

# NON-ISOTHERMAL DECOMPOSITION KINETICS OF COMPLEX OF Co(III), Ni(II) WITH O,O'-DIALKYLDITHIOPHOSPHATES AND ADDUCTS OF Ni-COMPLEX WITH PYRIDINES

Z. Lu<sup>1\*</sup>, S. Chen<sup>2</sup>, Y. Yu<sup>2</sup>, J. Sun<sup>1</sup> and S. Xiang<sup>1</sup>

<sup>1</sup>Testing and Analysis Centre, Suzhou University, Suzhou Jiangsu 215006

<sup>2</sup>Department of Chemistry, Zhenjiang, Teachers' College, Zhenjiang, Jiangsu 212003  
P. R. China

## Abstract

Thermal behaviour of tri(O,O'-diisopropylidithiophosphate)cobalt(III), Co(dtp)<sub>3</sub> and bis(O,O'-diethylidithiophosphate)nickel(II), Ni(detp)<sub>2</sub> and its adducts with pyridine, Ni(detp)<sub>2</sub>(py)<sub>2</sub> or 4-methylpyridine, Ni(detp)(mpy)<sub>2</sub> in a dynamic nitrogen atmosphere was investigated by TG-DTG and DSC techniques, which showed a medium endothermic peak for the evolution process of pyridine(or 4-methylpyridine) and a strong exothermic peak for that of O,O'-diethylidithiophosphate. The thermal stability and decomposition patterns for these compounds were compared and interpreted in terms of structural features such as bond character and steric effects. The kinetic parameters and mechanisms of every decomposition stage involved for all these complexes were obtained employing the non-isothermal kinetic analysis method suggested by Malek *et al.*, which showed the kinetics mechanism for pyrolysis of pyridine(or 4-methylpyridine) is an S-B empirical model with lower activation energy, while that of O,O'-dialkyldithiophosphate is a diffusion model. These results are in accord with the fact that two ligands are of different type.

**Keywords:** adducts, cobalt complex, DSC, kinetics, nickel complex, O,O'-dialkyldithiophosphate, pyridine, TG-DTG

## Introduction

O,O'-dialkyldithiophosphates (DATP) are known as effective extractants for extraction of some transition metals such as Co, Ni, and Mn [1]. The complexes of Co and Ni with these extraction agents have received a great deal of attention owing not only to their practical importance especially for biological use [2, 3], but also to the fact that being metal chelates in which the metal ions are coordi-

\* Author to whom all correspondence should be addressed.

natively unsaturated, they can act as electron acceptors to form adducts with neutral molecules which are electron donors [4]. Studies on the crystal structure, mass spectra and biological activity of some of these complexes have been reported [2, 4, 5–7]. However, a search of the literature reveals little information concerning thermal behaviour and even no information about thermal decomposition kinetics of these compounds.

TA is a powerful technique widely used for studying the thermal properties of complexes in solid state. In this paper, the thermal behaviour and decomposition kinetics under a nitrogen atmosphere were studied by means of TG-DTG-DSC for the title compounds, i.e.  $\text{Co}[(\text{C}_3\text{H}_7\text{O})_2\text{PS}_2]_3$ , (abbreviated as  $\text{Co}(\text{dptp})_3$ , where  $\text{dptp}=\text{O},\text{O}'$ -diisopropyldithiophosphate),  $\text{Ni}[\text{C}_2\text{H}_5\text{O})_2\text{PS}_2]_2$ , ( $\text{Ni}(\text{detp})_2$ ,  $\text{detp}=\text{O},\text{O}'$ -diethyldithiophosphate) and the adducts of  $\text{Ni}(\text{detp})_2$  with pyridine and 4-methylpyridine, i.e.  $\text{Ni}(\text{detp})_2(\text{py})_2$  and  $\text{Ni}(\text{detp})_2(\text{mpy})_2$ . As these target compounds in study cover many variations in structure such as bond character (including simple coordinate bond  $\text{Ni}-\text{N}$  and chelate ring  $\text{Ni} \left\langle \begin{array}{c} \text{S} \\ \text{S} \end{array} \right\rangle \text{P}$ ) the alkyl group type (ethyl and branched-chain isopropyl), metal ion (Co and Ni) and coordination number, another aim of this work which may be more important is to correlate their thermal behaviour and kinetic parameters of decomposition with these structural features.

## Experimental

### *Preparation and identification of sample*

The nickel complex of  $\text{Ni}(\text{detp})_2$  and its adducts,  $\text{Ni}(\text{detp})_2(\text{py})_2$  and  $\text{Ni}(\text{detp})_2(\text{mpy})_2$  were prepared by the procedures described elsewhere [2, 5, 6]. The cobalt complex  $\text{Co}(\text{dptp})_3$  was prepared using the method described in a previous paper [7] with the exception of using isopropanol instead of ethanol.

All the chemicals used in the preparation were Analar grade. Using UV-Vis, MS, PET and etc., the quality of the samples for TA study was identified with that of the samples for single crystal XRD study which has been reported earlier [6, 7].

### *Thermal analysis*

Thermogravimetric analyses were carried out on a Perkin-Elmer TGA-7, at different heating rates (2.5, 5, 10,  $15^\circ\text{C min}^{-1}$ ) from  $30$ – $600^\circ\text{C}$  under  $\text{N}_2$  ( $35 \text{ ml min}^{-1}$ ). Differential scanning calorimetry measurements were carried out on a Perkin-Elmer DSC-7 at a heating rate of  $5^\circ\text{C min}^{-1}$  from  $30$ – $500^\circ\text{C}$  under flowing  $\text{N}_2$  ( $30 \text{ ml min}^{-1}$ ). All the samples were crushed with a pestle and mortar, and a mass of 3–5 mg was used. Prior to the experiments, calibrations for both TGA-7 and DSC-7 were performed using the standards from the calibration kit provided by the P-E Corp. The temperature could be read from the record to two

decimal points but it is better to regard the temperature as correct to within one degree.

## Methodology and kinetic analysis

Heterogeneous reactions have proved extremely complicated [8–10]. It was shown that the activation energy  $E$  and preexponential factor  $A$  in the kinetic equation commonly used are mutually correlated, known as 'kinetic compensation effect' (KCE). From this point of view, it seems that the methods of kinetic analysis aiming to ascertain all kinetic parameters from only one experimental TA curve are somewhat problematic [8, 9]. Taking these facts into account, the data obtained from mass loss measurements were processed kinetically using the method proposed by Malek *et al.* [11, 12] in the present study, which, according to our experience [13, 14], can usually give more satisfactory results than some other methods. In the course of data processing in this work, the activation energies  $E$  were evaluated using both Kissinger [15, 16] and expanded Friedman methods [16, 17]. The latter was also used to check the constancy of  $E$  during the course of every decomposition stage.

## Results and discussion

### *Thermal behaviour*

Thermal analytical data measured at  $\beta=2.5^\circ\text{C min}^{-1}$  for all the complexes are presented in Table 1. The percentage mass loss and the probable composition of the expelled groups are also given. Two representative TG-DTG-DSC curves for complex  $\text{Ni}(\text{detp})_2$  and its adduct  $\text{Ni}(\text{detp})_2(\text{py})_2$  are shown in Figs 1 and 2, respectively.

Concerning the decomposition pattern, we observe that the TG-DTG curves for either  $\text{Ni}(\text{detp})_2$  or  $\text{Co}(\text{dtp})_3$  show only one peak clearly related to the loss of ligand molecules in one step; while the DTG curve for the adduct of the nickel complex with either pyridine or 4-methylpyridine shows two well-resolved peaks, which, according to the mass loss percentage, can be assigned to the elimination of two pyridine (or 4-methylpyridine) molecules and then of two O,O'-diethyldithiophosphate molecules, respectively. In contrast to the result reported earlier [2], in the present study, the TG measurement of either  $\text{Ni}(\text{detp})_2(\text{py})_2$  or  $\text{Ni}(\text{detp})_2(\text{mpy})_2$  exhibits no sign of the existence of the unstable species  $\text{Ni}(\text{detp})_2(\text{py})$  or  $\text{Ni}(\text{detp})_2(\text{mpy})$ . This is confirmed by the DTG curves recorded at different heating rates, which is generally considered as a technique which reveals the nature of the reaction when competitive and independent reactions proceed concurrently in a system [18, 19]. For all the compounds studied, the residue after the final stage of decomposition was found to be metal Ni or Co.

Table 1 The thermal behaviour of the complexes

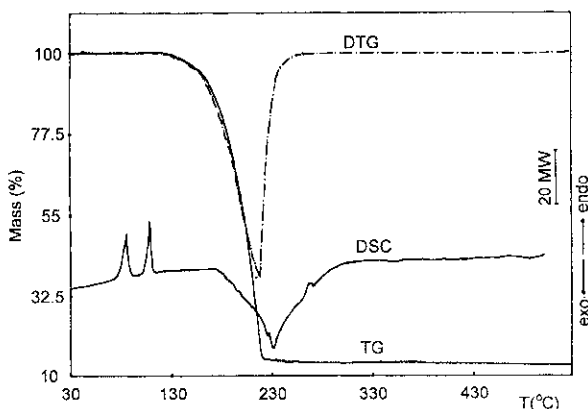
Complex <sup>a</sup>	DSC temp./°C $T_p$	TG-DTG temperature/°C		Mass loss/%		Probably expelled composition
		range	$T_p$	TG	theory	
Ni(detp) <sub>2</sub>	82, 105 (endo), 231 (exo)	123-510	216	87.14	86.43	2 detp
Ni(detp) <sub>2</sub> (py) <sub>2</sub>	112 (endo)	I 60-145	109	26.32	26.20	2 py
	210 (exo)	II 145-506	217	63.98	63.74	2 detp
Ni(detp) <sub>2</sub> (mpy) <sub>2</sub>	126 (endo)	I 58-139	120	30.80	30.25	2 mpy
	199 (exo)	II 139-524	203	59.86	60.20	2 detp
Co(dtp) <sub>3</sub> <sup>b</sup>	143 (endo), 219 (exo)	86-592	184	90.95	91.56	3 dtp

<sup>a</sup> *dtp*=O,O'-diisopropylidithiophosphate, *detp*=O,O'-diethyldithiophosphate, *p*=pyridine, *mpy*=4-methylpyridine

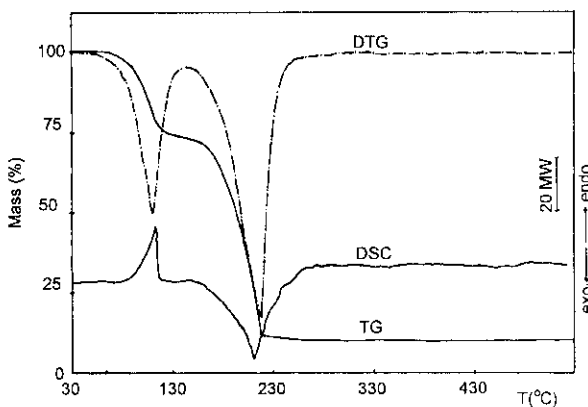
<sup>b</sup> both peaks in DSC curve for Co complex are very weak

It can be seen from Table 1 and Figs 1 and 2 that for nickel compounds the stage of pyridine (or 4-methylpyridine) evolution is associated with a medium endothermic peak; while the evolution of O,O'-diethyldithiophosphate is associated with a strong exothermic peak in DSC curves. It is interesting to note there are two small but sharp peaks in the DSC curve for Ni(detp)<sub>2</sub> appearing before the decomposition initiates, and that these are accompanied by no mass loss, corresponding to some possible solid state phase transitions or melting. Unfortunately, the DSC curve for Co(dtp)<sub>3</sub> provides information of no significance as it shows only two very weak peaks in the temperature range of decomposition with no parallel DTG peaks.

With regard to thermal stability, the complexes with simple ligand, namely Ni(detp)<sub>2</sub> and Co(dtp)<sub>3</sub> are evidently higher than the adducts Ni(detp)<sub>2</sub>(py)<sub>2</sub> and Ni(detp)<sub>2</sub>(mpy)<sub>2</sub>. The adducts start to decompose at a temperature as low as



**Fig. 1** TG-DTG-DSC curve for complex Ni(detp)<sub>2</sub>; heating rate: TG: 2.5°C min<sup>-1</sup>; DSC: 5.0°C min<sup>-1</sup>



**Fig. 2** TG-DTG-DSC curve for complex Ni(detp)<sub>2</sub>(py)<sub>2</sub>; heating rate: TG: 2.5°C min<sup>-1</sup>; DSC: 5.0°C min<sup>-1</sup>

about 60°C. This behaviour is expected from chemical consideration: being an additive, although pyridine or 4-methylpyridine molecules are also coordinated to the Ni ion through N atom, the bond energy of Ni–N, after all, is smaller than that of chelate ring, Ni– $\overset{\text{S}}{\text{S}}\text{P}$  through which O,O'-diethyldithiophosphate molecules are coordinated. This fact is also consistent with the result obtained earlier by Shun'ichiro Ooi *et al.* [4]: the Ni–N bond in these compounds does not have any double-bond character. It can also be seen from the thermal decomposition data that the existence of methyl group in pyridine molecule has almost no effect on the thermal behaviour of the compound. A comparison between Ni(detp)<sub>2</sub> and Co(dptp)<sub>3</sub> shows that the former has a higher thermal stability than the latter, which may be interpreted as below. First of all, the different metal ions would make a difference in thermal stability. Besides, the steric effects of the alkyl groups can destabilize the Ni–S bond. In fact, the branch-chain alkyl groups(isopropyl) in the ligand molecules of Co(dptp)<sub>3</sub> cause crowding about the phosphorus atom, leading to an increase in the phosphorus tetrahedral bond angles. This in turn causes strain in four-membered P– $\overset{\text{S}}{\text{S}}\text{Ni}$  ring, thereby weakening the Ni–S bond [2].

### Thermal decomposition kinetics

All the results from kinetic analysis of TG data using the method suggested by Malek *et al.* are summarized in Table 2. The *E* values listed under Friedman are all the average of those obtained at various  $\alpha$  which have been used to check the invariance of *E* with respect to  $\alpha$ . As shown in Table 2, the activation energy values determined by Kissinger and Friedman methods are in reasonable agreement, and therefore the *E* values by the Kissinger method were used in the rest of

**Table 2** Kinetic parameters obtained using the method by Malek *et al.* for decomposition of the complexes

Complex <sup>a</sup>	<i>E</i> /kJ mol <sup>-1</sup>		lnA	KM <sup>c</sup>	<i>m</i>	<i>n</i>	
	Kissinger	Friedman <sup>b</sup>					
Ni(detp) <sub>2</sub>	98.73	105.49	28.59	D2			
Ni(detp) <sub>2</sub> (py) <sub>2</sub>	I	79.74	82.64	23.86	SB	0.3577	0.6892
	II	106.82	106.33	29.31	D2		
Ni(detp) <sub>2</sub> (mpy) <sub>2</sub>	I	80.65	85.92	25.61	SB	0.2506	0.7254
	II	112.68	108.21	29.49	D2		
Co(dptp) <sub>3</sub>	125.03	121.78	29.59	D3			

<sup>a</sup> *drip*=O,O'-diisopropylidithiophosphate, *detp*=O,O'-diethyldithiophosphate, *py*=pyridine, *mpy*=4-methylpyridine

<sup>b</sup> The average value of *E* by the Friedman method at various  $\alpha$ ; c: kinetic model

calculations. From Table 2, it can also be seen that the first step of decomposition for both adducts, corresponding to the evolution of two pyridine molecules or two 4-methylpyridine molecules, is controlled by the S-B model, an empirical kinetic model proposed by Šesták and Berggren [20]:  $f(\alpha) = \alpha^m(1-\alpha)^n$ . It is concluded from the calculated parameters that pyrolysis of adductive molecules, i.e. pyridine or 4-methylpyridine, is a low-energy process, as evidenced by the low activation energy, as compared with that of O,O'-dialkyldithiophosphate molecules which are controlled by the D2 (nickel complex) and D3 (cobalt complex) diffusion mechanisms.

The variations in the  $E$  value and the decomposition mechanism determined in this work seem to be in accord with the fact that the two ligands are of different type, that is, the additive pyridine (or 4-methylpyridine) and chelating type ligand O,O'-diethyldithiophosphate (or O,O'-diisopropyldithiophosphate).

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