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THERMAL ANALYSIS OF COPPER DITHIOCARBAMATES

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ABSTRACT

Seven copper(II) dithiocarbamate complexes [$Cu(R_2Dtc)_2$: $R_2 = Me_2$, Et_2, nPr_2, nBu_2, $cycHex_2$, Et Ph, pyrrol and pip] have been prepared and examined by thermogravimetric analysis (TG). All the complexes show similar TG profiles whether heated in an atmosphere of air or nitrogen. Complete TG, DTA data are reported for copper diethyldithiocarbamate (air, nitrogen and vacuum atmospheres). Copper diethyldithiocarbamate is completely volatile (190–260°C) under vacuum (0.8τ), but in air and nitrogen only partial volatility is exhibited; thermal decomposition begins at 220°C and a residue of cuprous sulphide results at 350°C.

INTRODUCTION

Few investigations have been reported concerning the thermal properties of metal xanthate and dithiocarbamate complexes.

D'Ascenzo and Wendlandt[1] examined a number of metal diethyldithiocarbamates including the cobalt, copper, nickel, zinc and cadmium complexes. The same authors also reported $Fe(Et_2Dtc)_3$ as a new volatile metal chelate[2] and later showed that $Sn(Et_2Dtc)_2Cl_2$ was essentially non-volatile in character.

Bernard and Borel[4] studied the thermal properties of lead, zinc and cadmium dithiocarbamates $M(H_2Dtc)_2$ by TG and DTA, and claimed that lead dithiocarbamate decomposes to give carbon disulphide and ammonium thiocyanate.

Recently this laboratory reported the thermal properties of nickel and palladium xanthates[5,6]. The present paper reports the thermal properties of a series of copper dithiocarbamates, $Cu(R_2Dtc)_2$ where $R_2 = Me_2$; Et_2; nPr_2; nBu_2; $cycHex_2$; Et,Ph; pyrrol; pip.

EXPERIMENTAL

The copper dithiocarbamate complexes were prepared by adding an aqueous solution of AnalaR $CuCl_2 \cdot 6H_2O$ to an aqueous solution of excess ligand. The brown

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*Shell Chemical (Australia) Proprietary Limited, 155 William Street, Melbourne, Victoria 3000, Australia.

precipitate that formed was filtered, washed several times with water and dried in a vacuum desiccator over P_2O_5. The complexes were recrystallised from chloroform to give lustrous black crystals. Melting point and microanalysis data are given in Table 1.

TABLE 1

MELTING POINTS AND MICRO ANALYSIS DATA FOR $Cu(R_2Dtc)_2$ COMPLEXES

	M.p.	*Found*			*Calc.*		
		C	*H*	*S*	*C*	*H*	*S*
$Cu(Me_2Dtc)_2$	262	23.96	3.77	42.3	22.71	3.98	42.2
$Cu(Et_2Dtc)_2$	196	33.56	5.47	35.5	33.34	5.60	35.6
$Cu(npr_2Dtc)_2$	101	40.49	6.87	30.6	40.39	6.78	30.8
$Cu(nBu_2Dtc)_2$	57	45.42	7.61	27.3	45.76	7.68	27.2
$Cu(Et,Ph\ Dtc)_2$	205 dec	47.13	4.34	28.3	47.40	4.39	28.1
$Cu(pyrrolDtc)_2$	264 dec	33.82	4.32	36.1	33.73	4.53	36.0
Cu(pipDtc)	255 dec	37.28	4.96	33.2	37.52	5.24	33.4

The complexes showed varying degrees of volatility under reduced pressure (approx. 10^{-2} mm Hg), the most volatile being the diethyl and di-n-propyl complexes.

Microanalyses for C, H and S were carried out by the CSIRO Microanalytical Service, Melbourne University.

A Rigaku-Denki thermal analysis system was used to obtain the TG and DTA curves for the copper dithiocarbamates in air, nitrogen and under vacuum (0.8 mm Hg). Sample sizes ranged in mass from 5 to 10 mg and a furnace heating rate of 20 °C min^{-1} was used.

RESULTS AND DISCUSSION

All of the complexes were studied by thermogravimetric analysis from 0–800 °C in nitrogen. The main decomposition step for each complex is shown in Fig. 1. The thermograms and DTA profiles of $Cu(Et_2Dtc)_2$ in air, nitrogen and under vacuum are shown in Fig. 2. The thermograms obtained for most of the complexes were very similar in character, whether examined in air or nitrogen.

In general, decomposition begins between 175 and 245 °C followed by a rapid weight loss in which over 60% of the molecule is lost. No further change takes place in nitrogen (Fig. 2). In air the main decomposition step is followed by an increase in weight around 350 °C and a final weight loss occurs around 700 °C leaving a stable residue of CuO at 780 °C. $Cu(Et_2Dtc)_2$ was also heated under vacuum (0.8 mm Hg) over the range 0–800 °C. Initial weight-loss commenced at 185 °C and continued up to 290 °C resulting in a total loss of weight and an empty sample holder at 800 °C.

All thermograms show a rapid major weight-loss step in the temperature range 175–370 °C (Fig. 1), which represents the major thermal decomposition mode of all the copper dithiocarbamates. From the initial decomposition temperatures, it is apparent that the di-n-butyl and pyrrolidyl complexes are among the most stable within the series studied. A representative complex, Cu(Et$_2$Dtc)$_2$ was selected for detailed study.

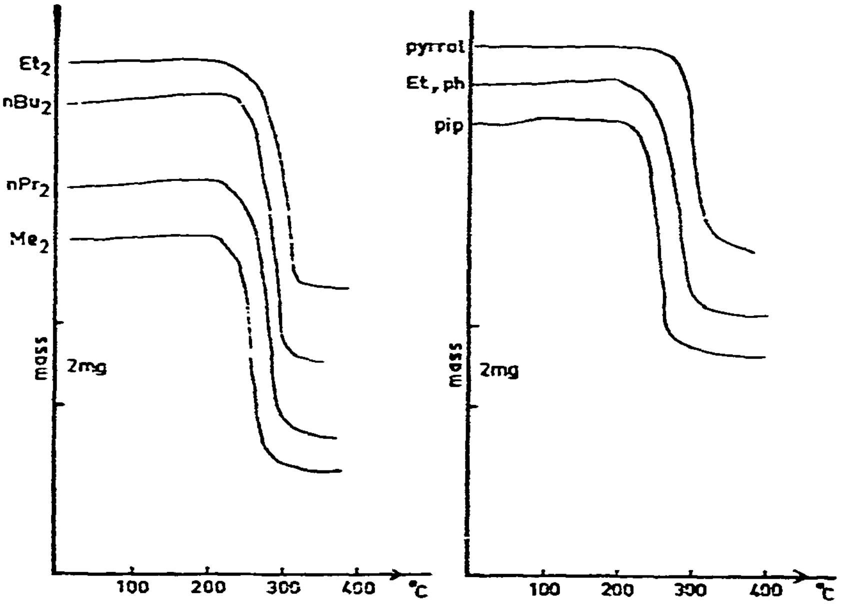

Fig. 1. Main decomposition step for copper dithiocarbamates.

THERMAL ANALYSIS OF Cu(Et$_2$Dtc)$_2$

A sample of Cu(Et$_2$Dtc)$_2$ (6.4 mg) was heated from ambient –800 °C in a vacuum of 0.8 mm Hg. The thermogram (Fig. 2) shows a weight-loss over the region 190–260 °C corresponding to complete sublimation of the complex. The DTA profile (Fig. 2) shows a sharp endothermic peak at 198 °C and a broad endothermic peak which has a maximum at 225 °C. The peak at 198 °C corresponds to the melting point of the complex and occurs in all of the DTA profiles for Cu(Et$_2$Dtc)$_2$. The broader peak at 225 °C is due to volatilisation of the sample in the range 190–260 °C leaving an empty sample container at 300 °C.

A sample of Cu(Et$_2$Dtc)$_2$ (8.9 mg) was heated in air from ambient 800 °C and analysed by TG and DTA. The thermogram (Fig. 2) shows an initial weight-loss from 200–320 °C of 6.6 mg. If it is presumed that cuprous sulphide, Cu$_2$S, was formed at the end of this step, the calculated weight-loss is 6.8 mg, showing close agreement with the experimental value. The residue at 350 °C was also analysed on sulphur content. The experimental value of 19.2% agrees with the theoretical value of 20.1% sulphur for Cu$_2$S. From 350–550 °C, the thermogram shows an increase in weight followed by a stable plateau and a corresponding decrease from 670–760 °C. The increase in weight is due to oxidation of Cu$_2$S to CuO and CuSO$_4$. According to Duval[7] the equation

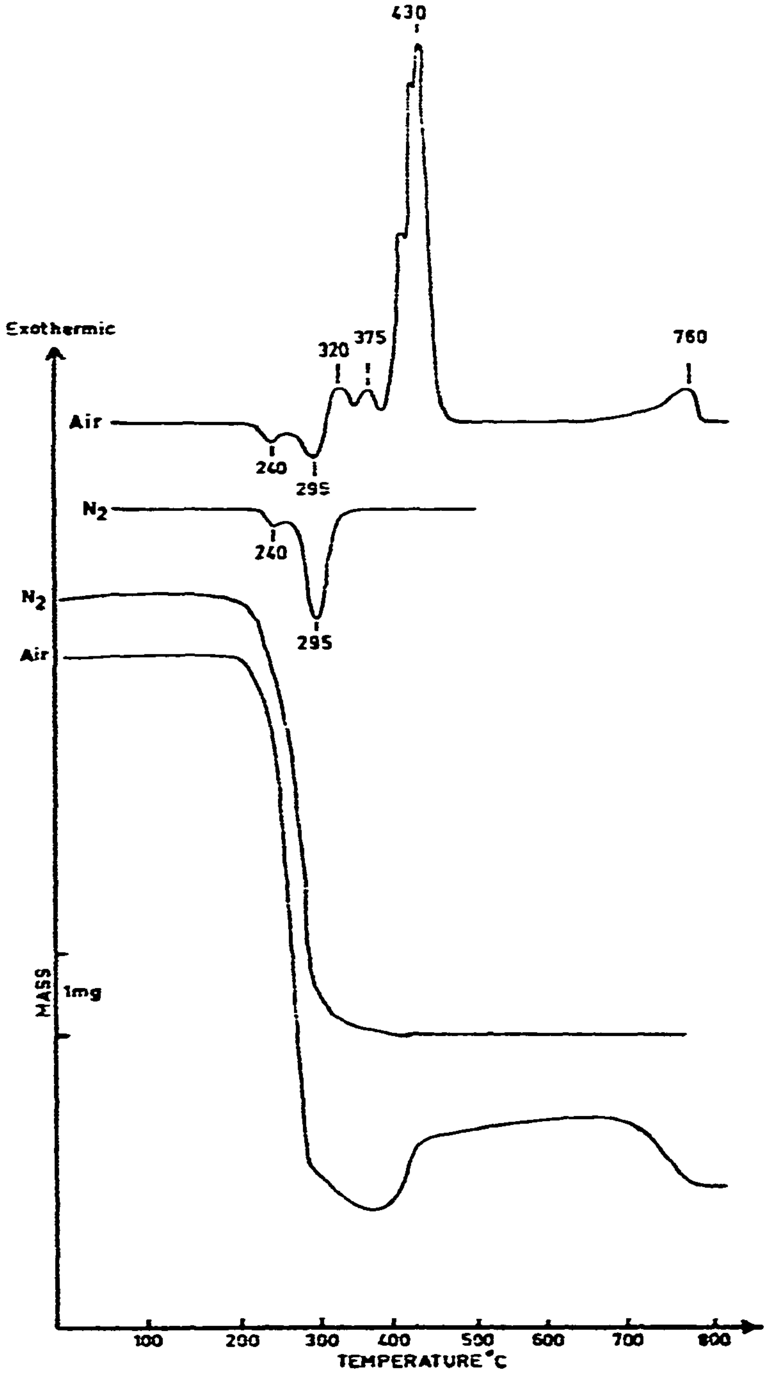

Fig. 2. TG and DTA curves for $Cu(Et_2Dtc)_2$.

for the reaction is

$$2Cu_2S + 5O_2 \rightarrow 2CuO + 2CuSO_4$$

The decrease in weight is due to decomposition of the sulphate,

$$CuSO_4 \rightarrow CuO + SO_3$$

leaving a final residue of CuO at 800°C. The residue at 800°C (2.1 mg) compared with a theoretical CuO residue of 2.0 mg.

The DTA profile for $Cu(Et_2Dtc)_2$ in air (Fig. 2) shows a sharp endothermic peak at 198°C corresponding to the melting point followed by a broad endothermic peak which has a maximum at 285°C. This may be assigned to the main decomposition, as it is also present in the DTA curve obtained in nitrogen. It is also interesting to note that the peak due to volatilisation at 255°C does not appear in the DTA curves obtained for air and nitrogen atmospheres. Thus if volatilisation occurs in air or nitrogen, it is only to a very small extent. Such results contradict some of the findings of D'Ascenzo and Wendlandt in an earlier report[1]. They found that for $Cu(Et_2Dtc)_2$ heated in a nitrogen atmosphere, complete volatilisation occurs and explained the corresponding exothermic DTA peak at 310°C, as being due to volatilisation of the sample. In the present work, it has been shown that complete volatilisation of $Cu(Et_2Dtc)_2$ only takes place under vacuum.

For the DTA curve in air (Fig. 2), three exothermic peaks occur at 332, 380 and 465°C, which appear to be due to the oxidation of the Cu_2S to CuO and $CuSO_4$ as the peaks are not present in the nitrogen DTA curve. The final endothermic peak at 140°C in air is due to the decomposition of $CuSO_4$ to CuO. The TG and DTA curves of $Cu(Et_2Dtc)_2$ in nitrogen (Fig. 2) were similar to those in air except that no oxidation of the Cu_2S takes place.

Attempts were made to determine the volatile organic decomposition products using a technique similar to that employed previously[5,6], however, the samples obtained were too contaminated to yield meaningful results.

From the results of the TG and DTA curves, the thermal properties of $Cu(Et_2Dtc)_2$ in different atmospheres can be summarised as:

(i) in air, the complex decomposes at around 220°C leaving a residue of Cu_2S at 350°C. The Cu_2S is oxidised to $CuSO_4$ and CuO from 360–550°C and the $CuSO_4$ is finally decomposed at around 700°C leaving a residue of CuO at 800°C;

(ii) in nitrogen, the complex decomposes around 220°C resulting in Cu_2S as residue at 350°C. No further change is apparent;

(iii) under vacuum (0.8 mm Hg), the complex volatilised completely in the range 190–260°C leaving an empty sample container at 300°C.

As all the copper dithiocarbamate complexes studied show similar TG curves in nitrogen, it appears that thermal decomposition mode of these complexes parallels that of copper diethyldithiocarbamate.

REFERENCES

1 G. D'Ascenzo and W. W. Wendlandt, *J. Thermal Anal.*, 1 (1969) 423.
2 G. D'Ascenzo and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, 32 (1970) 2431.
3 G. D'Ascenzo, V. Carunchio and A. Messina, *Thermochim. Acta*, 2 (1971) 211.
4 M. A. Bernard and M. M. Borel, *Bull. Soc. Chim. Fr.*, 9 (1969) 3066.
5 K. J. Cavell, C. G. Sceney, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 5 (1973) 319.
6 C. G. Sceney, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 6 (1973) 111.
7 C. Duval, *Inorganic Thermogravimetric Analysis*, Elsevier, Amsterdam, 2nd ed., 1963.