THE DIFFERENT PATHWAYS OF THE THERMAL DECOMPOSITION OF METAL NICOTINATES AND ISONICOTINATES

ELSA E. SILEO [1], PEDRO J. MORANDO [1,2] and MIGUEL A. BLESA [1,2]

[1] *Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón II, Ciudad Universitaria, 1428 Buenos Aires (Argentina)*
[2] *Departamento Química de Reactores, Comisión Nacional de Energía Atómica, Avenida del Libertador 8250, 1429 Buenos Aires (Argentina)*

ABSTRACT

The thermal decomposition (TD) of basic iron nicotinate and isonicotinate proceeds in several stages: (a) dehydration to yield a hydroxocompound; (b) dehydration of hydroxide bridges, overlapping with water attack on the anion and release of H(nic) and H(isonic); (c) homolytic RC(O)O–Fe(III) bond breaking; (d) formation of metallic iron. Sodium salts decompose yielding $Na_2CO_3 + C$, that later evolves CO. The different types of chemical reactions involved in the TD of metal nicotinates and isonicotinates are compared.

INTRODUCTION

In a previous work [1] we reported the thermal behaviour of several complexes of the type $[M_m Fe(CN)_5 L] \cdot x H_2O$, where M is a divalent or trivalent transition metal cation and L is an aromatic amine derived from pyridine or pyrazine; anionic ligands L featuring a carboxylate group bound to Cu(II) or Fe(III) decompose at lower temperatures than neutral L ligands such as pyridine.

We now report the thermal decomposition (TD) of basic Fe(III) nicotinates and isonicotinates under nitrogen; the corresponding simple copper salts were studied previously [2]. These systems allow us to characterize (i) the importance of homolytic M–OC(O)R bond breaking to trigger decomposition, and (ii) the role played by hydroxide groups bound to Fe(III) in the subsequent evolution of the organic acids and their decomposition products. Previous work on Fe(III) carboxylates includes studies of the formate [3], propionate [4], butyrate [4], oxalate [5–7], succinate [8], adipate [8], basic benzoate [9] and phthalate [9], and mellitate [10]; among these salts only formate was decomposed in nitrogen atmosphere, mellitate and basic benzo-

ate and phthalate were thermolysed in vacuum and all others were studied in air.

EXPERIMENTAL

Preparation and chemical analyses

$Fe_2(OH)_5L$ $(L = nicotinate$ or $isonicotinate)$

A three-fold excess of sodium nicotinate or isonicotinate was added to a 5×10^{-2} mol dm^{-3} Fe(NO$_3$)$_3$ acid solution and the pH was adjusted to 2.5. The solution thus obtained was refluxed at 70–80°C for 2 h until a brown solid was precipitated. The solid was centrifuged and washed several times with bi-distilled water and finally dried over CaCl$_2$.

The metal content was determined using a Varian Techtrom A-A5R atomic absorption spectrometer; nicotinate and isonicotinate were assayed by acid–base titration and the water content was determined thermogravimetrically. (Found for Fe$_2$(OH)$_5$nic · 0.75H$_2$O: Fe, 33.59%; nic, 36.92%; H$_2$O, 3.99%. Calculated: Fe, 33.60%; nic, 37.02%; H$_2$O, 4.06%. Found for Fe$_2$(OH)$_5$isonic · H$_2$O: Fe, 33.53%; isonic, 35.52%; H$_2$O, 5.33%. Calculated: Fe, 33.17%; isonic, 36.23%; H$_2$O, 5.34%.)

Sodium salts

Sodium nicotinate and isonicotinate were prepared by neutralization of nicotinic and isonicotinic acids with sodium hydroxide. The resulting solutions were evaporated at 40°C. (Found for Na(nic): Na, 15.77%. Calculated: Na, 15.86%. Found for Na(isonic) · H$_2$O: Na, 14.12%; H$_2$O, 8.60%. Calculated: Na, 14.10%; H$_2$O, 8.59%.)

Spectral characterization

X-ray diffraction patterns were recorded on a Philips P.W. 1390–1394 diffractometer; IR spectra were recorded on a Beckman 4260 spectrophotometer. In the case of solids, samples were prepared in the form of KBr disks.

DTA–TG

Thermogravimetric (TG) experiments were performed in a Mettler Recording Thermoanalyser 1 with samples of about 15 mg under a nitrogen atmosphere in the temperature range 25–800°C with a heating rate of 6°C min^{-1}. Identification of evolved products was performed by collecting gases and condensed liquids released under isothermal conditions in a tubular furnace, and recording their IR spectra.

RESULTS AND DISCUSSION

Basic ferric salts

The complexity of the TD of the basic ferric salts can be appreciated from the shape of the TG and DTA curves (Fig. 1a, b) that can be resolved into four regions (Table 1).

The first step at $80\,^{\circ}C$ is an endothermic dehydration; weight loss at this stage was used to establish the degree of hydration reported before.

The second zone between 185 and $300\,^{\circ}C$ approximately is composed of various exothermic DTA peaks in the case of the basic nicotinate and only one for the isonicotinate derivative.

TABLE 1

Thermogravimetric data for the basic iron salts

T_p ($^{\circ}C$)	DTA	Evolved products	Weight loss (%)
$Fe_2(OH)_5(nic)\cdot 0.75\ H_2O$			
80	Endo	H_2O	3.99
185	Exo	H(nic)	19.6
210	Endo	CO_2	
282	Endo	py	
		H_2O	
383	Endo	H(nic)	23.6
		CO_2	
		py	
		H_2O	
594	Endo	ND	38.4
676	Exo	(CO?)	
740	Endo		
$Fe_2(OH)_5(isonic)\cdot H_2O$			
80	Endo	H_2O	5.3
210	Exo	H(isonic)	16.5
		CO_2	
		py	
		H_2O	
370	Endo	H(isonic)	14.7
435	Endo	CO_2	
		py	
		H_2O	
500–800	Continuous loss	ND	16.7
		(CO?)	

ND, not determined.
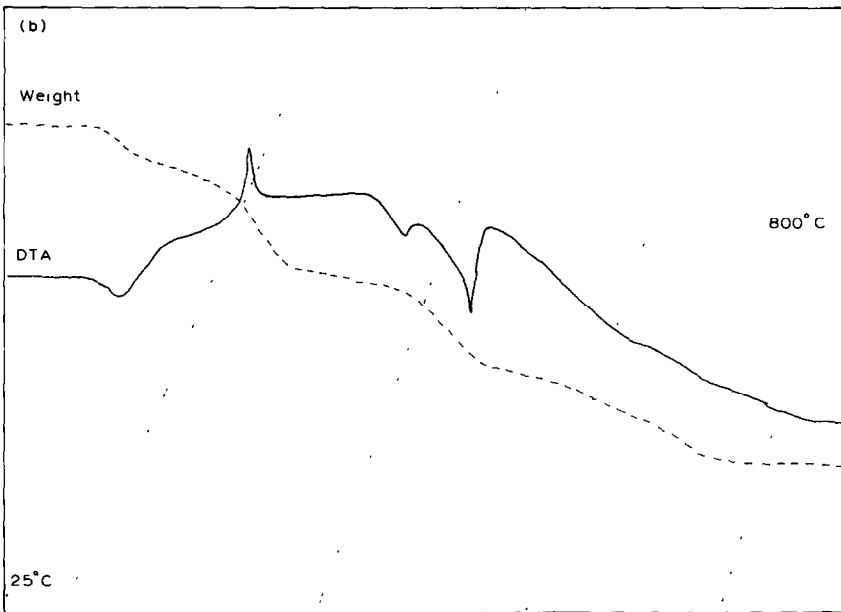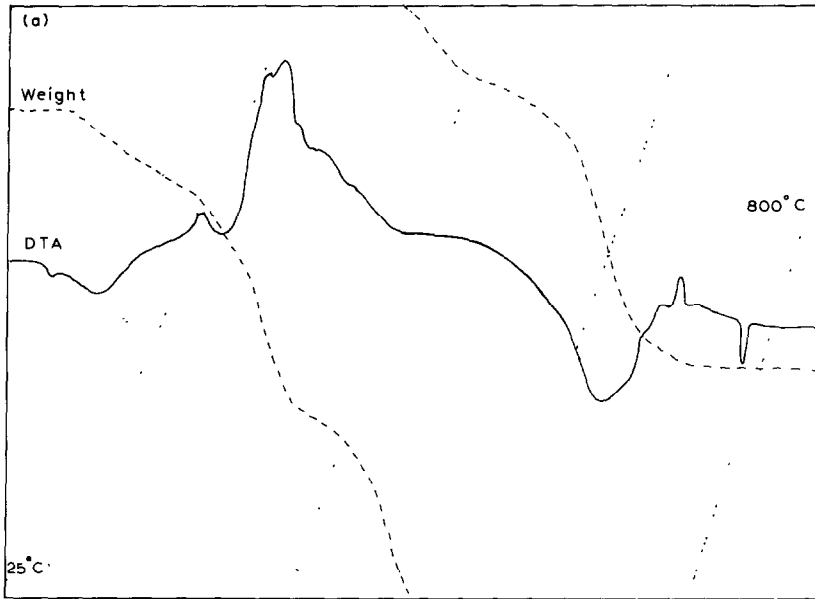
Fig. 1. TG ($\cdot-\cdot-\cdot$) and DTA (———) curves for (a) $Fe(OH)_5(nic)\cdot0.75H_2O$ and (b) $Fe(OH)_2(isonic)\cdot H_2O$. Linear heating is also shown.

The amorphous residues obtained by thermolysis at 300 and 240°C contained nicotinate or isonicotinate, respectively; in the evolved gases pyridine, carbon dioxide, water and nicotinic or isonicotinic acid could be detected.

These observations can be explained by accepting that, overlapping the main dehydration reaction,

$$RCO_2Fe(III)(OH)_5Fe(III)(s) \rightarrow RCO_2Fe(III)O_{2.5}Fe(III)(s) + 2.5H_2O(g)$$

(1)
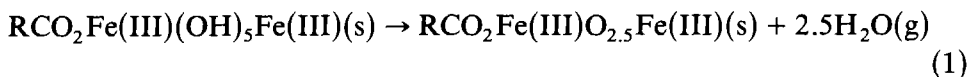
water attack on the organic anion takes place, through the following equations

$$RCO_2FeO_{2.5}Fe + H_2O \rightarrow RCO_2H(g) + HOFeO_{2.5}Fe$$ (2)

$$RCO_2H \rightarrow RH + CO_2$$ (3)
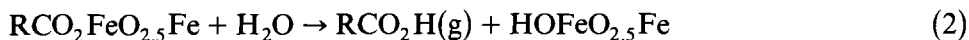
The exothermic character of the process is surprising, but the prevalence of reaction (1) is confirmed by the titration of Fe(II) in the residue, that shows less than 6% of total iron is present as Fe(II). It is possible that a minor contribution from an internal electron transfer $L^- \rightarrow Fe(III)$ (see below) is also embodied in this peak.

The weight loss expected according to eqn. (1) is 14.1%; this figure should be compared with 16.5 and 19.6% found for isonicotinate and nicotinate, respectively. The difference must be attributed to reactions (2) and (3) and/or the internal redox process already mentioned. The different volatilities of H(isonic) and H(nic) (both compounds undergo sublimation and their melting points are 313 and 236°C, respectively [11]) account for the different contribution of reaction (2) to the weight loss (2.4 and 5.5%, respectively).

The observed weight losses suggest that by the end of this state the compositions of the residues are $Fe_2(nic)_{0.86}O_{2.57}$ and $Fe_2(isonic)_{0.94}O_{2.54}$.

The third stage occurs at ca. 383°C (nic) and 435°C (isonic). The nature of the products indicates that this stage corresponds to the redox reaction between the ligand and Fe(III). This reaction is equivalent to the homolytic breakage of an Fe(III)–OC(O)R bond

$$R(O)CO-Fe(III)O_{2.5}Fe(III)(s) \rightarrow R(O)CO^{\cdot} + Fe(II)O_{2.5}Fe(III)(s)$$ (4)
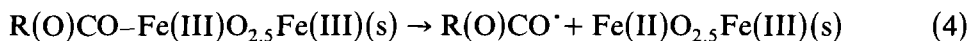
that must be followed by further decomposition reactions of the organic radicals. In the absence of interactions with the residual solid, these reactions should be decarboxylation

$$\rightarrow NC_5H_4^{\cdot} + CO_2$$ (5)

and hydrogen abstraction reactions among the pyridyl radicals

$$5NC_5H_4^{\cdot} \rightarrow 4py(g) + 0.5N_2(g) + 5C(s)$$ (6)
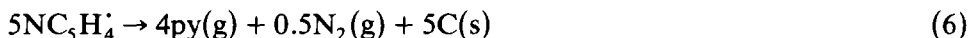
This sequence is responsible for the CO_2 and py observed in the evolved gas, and has been postulated also to take place during the thermolysis of the corresponding copper(II) salts [2].

TABLE 2

X-ray diffraction data for the sodium salts

Sodium nicotinate			Sodium isonicotinate		
2θ (deg.)	d (Å)	I/I_0	2θ (deg.)	d (Å)	I/I_0
7.64	11.54	100	3.70	23.88	5
14.70	6.026	2	6.30	14.03	100
15.25	5.809	1	7.40	11.95	4
16.80	5.277	34	8.20	10.78	3
18.70	4.745	3	14.50	6.11	5
18.90	4.695	6	14.60	6.07	9
19.70	4.506	1	14.80	5.98	8
24.10	3.693	7	15.20	5.83	6
24.90	3.575	39	16.40	5.40	48
26.70	3.338	6	17.20	5.15	2
29.50	3.028	1	18.30	4.85	22
29.60	3.018	1	19.40	4.57	24
30.80	2.903	24	20.30	4.37	9
31.70	2.822	5	22.25	4.42	6
31.90	2.805	4	23.30	3.81	2
32.60	2.746	1	24.70	3.60	50
33.60	2.667	1	25.70	3.50	20
34.00	2.637	1	26.30	3.38	14
34.40	2.607	1	26.60	3.35	14
35.10	2.556	1	27.90	3.19	9
35.80	2.508	1	28.30	3.15	9
37.85	2.376	6	28.40	3.14	10
38.20	2.356	2	29.40	3.04	16
42.20	2.141	1	30.40	2.94	25
43.20	2.094	1	30.80	2.90	12
46.80	1.941	3	31.30	2.86	4
47.20	1.925	1	31.70	2.82	5
47.70	1.906	1	32.40	2.76	6
48.80	1.8601	1	32.90	2.72	12
49.25	1.8501	1	33.85	2.65	3
49.90	1.8275	1	34.90	2.57	4
51.20	1.7841	1	37.20	2.41	23
			38.40	2.344	1
			39.80	2.264	2
			44.60	2.031	4
			45.40	1.997	5
			45.90	1.977	8
			46.00	1.972	7
			46.40	1.957	3
			49.10	1.255	9

I/I_0: intensity ratio to maximum diffraction peak.

The free acids are also observed in the evolved gas, indicating that hydrogen abstraction by RCO_2^- may also take place (alternatively, some hydroxide groups may have survived the first stage).

At these high temperatures, the pyrolysis of pyridine and the free acids may also overlap, leaving behind larger amounts of carbon in the solid residue.

The residual solid is magnetic, as expected for a ferrous–ferric oxide, see eqn. (4).

The fourth region in both cases corresponds to the reduction of the magnetic oxide to Fe^0, characterized by X-ray diffraction, in a process similar to the well-known reaction:

$$Fe_3O_4 + 4C \rightarrow 3Fe(s) + 4CO(g) \tag{7}$$

Sodium salts

Whilst sodium nicotinate crystallizes as an anhydrate, sodium iso-nicotinate loses water at $110\,^\circ C$ in an amount that agrees with the formula $Na(isonic) \cdot 4H_2O$. This salt shows a second, small endothermic peak at $243\,^\circ C$ that corresponds to a transition without weight loss. Diffraction patterns obtained before and after this transition did not show any difference with the one obtained for the original dehydrated solid (Table 2).

Nicotinate and isonicotinate start to decompose with melting at 417 and $430\,^\circ C$, respectively; the DTA shows two endothermic peaks at 417 and $440\,^\circ C$ for the former solid, and at 440 and $495\,^\circ C$ for the latter solid. The residual solid was Na_2CO_3 in both cases, as seen by X-ray diffraction and IR spectroscopy. In the evolved gas, py, $(CN)_2$ and CO_2 were identified. No attempt was made to establish the stoichiometry of the reaction, which can be written qualitatively as

$$2\,Na^+ \; N\langle\text{—}\rangle\,CO_2^-\;(s) \rightarrow Na_2CO_3(s) + xC(s) + \left[py + (CN)_2 + CO_2 + H_2 + N_2\right] \tag{8}$$
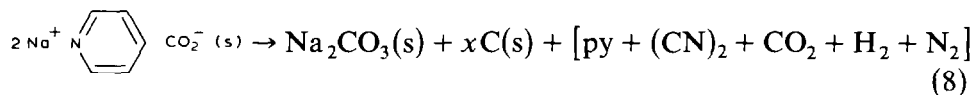
Residual carbon and evolved hydrogen and nitrogen are required by stoichiometry; the former is probably responsible for the further weight loss observed at higher temperatures

$$Na_2CO_3(s) + C(s) \rightarrow Na_2O(s) + 2CO(g) \tag{9}$$
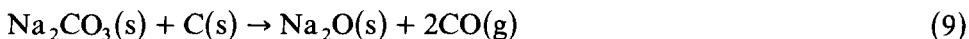
CONCLUSIONS

Our studies of the TD of the nicotinates and isonicotinates of sodium, copper [2] and iron(III) show the operation of three different mechanisms corresponding to very different reaction products.

(a) Copper(II) salts decompose easily through a redox process that yields Cu^0 and decomposition products of the organic radical [2]. The decomposition is fast and gives rise to highly mobile copper atoms, in good agreement with the behaviour of other salts of Cu(II) [12].

(b) Sodium salts decompose at much higher temperatures, in a process in which C–O and/or C–C bonds, rather than M–O bonds, are homolytically broken. Thermolysis of the radicals and the high reactivity of Na_2O give rise to Na_2CO_3.

(c) Basic ferric salts decompose in two stages, the first one corresponding to the attack of released water or mobile protons on the O–M bond with the release of the acid (equivalent to a heterolytic bond rupture). At higher temperatures, the oxo salts decompose in a fashion similar to the copper salts, but yielding ferrous–ferric oxides.

The order of composition temperatures for these processes is Fe(III) hydroxo salts (mode I) < Cu(II) salts < Fe(III) oxo salts (mode II) < Na salts.

In particular, the order for Cu(II) salts and Fe(III) oxo salts (mode II) is dictated by the relative stabilities of the oxidized forms of both metals.

REFERENCES

1   E.E. Sileo, M.G. Posse, P.J. Morando, M.A. Blesa, H. Herrera, C.A. della Vedova and A. Esteban, Polyhedron, 9 (1987) 1757.
2   E.E. Sileo, P.J. Morando, C.A. della Vedova and M.A. Blesa, Thermochim. Acta, 138 (1989) 233.
3   P.J. Morando, N. Piacquadio and M.A. Blesa, Thermochim. Acta, 117 (1987) 325.
4   P.S. Bassi, B.S. Randhawa and H.S. Jamwal, Thermochim. Acta, 62 (1983) 209.
5   D. Dollimore and D. Nicholson, J. Chem. Soc., (1962) 960.
6   D. Dollimore and D. Nicholson, J. Chem. Soc. A, (1966) 281.
7   P.K. Gallagher and C.R. Kurkjian, Inorg. Chem., 5 (1966) 214.
8   P.S. Bassi, B.S. Randhawa and H.S. Jamwal, Thermochim. Acta, 65 (1983) 1.
9   A.K. Galwey, J. Chem. Soc., (1965) 4235.
10 A.K. Galwey, J. Chem. Soc., (1966) 87.
11 R.C. Weast, S.M. Selvy and C.D. Hodgman (Eds.), Handbook of Chemistry and Physics, The Chemical Rubber Co., Cleveland, OH, 1964, p. 520.
12 N.J. Carr and A.K. Galwey, Proc. R. Soc. London, Ser. A, 404 (1986) 127.