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The thermogravimetric analysis of copper alkanoate–pyridine complexes

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Abstract

Two crystalline products derived from solutions of copper(II) dodecanoate in pyridine were shown by thermogravimetric analysis to be pure forms of pyridine–copper(II) dodecanoate complexes of molar ratios 1:1 and 2:1. Similar complexes form with the octadecanoate. Such complex formation and subsequent removal of pyridine could serve as a means of purifying the carboxylates.

INTRODUCTION

In the course of studies of the thermal behaviour of long chain metal alkanoates in the presence of a second component, the interaction of copper(II) dodecanoate and copper(II) octadecanoate with pyridine was investigated.

Koenig [1] attempted to prepare the pyridine adducts of metal hexadecanoates and octadecanoates and qualitatively studied their solubility in a number of solvents, and Malik and Ahmad [2] attributed the lack of a critical solution temperature for chromium hexadecanoate and octadecanoate in pyridine to complex formation. Gilmour and Pink [3] studied the magnetic properties of monopyridine–copper(II) dodecanoate ($(C_{11}H_{23}COO)_2Cu \cdot C_5H_5N$) but failed to isolate the dipyridine complex ($(C_{11}H_{23}COO)_2Cu \cdot 2C_5H_5N$). Satake and Matuura [4] have reported X-ray diffraction, infrared and magnetic studies of both mono- and dipyridine complexes of copper(II) octadecanoate, and more recently Pardeshi et al. [5] have described the magnetic and electronic spectral properties and relatively large-scale non-isothermal decomposition of

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monopyridine–copper(II) hexadecanoate and octadecanoate complexes. In 1987, Szpakowska et al. [6] reported thermogravimetric investigations of complexes of copper(II) ethanoate and pyridine derivatives, relating pK_a values of the base ligand to thermal stability.

In this study, two brightly coloured complexes of both copper(II) dodecanoate and copper(II) octadecanoate with pyridine were isolated in pure form, and their thermogravimetric analysis is reported here. Similar adducts with piperidine have been investigated also.

EXPERIMENTAL

Preparations

Copper(II) dodecanoate was prepared by mixing filtered, hot, ethanolic copper(II) ethanoate (1% w/v) and dodecanoic acid (2.5% w/v) solutions. The resulting precipitate was washed with water, ethanol and acetone and dried first in air then in vacuo at 353 K over P_4O_{10}. Analysis: Cu found (by EDTA volumetric analysis) 13.69%; theory 13.75%; C found 63.02%; theory 62.37%; H found 10.10%; theory 10.03%.

Copper(II) octadecanoate was similarly prepared using octadecanoic acid and was found to be of similar percentage purity.

Dried copper(II) dodecanoate (0.4 g) was dissolved in dry pyridine (8 cm^3) at 333 K. A royal blue crystalline product (designated W) which formed on cooling to 273 K was filtered off, dried between filter paper and stored at 273 K. A similar preparation (but using 0.04 g and 8 cm^3) was carried out with copper(II) octadecanoate, but the royal blue product, after filtration, was air dried at room temperature for 24 h (sample Y). A quantity of W was air dried at room temperature, whereupon it slowly turned to a green solid. This was freeze dried for 3 h, giving sample X.

A green product (Z) was also crystallised, at 273 K, from copper(II) octadecanoate (0.4 g) and dry pyridine (8 cm^3). A similar product was produced by prolonged freeze drying of sample Y.

Thermogravimetry

For the mass loss determinations, a Stanton Redcroft TG750 thermobalance was used. Amounts of 1–2.5 mg of sample were contained in Pt crucibles over which "white spot" N_2, dried with molecular sieves, was passed at 25 cm^3 min^{-1}.

RESULTS

Composition of complexes

In Fig. 1(I) are shown the differential thermogravimetry traces for pure copper(II) dodecanoate (curve a) and the pyridine complexes, namely

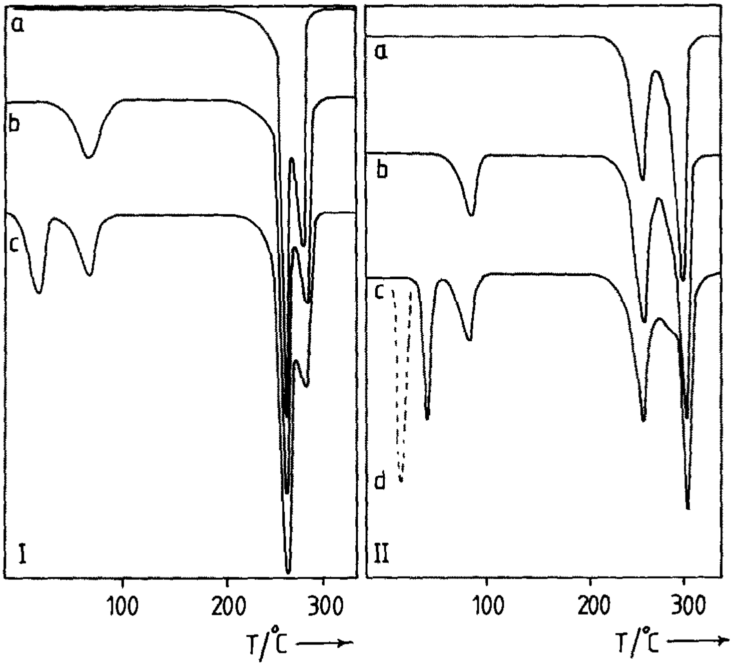

Fig. 1. Differential thermogravimetric analysis of (I) curve a, copper(II) dodecanoate; curve b, solid X; curve c, solid W; (II) curve a, copper(II) octadecanoate; curve b, solid Z; curve c, solid Y; curve d, unbound pyridine.

(curve b) green solid X and (curve c) blue solid W. The corresponding traces for copper(II) octadecanoate are shown in Fig. 1(II). An extra peak (curve d) was observed when the blue solid was insufficiently dried, and this corresponds to the liberation of excess uncomplexed pyridine.

The results of the analysis of these traces (on the assumption that the low temperature peaks are due to pyridine and the high temperature peaks to copper(II) alkanoate decomposition) are shown in Table 1. These confirm that the blue solids (W and Y) are 2:1 molar complexes of pyridine and copper(II) alkanoate and the green solids (X and Z) are 1:1 complexes. It is concluded that the pyridine can complex to these long chain Cu(II) complexes in at least two different ways and that the pyridine–alkanoate bond strength changes as transition from the blue to the green complex takes place.

Similar crystalline products have been obtained from the interaction between copper(II) alkanoates and piperidine. Copper(II) dodecanoate, for example, forms a royal blue crystalline solid which slowly converts to a green product, apparently through a violet intermediate. The corresponding royal blue octadecanoate complex is more stable, conversion occurring extremely slowly even under reduced pressure. However, the peaks in the thermogravimetry traces obtained with these solids were not as well

TABLE 1

Analysis of thermograms for copper(II) alkanoate–pyridine complexes

Solid	Molar ratio [a] pyridine–alkanoate		
	310 K peak	*348 K peak*	*Overall*
W	1.01	0.98	1.99:1
X	–	1.03	1.03:1
	324 K peak	*357 K peak*	*Overall*
Y	1.02	1.02	2.04:1
Z	–	1.00	1.00:1

[a] (Mass loss of low temperature peak/relative molar mass of pyridine)/(Mass loss of high temperature peak/relative molar mass of alkanoate).

resolved as they were for the pyridine complexes, thus preventing accurate analysis and any confident statement about their stoichiometry.

Kinetics of decomposition

Pardeshi et al. [5] reported that, in almost all cases, the order of the depyridinisation reaction of the complexes they studied was nearly zero. They also quoted values for the activation energy of this reaction involving the 2:1 pyridine–copper octadecanoate complex of 7.241 kcal mol^{-1} (30.4 kJ mol^{-1}) for the first pyridine loss and 7.760 kcal mol^{-1} (32.6 kJ mol^{-1}) for the second stage. These values were deduced from an application of the Freeman and Carroll [7] procedure. Analysis of the data reported in this present paper by the same procedure gave orders again less than 0.5 and activation energies of 37 and 162 kJ mol^{-1} for the first and second stages respectively.

An alternative method of kinetic analysis, and one preferred by some [8], is that due to Coats and Redfern [9]. The best correlation coefficients from linear regression analysis of data involved in this analysis favoured, in general, zero or first order decomposition kinetics for the two depyridinisation stages. It was not possible to distinguish between these two orders with any certainty. The activation energies obtained from this kinetic analysis of all the complexes studied were always similar when zero and first order kinetics were assumed. (The first order values were on average 15% higher.) When orders of 0.5 and 0.75 were tried the activation energies were always very much lower (typically 60% lower in the case of 0.5 order and 75% for first order).

For copper(II) octadecanoate the Coats and Redfern method gave activation energies of 61 and 168 kJ mol^{-1} for the first and second stages of pyridine loss.

CONCLUSIONS

Copper(II) alkanoates readily form complexes with pyridine which can be isolated as crystalline materials of molecular ratio 1:1 and 2:1 as pyridine–alkanoate. These complexes could be used as a means of purifying the alkanoates because the pyridine can be quantitatively removed at elevated temperatures.

Neither the Freeman and Carroll nor the Coats and Redfern method fully explains the kinetics of the loss of pyridine from these complexes, but the latter appears to be the more successful method.

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REFERENCES

1 A.E. Koenig, J. Am. Chem. Soc., 36 (1914) 951.
2 W.U. Malik and S.I. Ahmad, J. Am. Oil Chem. Soc., 42 (1965) 454.
3 A. Gilmour and R.C. Pink, J. Chem. Soc., (1953) 2198.
4 I. Satake and R. Matuura, Kolloid-Z., 176 (1961) 31.
5 L. Pardeshi, A. Rasheed and R.A. Bhobe, Rev. Roum. Chim., 23(8) (1978) 1291.
6 M. Szpakowska, I. Uruska and R. Teszner, J. Therm. Anal., 32 (1987) 717.
7 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
8 J.H. Sharp and S.A. Wentworth, Anal. Chem., 41 (1969) 2060.
9 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.