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THE THERMAL DECOMPOSITION OF COPPER(II) NICOTINATE AND ISONICOTINATE

ELSA E. SILEO, [1] PEDRO J. MORANDO, [1,2] CARLOS O. DELLA VEDOVA [3]
and MIGUEL A. BLESA [1,2]

[1] *Departamento de Quimica Inorgánica, Analitica y Quimica Fisica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón II, Ciudad Universitaria, 1428 Buenos Aires (Argentina)*
[2] *Departamento Quimica de Reactores, Comisión Nacional de Energia Atómica, Avenida del Libertador 8250, 1429 Buenos Aires (Argentina)*
[3] *Programa QUINOR, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Calle 47 y 115; (1900) La Plata (Argentina)*

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ABSTRACT

The thermal decomposition of copper(II) nicotinate and isonicotinate yields, in a sharp transition, metallic copper as the final solid residue along with the release of carbon dioxide and pyridine. In the case of the nicotinate, small amounts of nicotinic acid are also detected. The decomposition is started by homolytic RC(O)O–Cu bond scission, which is equivalent to electron transfer from $RC(O)O^-$ to Cu(II).

INTRODUCTION

Several studies of the thermolysis behaviour of copper(II) salts of organic acids are found in the literature: formate [1–5], acetate [6–8], other alkanoates [4], oxalate [9], maleate [10,11], fumarate [10,11], malonate [11,12], tartrate [13,14], adipate [12], benzoate [12], salicylate [12], salicylaldoximate [15,16], indolecarboxylate [16], resacetophenoneoximate [15] and mellitate [17]. Inspection of the available data shows that it is generally true that copper(II) salts decompose at lower temperatures that the corresponding salts of other divalent metals (e.g. manganese(II), cobalt(II), zinc(II)). There is, however, no general agreement between the proposed mechanisms, and electron transfer from the anion to Cu(II), O–C bond scission or cleavage of other bonds of the anion have all been suggested as triggering chemical reactions. In spite of the number of systems studied, there is a lack of adequate data to draw general mechanistic conclusions. The present paper discusses the thermal behaviour of copper(II) nicotinate and isonicotinate, and is the first report of a systematic study of copper(II) carboxylates pyrolyses.

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There is scant information in the literature concerning copper(II) nicotinate and isonicotinate. Therefore, prior to the study of the thermolytic behaviour some effort was devoted to the preparation and characterization of both salts.

EXPERIMENTAL

Copper(II) salts of 3- and 4-pyridinecarboxylic acid (Cu(nic)$_2$ and Cu(isonic)$_2$) were prepared by mixing 5×10^{-2} mol dm^{-3} $CuSO_4$ solution with the stoichiometric amount of 0.1 mol dm^{-3} Na(nic) or Na(isonic) solution (pH 5). The copper salts that precipitated inmediately were washed several times with bidistilled water until no sulphate ion could be detected in the rinse water. The solids were dried over $CaCl_2$. Copper contents were determined using a Varian Techtrom A-A5R atomic absorption spectrometer (calculated for Cu(nic)$_2$ 20.66%, found 20.62%; calculated for Cu(isonic)$_2 \cdot 4H_2O$ 16.74%, found 16.68%). Elementary analyses were performed by UMYMFOR, UBA using standard techniques (for Cu(nic$_2$): C calculated 46.82%, found 46.62%; H calculated 2.60%, found 2.81%; N calculated 9.10%, found 8.83%; for Cu(isonic)$_2 \cdot 4H_2O$: C calculated 37.94%, found 38.14%; H calculated 4.21%, found 4.05%; N calculated 7.37%, found 7.38%).

Water contents were determined thermogravimetrically for Cu(isonic)$_2 \cdot 4H_2O$ (H_2O calculated 18.97%, found 18.44%).

X-ray diffraction data were recorded with a Philips X-ray Generator PW 1130 and IR spectra with a Perkin-Elmer 580 B spectrophotometer.

Thermogravimetric experiments were performed using a Rigaku Denki CV 8002 L2 thermobalance with samples of about 15 mg under a N_2 atmosphere in the temperature range 25–450 °C at a heating rate of 10 °C min^{-1}.

Scanning electron micrographs were obtained using a JEOL S 25 II apparatus.

Identification of evolved products was performed qualitatively by IR spectroscopy of gases and condensed liquids released under isothermal conditions in a tubular furnace.

RESULTS AND DISCUSSION

Characterization of Cu(nic)$_2$ and Cu(isonic)$_2 \cdot 4H_2O$

Banerjee and Ray [18] have reported X-ray diffraction data on copper isonicotinate and mention also copper nicotinate; these substances are reported to be isostructural with analogous Ag(II) salts. Although the

TABLE 1

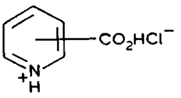
X-ray diffraction data

Cu(isonic)$_2$[a]			Cu(isonic)$_2$·4H$_2$O			Cu(isonic)$_2$		
2θ(°)	d (Å)	VI[b]	2θ	d (Å)	VI[b]	2θ (°)	d (Å)	VI[b]
10.9	8.10	vs	10.2	8.66	w	10.8	8.18	s
14.3	6.17	w	13.9	6.36	w	14.1	6.28	w
19.5	4.55	m	15.5	5.71	vs	15.6	5.67	vs
22.1	4.02	s	16.7	5.30	vw	18.3	4.84	vw
23.8	3.74	m	18.6	4.76	m	19.0	4.67	w
25.8	3.45	w	19.5	4.55	m	19.6	4.52	vw
27.8	3.21	w	20.5	4.33	m	21.0	4.23	w
29.2	3.05	w	21.6	4.11	m	21.7	4.09	m
30.4	2.94	w	23.1	3.85	m	22.8	3.90	m
32.7	2.74	w	24.7	3.60	vw	23.5	3.78	w
33.8	2.65	w	25.7	3.46	vw	26.8	3.32	s
37.8	2.37	w	26.7	3.33	s	27.5	3.24	m
40.4	2.23	w	27.4	3.25	m	28.3	3.15	m
42.7	2.11	m	28.2	3.16	m	30.3	2.95	w
45.0	2.01	w	30.1	2.97	vw	31.8	2.81	w
47.9	1.90	w	32.3	2.77	w	32.8	2.73	w
49.0	1.86	w	34.4	2.60	w	34.5	2.60	w
53.3	1.72	w	37.0	2.43	w	37.0	2.43	w
			38.7	2.32	vw	39.9	2.26	m
			39.8	2.26	s	41.8	2.16	w
			42.5	2.10	vw	44.2	2.05	vw
			43.7	2.06	vw	46.9	1.94	vw
			44.6	2.03	vw	48.6	1.87	vw
			46.0	1.97	vw	53.2	1.71	vw

[a] from ref. 18.

[b] Visual intensities: vs very strong, s strong, m medium, w weak, vw very weak.

preparative procedure for copper salts is not given, it may be inferred that these authors prepared complexes in which Cu(II) is bound to nitrogen, at variance with the usual behaviour of copper(II) as reported by Paris et al. [19]. These authors demonstrate binding to carboxylate in Cu(nic)$_2$ and Cu(isonic)$_2$ through the different behaviour of ring vibrations in these compounds as opposed to



Cu(isonic)$_2$ · 4H$_2$O as prepared by us exhibits an X-ray diffraction pattern (data collected in Table 1) very different to that reported in ref. 18; IR spectral data show good agreement with values given in ref. 19 and indicate the presence of bands assigned to carboxylate ν asym and ν sym at 1604–1545 and 1420–1380 cm^{-1} that are indicative of a salt-like behaviour where the interaction between Cu(II) and the anions is essentially electrostatic.

THERMOGRAVIMETRIC BEHAVIOUR

Thermograms of both salts are shown in Fig. 1. In the lower temperature range, $Cu(isonic)_2 \cdot 4H_2O$ shows an endothermic dehydration at 146 °C and an exothermic transition at 200 °C without weight change, features that are not present in the thermogram of $Cu(nic)_2$. These features are discussed first.

Dehydration weight loss of $Cu(isonic)_2 \cdot 4H_2O$ indicates that the starting material is a tetrahydrate; X-ray examination of the resulting material shows that a new crystalline phase is formed (anhydrous $Cu(isonic)_2$); the exothermic transition is not accompanied by structural changes evidenced by

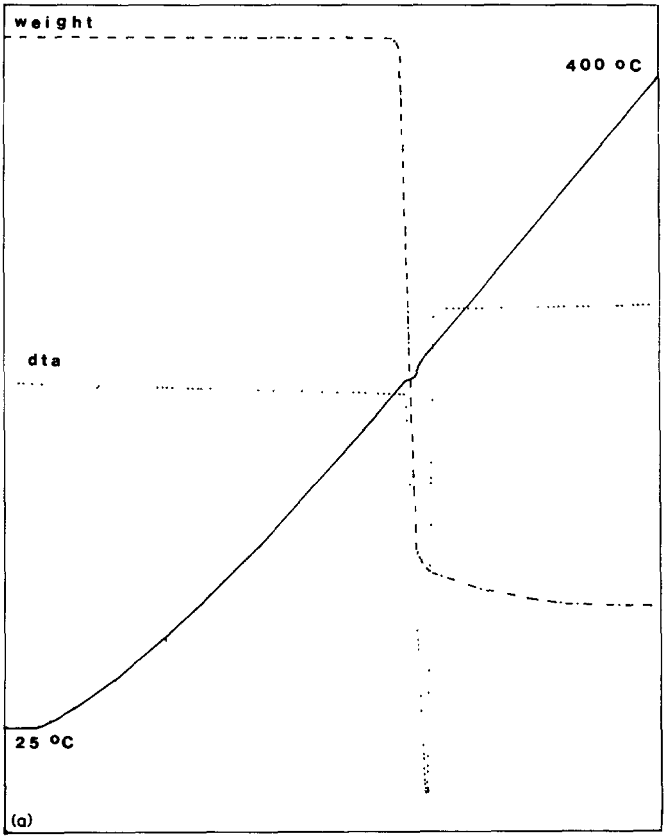


Fig. 1. TGA (·—·—·) and DTA (······) curves for (a) $Cu(nic)_2$ and (b) $Cu(isonic)_2 \cdot 4H_2O$. Linear heating is also shown (———).

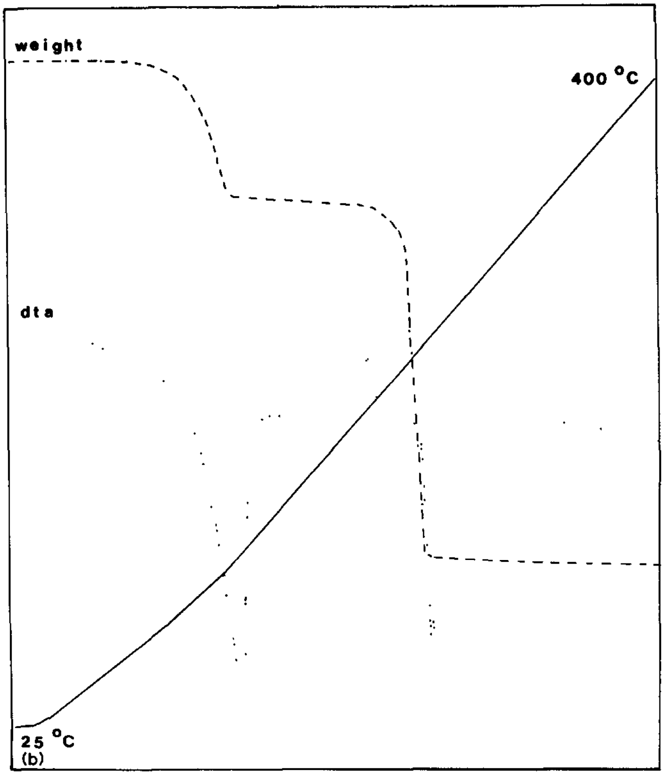


Fig. 1 (continued).

spacing and/or sharpness of the diffraction lines. The diffraction data for anhydrous Cu(isonic)$_2$ are included in Table 1.

At ~278 and 280 °C a fast weight loss is observed in Cu(nic)$_2$ and Cu(isonic)$_2$, respectively. The overall weight loss is in agreement with the stoichiometry

$$5\ \mathrm{Cu(NC_5H_4CO_2)_2(s)} \rightarrow 5\ \mathrm{Cu(s)} + 10\ \mathrm{CO_2(g)} + 8\ \mathrm{NC_5H_5(g)} + \mathrm{N_2(g)} + 10\ \mathrm{C(s)} \qquad (1)$$

Carbon dioxide was detected as the main gaseous product through the formation of $BaCO_3$ upon bubbling the released gases in aqueous $Ba(OH)_2$, and this was confirmed by IR spectroscopy of the evolved gases. Pyridine is also formed and partially condenses; it can be identified both in the gas and condensed liquid through IR spectra.

A small amount of nicotinic acid was isolated in some isothermal experiments; we can offer no explanation for this product, but its formation requires the presence of moisture or some other proton-containing substance (its formation has been observed by us during the thermolysis of iron(III) nicotinates, and attributed to the presence of OH^- and/or H_2O [20]).

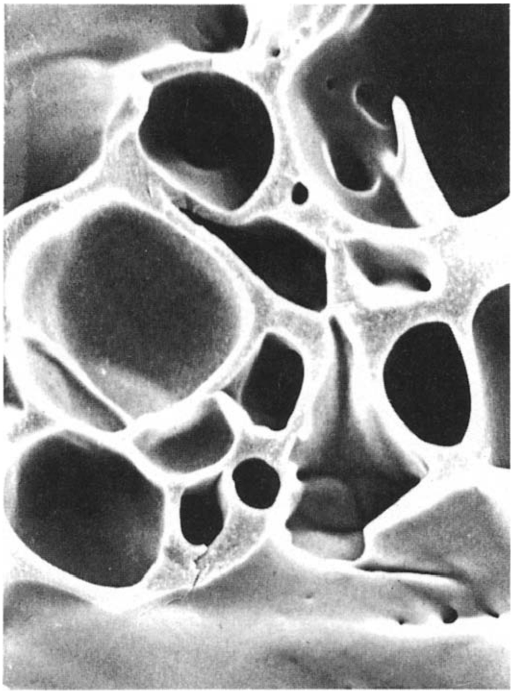


Fig. 2. SEM picture of the pyrolysis (400 ° C) product of $Cu(nic)_2$.

In order to explore the possibility that melting might trigger decomposition several isothermal experiments were performed at different temperatures below 278 and 280 ° C, respectively. The solids decompose over a rather wide temperature range (obviously at varying rates), and thus melting prior to decomposition is not substantiated by the data. On the other hand, the morphology of the copper residue (see Fig. 2) indicates that melting and/or volatilization may be involved, giving rise to appreciable migration of copper atoms. Similar results have been reported for copper(II) formate [5] and acetate [6–8] where intervention by volatile copper(I) alkanoates has been proposed. *

In our case, there is no evidence in favour of or against the possible intermediate formation of fleeting copper(I) species. In any case the reaction clearly starts through electron transfer from nicotinate to copper(II)

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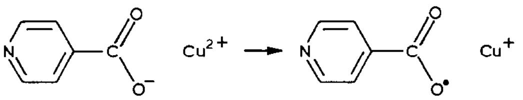
* Note added in proof: After completion of this paper, our attention was directed to two papers by N.J. Carr and A.K. Galwey (J. Chem. Soc., Faraday Trans. 1, 84 (1988) 1357 and Proc. R. Soc. London, Ser. A, 404 (1986) 101) which contain a thorough analysis of the isothermal decomposition of three copper(II) carboxylates which demonstrates the intervention of copper (I) salts.



(2)

This picture is of course equivalent to the homolitic breakage of the covalent bond RCOO–Cu, and corresponds to the transfer of the electron from an orbital essentially centered on oxygen to a metal-centered level. Re-examination of the thermolysis of copper(II) tartrate [13,14] has also shown that no oxide phases are formed, i.e. bond-breaking again takes place homolytically between copper and oxygen, rather than within the organic anion. It seems clear by now that all the well-documented cases of thermolysis of copper(II) carboxylate proceed directly to yield Cu(0), CO_2 and other decomposition fragments of the organic moiety in a process governed by the existence of easily accessible levels in copper(II) which can receive the electron.

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