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THERMAL AND KINETIC STUDY OF NICKEL TRIFLUOROMETHANESULPHONATE, TRIFLUOROACETATE AND ACETATE

Hiléia K. S. de Souza[*], *E. A. Sousa, M. D. M. Paiva, F. M. M. Borges, D. M. A. Melo and H. Scatena Jr.*

Universidade Federal do Rio Grande do Norte, Departamento de Química, C. P. 1662, 59078-970 Natal, RN, Brasil

The reason of comparing thermal behaviour and kinetics of some nickel compounds, is justified by the influence of anion on it, besides supplying information on the stability of the salts. In this work, $Ni(TMS)_2\cdot 6H_2O$, $Ni(TFA)_2\cdot 3H_2O$ and $Ni(Ac)_2\cdot 2H_2O$, were synthesized and characterized by microanalysis, atomic absorption molar, conductance and thermal analysis. Thermogravimetric curves indicate that the decomposition of the salts occurs in the range 295–1169 K and the NiO is the final residue. Non-isothermal kinetic evaluation from thermogravimetric data was used to determine energies of activation and pre-exponential factors.

Keywords: *kinetic study, nickel complexes, thermal analysis*

Introduction

The interest for nickel chelated $CF_3SO_3^-$ (TMS) results from its thermal stability and also from the possibility of being a mono-, bi- or tridentates ligand [1]. Trifluoroacetates CF_3COO^- (TFA) and acetates CH_3COO^- (Ac) may behave in a similar way, albeit forming nickel compounds with different amounts of hydration. Garner [2] was a precursor of the study of the whole series of transition metal trifluoromethane compounds with salts showing three hydration water molecules. Fujinaga and Sakamoto have been studied the electrochemical characteristics of trifluoro- methanesulphonic acid and its salts in nonaqueous solvents [3].

Transition complexes containing trifluoroacetate compounds with formulas: $Tm(CF_3COO)_3\cdot 3H_2O$, $Tm_2(CF_3COO)_6\cdot 2CF_3COOH\cdot 3H_2O$ [4] and $Ln(TFA)_3\cdot 3MMNO$ [5] were synthesized and studied. Trifluoroacetate compounds and their structures also have been described already [6].

Acetates complexes with several organic neutral ligands as heterocyclicamines [7], phenol derived [8], pyrazines [9], salicylidene derivatives [10], phenazone [11] dimethylaminobenzoic derivatives [12] were also prepared and characterized. In the solid-state, nickel acetates have been used as precursors for obtaining mixed nickel oxides with ‘*d*’ transition metals and also rare earths [13].

This work tries to correlate dehydration with thermal stability and to evaluate kinetic parameters, activation energies and pre-exponential factors from thermogravimetric curves of the nickel salts with different anions.

Experimental

Nickel trifluoromethanesulphonates (TMS), TFA and Ac salts were obtained from pentahydrated nickel chloride and characterized by microanalytical procedure (CHN), atomic absorption, nuclear electrolytic conductance and thermal analysis (TG and DSC). Carbon and hydrogen were determined with a Perkin Elmer 2400 Elemental Analyzer. Nickel percentages were measured on a SpectrAA 110 Varian atomic absorption spectrophotometer and molar conductance on Quimis E405 equipment. TG curves were obtained in a N_2 dynamic air atmosphere with $0.17\ K\ s^{-1}$ heating rate and $0.83\ cm^3\ s^{-1}$ flow in a Shimadzu TGA-50H system. DSC curves were obtained under the same heating and flow rate conditions with a Shimadzu DSC-50H equipment. Finally, kinetic study of the compounds was achieved using a domestic computer program developed in QBASIC using TG data.

Basic kinetic theory

Several methods have been used for obtaining kinetic parameters through TG techniques [14, 15]. Vyazovkin [16] and Scatena Jr. [17] analyzed the difficulty in obtaining kinetic parameters with small errors. In this work, custom-made software was used, simulating thermogravimetric data using the following kinetic equation in each process step:

$$\Delta m_{i,j} = -\frac{k_{0,i}}{\beta}\exp\left[-\frac{E_{ai}}{RT}\right] m_{i,j-1}\Delta T_j + \frac{M_{i+1}}{M_i}\Delta m_{i,j-1} \quad (1)$$

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[*] Author for correspondence: hileiak@yahoo.com

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

where $\Delta m_{i,j}$ is the mass increase of the compound i after the step j; $k_{0,i}$ is the pre-exponential factor and $E_{a,i}$ is the activation energy of compound i, M_i is the molar mass of compound i; β is the heating rate and ΔT_j is the temperature increase for step j.

The initial mass for the first compound is m_1. For the remaining components the initial mass is zero. With the use of block activation energies and pre-exponential factors it is possible to approximate visually the theoretical mass and the experimental one. The theoretical mass is given by:

$$m_j = \sum_i m_{i,j} \qquad (2)$$

where m_j is the total mass at step j. A reaction order of one was proposed for basic kinetic theory, since any other is theoretically difficult to justify.

The quality criterion for the approximation of calculated and observed curves is visual and therefore the first and second derivatives are helpful.

The advantages of determining the kinetic parameters by this method are:

- It is possible to study the whole temperature range of the thermogravimetric curve even with parallel or consecutive reactions.
- It is possible to predict the quantity and the molar mass of the reaction intermediate.
- Using the mechanistic proposal it is possible to determine the experimental curve and test the initial hypothesis.

Results and discussion

From the CHN microanalysis and atomic absorption (AA) results shown in Table 1, the following stoichiometrics are suggested for the salts: $Ni(TMS)_2{\cdot}6H_2O$, $Ni(TFA)_2{\cdot}3H_2O$ and $Ni(Ac)_2{\cdot}2H_2O$.

Conductance measurements in 10^{-3} mol L^{-1} water solution at 298 K indicate the existence of 1:2 electrolytes for the compounds TMS and AC. Electrolytes (1:1) to the TFA according to the intervals admits by Geary [18] (Table 2).

Thermal stability depends on the anions types, structure and chartered of the bond between ligands and central atom. The complexation of the different anions can be distinct effects on the thermal stability of the complexes as results of the different chemical environments. Thermogravimetric curves were recorded to evaluate the thermal stability of the salts. For $Ni(TFA)_2{\cdot}3H_2O$ and $Ni(Ac)_2{\cdot}2H_2O$ salts, the thermogravimetric curves show four-step decomposition. For the $Ni(TMS)_2{\cdot}6H_2O$, the decomposition process show five-step (Fig. 1). The first mass loss region for all salts is due to anhydrous salts formation. TMS compound starts the decomposition at 716 K, while the TFA and Ac compounds at 545 and 563 K, respectively. This clearly suggests a high stability of the TMS salt. Finally, nickel oxide was obtained as final residue for all the salts (Table 3).

DSC curves (300–780 K range), obtained under the same condition as TG exhibit different behavior and showed endothermic peaks as indicative of dehydration of the compounds (Fig. 2). The exothermic process observed in acetate compounds is probably related to the evolution of acetate molecules. This exothermic peak evidence a less stability of the ace-

Table 2 Molar electrolytic conductance results

Compounds	Λ_M/Ω^{-1} cm^{-2} mol^{-1}
$Ni(TMS)_2{\cdot}6H_2O$	206.5
$Ni(TFA)_2{\cdot}3H_2O$	153.0
$Ni(Ac)_2{\cdot}2H_2O$	265.3

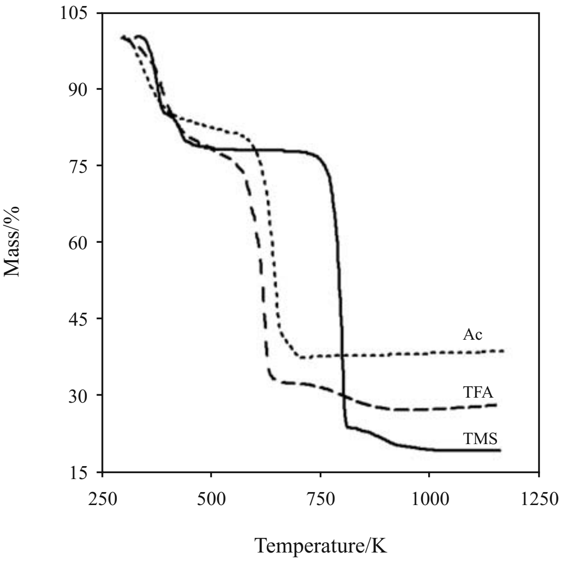

Fig. 1 TG curves for the TMS, TFA and Ac salts under flowing N_2 (50 cm^3 min^{-1}). Heating rate 0.083 K s^{-1}

Table 1 Elemental analysis results

Compounds	Ni/%		C/%		H/%	
	exp.	calc.	exp.	calc.	exp.	calc.
$Ni(TMS)_2{\cdot}6H_2O$	9.8	9.9	5.4	5.2	2.6	2.6
$Ni(TFA)_2{\cdot}3H_2O$	7.8	7.5	15.3	15.0	1.9	1.3
$Ni(Ac)_2{\cdot}2H_2O$	8.5	8.4	22.2	22.6	4.8	4.7

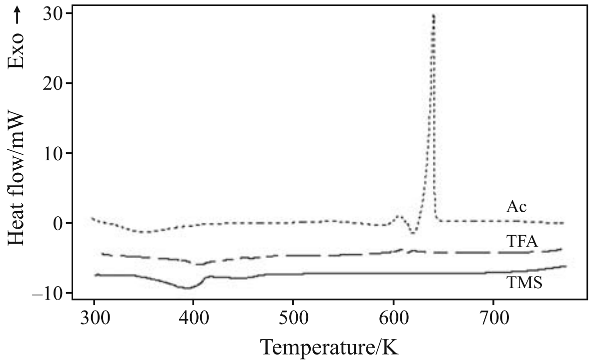

Fig. 2 DSC curve for salts (TMS, TFA and Ac), under flowing N_2 (50 cm^3 min^{-1}). Heating rate 0.083 K s^{-1}

tate compound in comparison with another ones. Due to the temperature range limited in DSC, was not possible to observe the final decomposition process of the TMS and TFA compounds.

According TG and DSC data, it is possible to suggest the following decomposition reactions:

$Ni(TMS)_2{\cdot}6H_2O$

$$Ni(CF_3SO_3)_2{\cdot}6H_2O \rightarrow Ni(CF_3SO_3)_2{\cdot}3H_2O+3H_2O\uparrow$$

$$Ni(CF_3SO_3)_2{\cdot}3H_2O \rightarrow Ni(CF_3SO_3)_2{\cdot}2H_2O+H_2O\uparrow$$

$$Ni(CF_3SO_3)_2{\cdot}2H_2O \rightarrow Ni(CF_2O)_2+2H_2O+2FSO_3$$

$$Ni(CF_2O)_2 \rightarrow NiO+C_2F_4O\uparrow$$

$Ni(TFA)_2{\cdot}3H_2O$

According Pedrosa *et al.* [5], the decomposition of TFA evolve gaseous products, especially CO, CO_2, CF_3OF and $(CF_3CO)_2O$. The decomposition of TFA continues up 1160 K, with the formation of NiO as final residue.

$Ni(Ac)_2{\cdot}2H_2O$

The decomposition of AC also evolves gaseous products, especially CO, CO_2, CH_3COO, $C_2H_6CO_2$ and C_2H_5CHO with NiO as final residue.

Figures 3–5 shows the observed and calculated thermogravimetric curves obtained by TG and kinetic studies respectively for the thermal decomposition of the $Ni(TMS)_2{\cdot}6H_2O$, $Ni(TFA)_2{\cdot}3H_2O$ and $Ni(Ac)_2{\cdot}2H_2O$. These figures also show the first and second derivatives of both calculated and observed TG curves for the three salts. E_a, k_0, and intermediate molar masses were determined by fitting the observed curves assuming that the reaction order was one. The first and second derivatives help with a visual approach between observed and calculated curves. The usual molar mass of the intermediate allows good approximation between observed and calculated curves. The proposed mechanism for thermoanalysis of the $Ni(TMS)_2{\cdot}6H_2O$, $Ni(TFA)_2{\cdot}3H_2O$ and $Ni(Ac)_2{\cdot}2H_2O$ is coherent with:

- Molar mass obtained from TG curves and
- Mass balance of each step.

Table 4 summarizes the thermodynamic parameters obtained from these plots as explained in the experimental section. Studies show that Ac is least hydrated and have major E_a in the step dehydrated (step 1) returning least stable. Step 2 only the TMS continue hydrated, while of the Ac and TFA starts the salts decomposition respectively, observed through values E_a. In this step, the value major E_a of the TFA is related due the fluor compound. In step 3 continue the salts Ac and TFA decomposition with E_a values 400 and 205 kJ mol^{-1}, respectively. The decomposi-

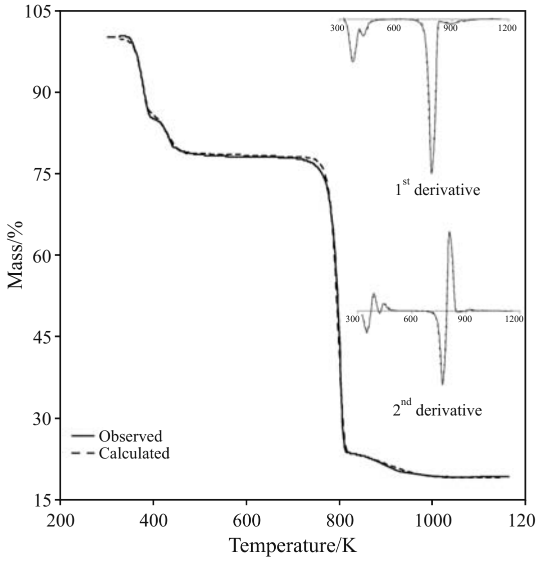

Fig. 3 Observed and calculated TG curves for the $Ni(TMS)_2{\cdot}6H_2O$ salt

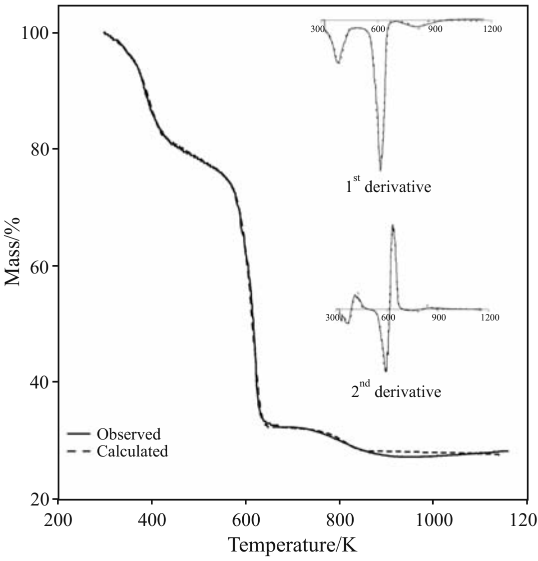

Fig. 4 Observed and calculated TG curves for the $Ni(TFA)_2{\cdot}3H_2O$ salt

Table 3 Kinetic study results

Step	TMS		TFA		Ac	
	k_0/s^{-1}	E_a/kJ mol^{-1}	k_0/s^{-1}	E_a/kJ mol^{-1}	k_0/s^{-1}	E_a/kJ mol^{-1}
1	$2.1\cdot10^{13}$	108.8	$4.6\cdot10^{6}$	67.0	$1.1\cdot10^{26}$	165.0
2	$8.5\cdot10^{5}$	66.4	$3.5\cdot10^{14}$	196.0	$3.0\cdot10^{9}$	75.0
3	$1.3\cdot10^{29}$	471.5	$8.0\cdot10^{10}$	205.0	$1.0\cdot10^{31}$	400.0
4	$3.0\cdot10^{2}$	88.7	–	–	–	–

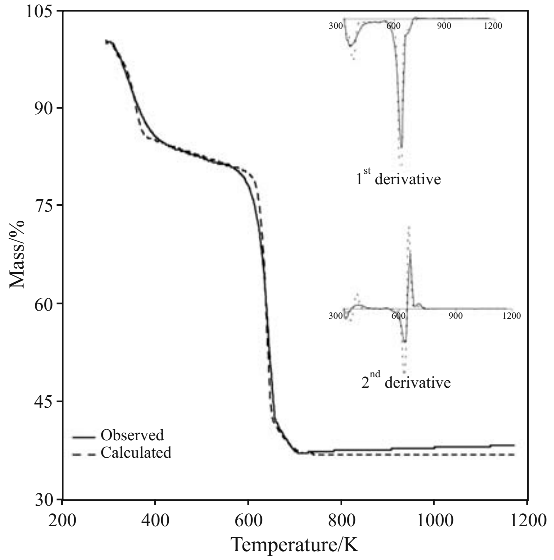

Fig. 5 Observed and calculated TG curves for the $Ni(Ac)_2\cdot2H_2O$ salt

tion of TFA and Ac continues in step 4 with the formation of NiO as a final residue. In the TMS case the NiO residue was obtained in step 5.

Conclusions

Thermal behavior of the nickel TMS, TFA and Ac salts have not been described in the literature. The thermal characterization was carried out by TG, DSC while the kinetic study using a QBASIC program infer the TG data as input. The proposed three mechanism for the observed thermal decomposition consists of consecutive of the organic intermediates. The method previously introduced [8] showed a good agreement with the plotted curves and suggests that each peak correspond to more than one reaction. The first and second derivatives indicated the high quality of the optimization of the mass curves.

The thermal decompositions and kinetic studies show that trifluoromethanesulphonate anion is much more stable than other anions taking into account the remarkable resistance to thermal decomposition.

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