of Dibrugarh University for X-ray powder diffraction photographs.

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Zusammenfassung — Es wird die Synthese und thermische Zersetzung von Nickel(II) - bis(oxalato) - nickelat(II) - pentahydrat beschrieben: $Ni[Ni(C_2O_4)_2].5H_2O$. Dieser Komplex wurde mittels Elementaranalyse, IR-Spektroskopie, ESR-Spektroskopie, der Messung des magnetischen Momentes sowie mittels Pulverdiffraktionsuntersuchungen charakterisiert. Im Ergebnis der thermischen Zersetzung entsteht NiO, in Luft bei etwa 338°, in Stickstoffatmosphäre bei ca. 720°. Die Aktivierungsenergien (E^*) der Dehydratations- und Zersetzungsreaktionen in Luft und in Stickstoff wurden ermittelt. Für die thermische Zersetzung des Komplexes in Luft bzw. in Stickstoff wurde ein Reaktionsmechanismus entwickelt.