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THERMAL DECOMPOSITION OF SOME N-OXIDE COMPLEXES OF COBALT(II), NICKEL(II) AND COPPER(II) CARBOXYLATES

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Thermal decomposition of mono pyridine N-oxide complexes of cobalt(II), nickel(II) and copper(II) propionates and mono quinoline N-oxide complex of copper(II) benzoate has been studied by TG and DTA techniques. These dimeric complexes are stable upto 350–380 K and decompose in two stages: (i) successive elimination of the two ligand molecules (mostly endothermic); and (ii) decomposition of the resulting anhydrous metal(II) carboxylates by an exothermic multistep process in air.

Thermal studies of hydrated metal(II) carboxylates have been quite interesting [1–9]. The reactions have been followed to study their kinetics [1–3, 6, 9] or the mechanism of decomposition [4, 5, 7]. However, the addition complexes of metal(II) carboxylates with amines and amine N-oxides have not been adequately studied [10–12]. The present communication deals with the thermal decomposition of mono pyridine N-oxide complexes of cobalt(II), nickel(II) and copper(II) propionates and mono quinoline N-oxide complex of copper(II) benzoate by TG and DTA techniques in static air atmosphere.

Experimental

The required metal(II) carboxylate complexes were prepared by mixing acetone or methanol solution of the appropriate metal(II) carboxylate and the corresponding ligand in 1 : 1.1 molar ratio and subsequent crystallisation. The samples obtained were crystalline products which gave satisfactory analytical results. The Stanton Thermobalance (Model No. AD-2) was used and heating rate of 4°/min was maintained. The amount of the samples taken varied from 250–450 mg. The differential thermal analysis curves were recorded on DTA-02-Universal apparatus at the same heating rate using alumina as a reference standard. As much identical conditions as possible were used. The nature of thermolysis curves was, however, independent of the mass of the samples used. The results of TG and DTA studies are presented in Figs 1 and 2.

Results and discussion

An examination of the TG curve (Fig. 1) of bis(propionato)pyridine-N-oxide-cobalt(II) indicates that the complex is stable upto ~ 350 K and beyond this

Table 1

Starting complex	Intermediates/Product proposed	Temperature, K	Weight loss, %	
			found	theoretical
$[Co_2(O_2CC_2H_5)_4(PyNO)_2]$	$[Co_2(O_2CC_2H_5)_4(PyNO)]$	400	14.84	15.83
	$[Co_2(O_2CC_2H_5)_4]$	450	30.86	31.67
	Co_3O_4	575	73.43	73.24
$[Ni_2(O_2CC_2H_5)_4(PyNO)_2]$	$[Ni_2(O_2CC_2H_5)_4(PyNO)]$	405	15.25	15.85
	$[Ni_2(O_2CC_2H_5)_4]$	435	30.71	31.70
	NiO	585	75.21	75.07
$[Cu_2(O_2CC_2H_5)_4(PyNO)_2]$	$[Cu_2(O_2CC_2H_5)_4(PyNO)]$	400	15.41	15.60
	$[Cu_2(O_2CC_2H_5)_4]$	435	31.47	31.20
	CuO	555	73.81	73.88
$[Cu_2(O_2CC_6H_5)_4(QNO)_2]$	$[Cu_2(O_2CC_6H_5)_4(QNO)]$	475	16.49	16.09
	$[Cu_2(O_2CC_6H_5)_4]$	525	32.43	32.18
	$CuCO_3$	700	72.97	72.58
	CuO	790	82.43	82.35

PyNO = Pyridine N-oxide
QNO = Quinoline N-oxide

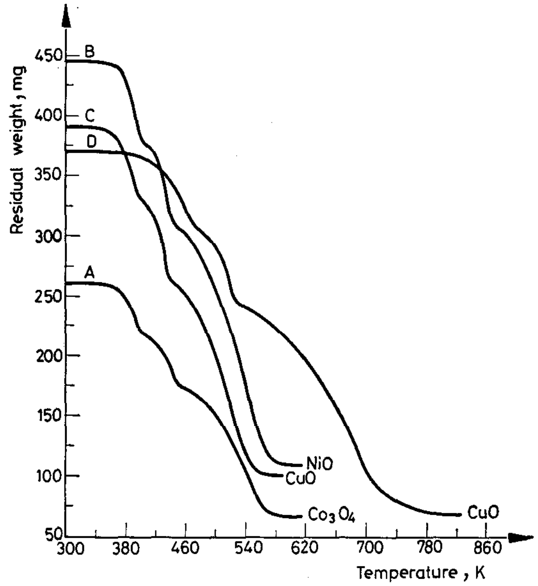

Fig. 1. TG curves of A: Bis(propionato)pyridine-N-oxidecobalt(II), B: Bis(propionato)pyridine-N-oxidenickel(II), C: Bis(propionato)pyridine-N-oxidecopper(II) and D: Bis(benzoato)quinoline-N-oxidecopper(II)

temperature decomposes without the formation of any stable, isolable intermediate giving Co_3O_4 as the final product at 575 K. However, the TG curve does show two discontinuities at 400 and 450 K corresponding to the formation of intermediate species $[Co_2(O_2CC_2H_5)_4(PyNO)]$ and $[Co_2(O_2CC_2H_5)_4]$ (Table 1) respectively.

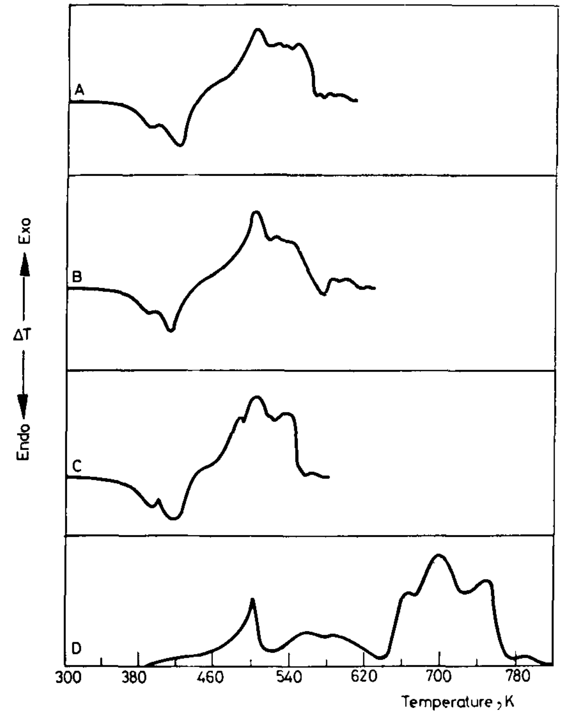

Fig. 2. DTA curves of A: Bis(propionato)pyridine-N-oxidecobalt(II), B: Bis(propionato)pyridine-N-oxidenickel(II), C: Bis(propionato)pyridine-N-oxidecopper(II) and D: Bis(benzoato)quinoline-N-oxidecopper(II)

Bis(propionato)cobalt(II) and its hemipyridine N-oxide complex could not be isolated because these start decomposing even before they are completely formed. The decomposition of bis(propionato)pyridine-N-oxide cobalt(II) may be represented schematically as below:

$$[Co_2(O_2CC_2H_5)_4(PyNO)_2] \xrightarrow{350-400K} [Co_2(O_2CC_2H_5)_4(PyNO)] \quad (1)$$

$$[Co_2(O_2CC_2H_5)_4(PyNO)] \xrightarrow{400-450K} [Co_2(O_2CC_2H_5)_4] \quad (2)$$

$$[Co_2(O_2CC_2H_5)_4] \xrightarrow{450-575K} Co_3O_4 + \text{Volatile products} \quad (3)$$

The DTA curve (Fig. 2) of this complex shows a broad endothermic band, split into two peaks centred at 390 and 420 K corresponding to the decomposition reactions represented by the Eqs (1) and (2) respectively. Strong exothermic peaks at 495,520 and 545 K then account for the decomposition of bis(propionato)-cobalt(II) (Eq. 3) and indicate that the decomposition of bis(propionato)-cobalt(II) to Co_3O_4 is a multistep process. The thermogravimetric curves (Fig. 1) of bis(propionato)pyridine-N-oxide nickel(II) and bis(propionato)pyridine-N-oxide copper(II) are comparable to that of bis(propionato)pyridine-N-oxide-cobalt(II), suggesting thereby that the thermal decomposition of these complexes also proceeds in a similar manner. The intermediates and the end products involved in each case are shown in Table 1 along with their weight-loss data. The DTA curve (Fig. 2) of nickel(II) complex shows two endotherms at 390 and 410 K and three exotherms at 500, 525 and 540 K. The DTA curve (Fig. 2) of copper(II) complex also shows a similar structure constituting of two endotherms at 390 and 415 K and three main exotherms at 490, 510 and 535 K. The close similarity of the DTA curves of the cobalt(II), nickel(II) and copper(II) propionate-pyridine N-oxide complexes further points out that the general mode of decomposition of these complexes is identical with one another.

The thermogravimetric curve (Fig. 1) of bis(benzoato) quinoline-N-oxide-copper(II) shows three discontinuities at 475, 525 and 700 K and final constant weight level at 790 K. Weight-loss data (Table 1) indicate that the intermediate species formed at these temperatures are $[Cu_2(O_2CC_6H_5)_4(QNO)]$, $[Cu_2(O_2CC_6H_5)_4]$ and $CuCO_3$ and the final product is CuO. The intermediates are too unstable to be isolated.

The DTA curve (Fig. 2) of bis(benzoato) quinoline-N-oxide copper(II) shows a strong exotherm at 500 K with a broad shoulder in the range 425 – 475 K. These exothermic structures correspond to QNO elimination reactions. It is notable that the thermal elimination of PyNO molecules from metal(II) propionate complexes discussed above is an endothermic process, whereas in the present case, the corresponding step is, on the contrary, exothermic. The remaining DTA curve shows two broad, highly complex exotherms observed in the regions 545 – 600 and 650 – 775 K. It is difficult to consider all the intermediate species produced because the decomposition process is in itself the result of many complicated factors.

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References

1. T. A. Clarke and J. M. Thomas, J. Chem. Soc., A, (1969) 2227, 2230.
2. T. R. Bhat, B. S. Mathur and J. Shankar, Ind. J. Chem., 8 (1970) 275.
3. D. Dollimore and D. Tinsley, J. Chem. Soc., A, (1971) 3043; and earlier papers.
4. L. Tournayan, H. Charcosset, B. R. Wheeler, J. M. McGinn and A. K. Galwey, J. Chem. Soc., A, (1971) 868; and earlier papers.

5. R. A. Hites and K. Biemann, J. Am. Chem. Soc., 94 (1972) 5772.
6. L. Walter-Levy, J. Perrotey and J. W. Visser, Compt. Rend. Acad. Sci., Ser. C, 277 (1973) 1351; Chem. Abstr., 80 (1974) 152317y.
7. K. Nagase, K. Muraishi, K. Sone and N. Tanaka, Bull. Chem. Soc. Japan, 48 (1975) 3184; and earlier papers.
8. M. D. Judd, B. A. Plunkett and M. I. Pope, J. Thermal Anal., 9 (1976) 83.
9. M. D. Karkhanavala and S. R. Dharwadkar, Ind. J. Chem., 7 (1969) 729.
10. C. A. Agambar and K. G. Orrell, J. Chem. Soc., A, (1969) 897.
11. S. Amasa, D. H. Brown and D. W. A. Sharp, J. Chem. Soc., A, (1969) 2892.
12. M. M. Borel, A. Busnot and A. Leclaire, J. Inorg. Nucl. Chem., 38 (1976) 235.

Résumé — On a étudié, par TG et ATD, la décomposition thermique des propionates des complexes mono-pyridine N-oxyde de cobalt(II), de nickel(II) et de cuivre(II) ainsi que du benzoate mono-quinoline N-oxyde de cuivre(II). Ces complexes dimères sont stables jusqu'à 350—380 K et se décomposent en deux étapes: (i) élimination successive des deux molécules-ligands (la plupart du temps endothermique); et (ii) décomposition des carboxylates anhydres des métaux(II) formés par un processus en plusieurs étapes dans de l'air.

Zusammenfassung — Die thermische Zersetzung der Monopyridin N-oxidkomplexe der Kobalt(II)-, Nickel(II) und Kupfer(II)-propionate sowie des Monochinolin N-oxidkomplexes von Kupfer(II)-benzoat wurden durch TG und DTA-Methoden untersucht. Diese dimeren Komplexe sind bis zu 350—380 K stabil und werden in zwei Stufen zersetzt: (i) sukzessive Eliminierung der zwei Ligandmoleküle (hauptsächlich endotherm); und (ii) Zersetzung der entstehenden wasserfreien Metall(II)carboxylate durch einen mehrstufigen exothermen Vorgang in Luft.

Резюме — Методами ТГ и ДТА было изучено термическое разложение моно пиридин-N-оксидных комплексов пропионатов кобальта (II), никеля (II) и меди (II), а также моно хинолин-N-оксидного комплекса бензоата меди (II). Эти димерные комплексы стабильны до температур 350—380 К и в дальнейшем разлагаются в две стадии: (1) последовательное выделение двух молекул лиганда и этот процесс большей частью эндотермический и (2) разложение образующихся безводных карбоксилатов металлов по экзотермическому многостадийному процессу в атмосфере воздуха.