A TG/GC/MS STUDY OF COPPER DIMETHYL-
AND DIETHYLDITHIOCARBAMATES

C. G. Sceney*, J. F. Smith, J. O. Hill** and R. J. Magee

Departments of Physical & Inorganic and *Analytical Chemistry, La Trobe University,
Bundoora, Melbourne, VICTORIA 3083, Australia
Shell Chemical (Australia) Proprietary Limited, Melbourne, 3000, Australia.

The thermal decomposition products of copper dimethyldithiocarbamate and copper diethyldithiocarbamate have been semi-quantitatively analyzed by a combined gas chromatography — mass spectrometry technique and thermal decomposition mechanisms for both complexes are proposed. The fragmentation pathway is strongly influenced by the nature of the terminal alkyl group attached to the dithiocarbamate moiety.

Until recently few data have been reported relating to the thermal behaviour of metal xanthate and dithiocarbamate complexes.

D'Ascenzo and Wendlandt studied the thermal properties of several metal dialkyldithiocarbamates and noted that most were volatile [1−3]. Bernard and Borel [4] examined the thermal decomposition of some metal dithiocarbamates $M(H_2Dtc)_2$ and found that the decomposition products were carbon disulphide, and ammonium thiocyanate leaving the metal sulphide as residue. Recently we reported some thermal properties of nickel xanthates [5], palladium xanthates [6] and copper dithiocarbamates [7]. In the latter report no thermal decomposition mechanism was proposed because the volatile organic decomposition products could not be isolated and identified.

This paper reports a gas chromatography/mass spectrometry technique for identifying the volatile organic decomposition products of copper dithiocarbamate complexes and thermal decomposition mechanisms for $Cu(Me_2Dtc)_2$ and $Cu(Et_2Dtc)_2$ are proposed.

Experimental

The copper dithiocarbamates were prepared as reported previously [7]. The TG and DTA curves for $Cu(Me_2Dtc)_2$ and $Cu(Et_2Dtc)_2$ in air, nitrogen and under vacuum (0.8 mm Hg) were obtained using a Rigaku−Denki thermal analysis (Thermoflex) system. Sample mass ranged from 5 to 10 mg and a furnace heating rate of 20° per minute was used.

The volatile organic decomposition products were identified using a gas chromatography-mass spectrometry (GC-MS) technique developed in the Department

** To whom correspondence should be addressed.

of Physical Chemistry, La Trobe University [8]. A Pye 104 gas chromatograph
was interfaced with a 12 inch radius 60° magnetic sector mass spectrometer con-
structed by the Department of Physical Chemistry, La Trobe University [9].
The following technique was employed: a small crystal of the complex to be
studied (approx. 3 mg) was placed in a special oven sampler (Fig. 1) which
consists of a GC syringe needle cemented to a small glass tube. The sampler was
inserted into a tubular heater (24 volts, 50 watts approx.). The top of the sampler
was sealed with a modified swagelok union and rubber "O" ring which permits
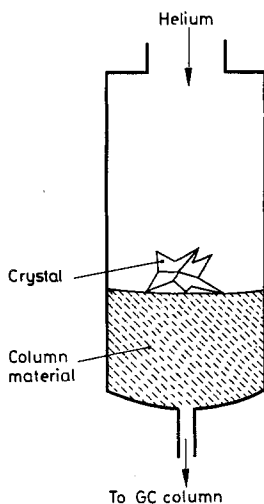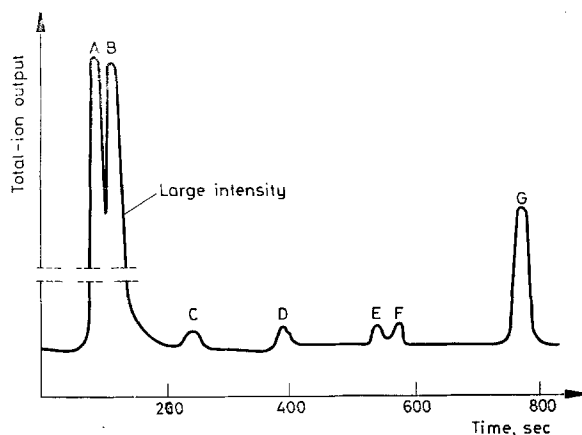

Fig. 1. Special oven sampler

Fig. 2. Total-ion monitor output obtained for the thermal decomposition of copper diethyl
dithiocarbamate

an appropriate valve system to divert carrier gas (helium) through the sampler. The needle of the sampler was injected into the GC column septum immediately before heating. A small amount of column packing material was placed at the
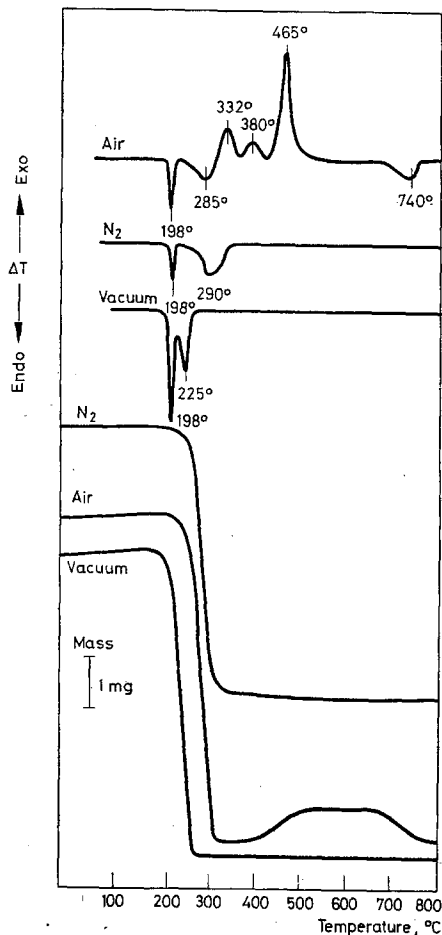

Fig. 3. TG and DTA profiles for copper diethyldithiocarbamate

bottom of the tube to prevent solid residue from entering the GC column. With carrier gas flowing over the sample, the oven sampler was heated for a suitable period depending on the temperature required. For both complexes the samples were heated for 30 seconds which resulted in a maximum decomposition temperature of approximately 300°. The evolved volatile products from the thermal decomposition of the complex were flushed onto the GC column which was maintained at 60°. After completion of the heating period, the sample was flushed with

carrier gas for a further minute. The carrier gas was then diverted back to its normal path through the GC column and the GC oven program commenced (oven heat from 60° to 200° at 4°/minute; flow of helium was 12 cm³/minute). The eluted compounds were suitably recorded on a chart recorder. The resulting chromatogram shows the separation of the individual components (Fig. 2). During elution of the compounds, the mass spectrometer was scanned repetitively at a rate of one scan every five seconds. The output of the mass spectrometer is interfaced to a computer which records the individual mass spectra together with tape storage. After the run is completed, the computer recovers the stored data and prints the mass spectra. In a typical analysis over a period of 800 seconds, 160 mass spectra were run.

Results and discussion

Copper diethyldithiocarbamate

The TG and DTA curves for $Cu(Et_2Dtc)_2$ in air, nitrogen and under vacuum (0.8 mm Hg) are shown in Fig. 3. As reported previously [7] the complex is completely volatile under vacuum but decomposes in air and nitrogen at approximately 220° leaving a residue of Cu_2S at 350°. To determine the thermal decomposition mode of the complex it was necessary to firstly separate and then identify the volatile organic decomposition products. This proved difficult by normal techniques [7] but using the present GC/MS technique the individual decomposition products were readily separated as shown in Fig. 2.

A comparison of reference mass spectra given by Cornu and Massot [10] with those obtained for the major peaks at *A* and *B*, identified them as carbon disulphide and diethylamine respectively. In peak *B* there were also traces of carbon disulphide and chloroform. The carbon disulphide is a result of tailing from peak *A* and the chloroform is believed to be solvent of crystallisation as the complexes were recrystallised from chloroform. The compound at peak *G* (Fig. 2) occurs to a significant extent (the size of the peak indicates that it forms about 15% of the total products) and must be considered in the overall decomposition process. Although the mass spectrum is not listed in reference mass spectra literature, the structure of the compound can be deduced as tetraethylthiourea, (molar mass
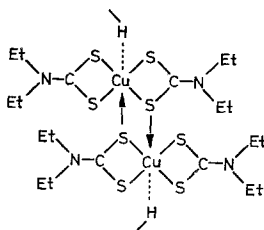

Fig. 4. Crystal structure of copper diethyldithiocarbamate

188 g mol^{-1}), $(C_2H_5)_2$ N.CS.N$(C_2H_5)_2$. The other four compounds (peaks $C, D.E$ and F) only occur in trace amounts and are not significant in the overall decomposition process. The compound at peak C was identified as ethyl isothiocyanate, $C_2H_5 - N = C = S$, according to Cornu and Massot [10]. The remaining three compounds do not appear in the literature and it is difficult to determine their structure unambiguously.
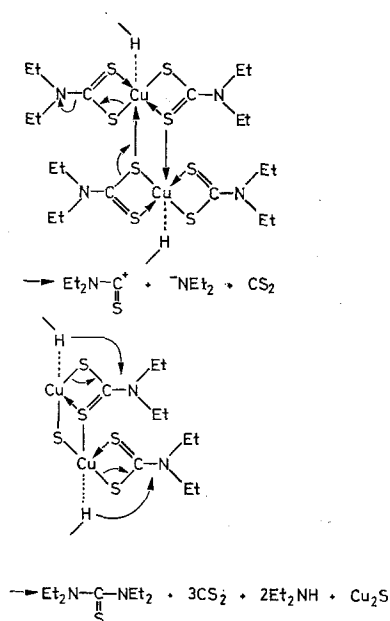

Fig. 5. Thermal decomposition mechanism, copper diethyldithiocarbamate

From the GC-MS results it appears that the major decomposition step involves breakdown of the complex to carbon disulphide, diethylamine and tetraethylthiourea with Cu_2S remaining as a solid residue. To account for these products, it is necessary to refer to the crystal structure of $Cu(Et_2Dtc)_2$. In 1965 Bonamico et al. [11], determined the crystal and molecular structure of $Cu(Et_2Dtc)_2$ and found it to exist as a dimer in the solid state (Fig. 4). Each copper atom has a distorted tetragonal-pyramidal coordination of four sulphur atoms at an average distance of 2.32 Å and a fifth apical sulphur atom at 2.85 Å. The sixth octahedral position is occupied by a hydrogen atom, from a neighbouring ethyl group, at a distance of 2.86 Å.

The thermal decomposition products may be explained if the dimeric molecule is considered to fragment in the manner shown schematically in Fig. 5. The final proposed products, tetraethylthiourea, carbon disulphide, diethylamine and cuprous sulphide agree with those indicated by mass spectrometric and thermo-

gravimetric analysis. In the decomposition process, the copper atom is reduced from an oxidation state of $+2$ to $+1$. This reduction is balanced by the gaining of two hydrogen atoms from adjacent ethyl groups. The other products that emerge in trace amounts, such as ethyl isothiocyanate and those represented by peaks
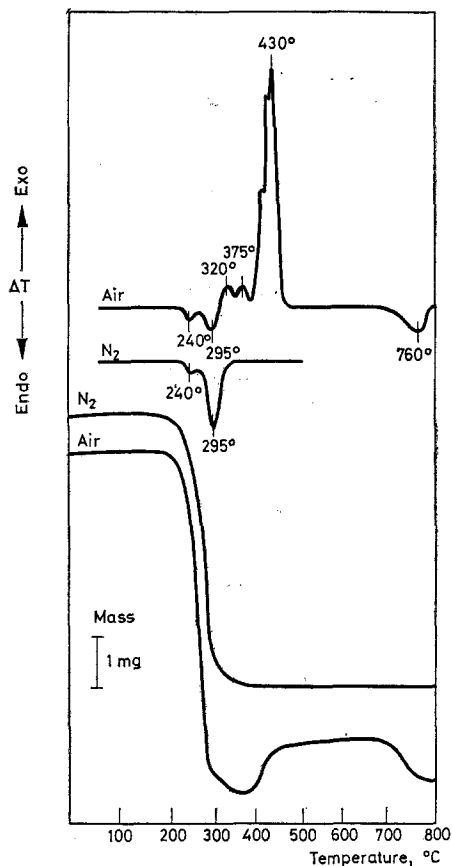

Fig. 6. TG and DTA profiles for copper dimethyldithiocarbamate

$D-F$ (Fig. 2), probably arise from minor decomposition processes, some of which are needed to account for the hydrogen atoms required in the main decomposition process. The compound at peak D contains chlorine and clearly arises from a minor reaction involving the small amount of chloroform trapped in the crystalline lattice. From the chromatogram obtained (Fig. 2), the CS_2 and Et_2NH peaks are of approximately similar area with some tailing of the CS_2 into the Et_2NH peak. The small peak area for tetraethylthiourea (about 15% of the total products), agrees with the decomposition process outlined in Fig. 5 which accounts for the production of three molecules of CS_2, two molecules of diethylamine, and one molecule of tetraethylthiourea.

Copper dimethyldithiocarbamate

$Cu(Me_2Dtc)_2$ was examined similarly to $Cu(Et_2Dtc)_2$. The TG and DTA profiles in air and nitrogen are shown in Fig. 6, and the total ion-monitor output for the thermal decomposition of $Cu(Me_2Dtc)_2$ is shown in Fig. 7. The DTA curves appear similar to those of $Cu(Et_2Dtc)_2$ although there is one major difference. The two endothermic peaks for $Cu(Et_2Dtc)_2$ at 198° and 285° are due to
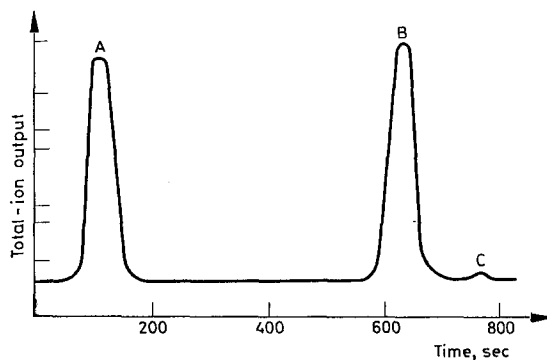

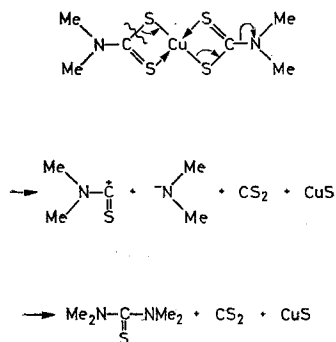Fig. 7. Total ion-monitor output obtained for the thermal decomposition of copper dimethyldithiocarbamate

Fig. 8. Thermal decomposition mechanism, copper dimethyldithiocarbamate

fusion and decomposition respectively. In the case of $Cu(Me_2Dtc)_2$ the two endothermic peaks at 240° and 295° are both due to decomposition as the complex decomposes without melting. The broadness of the peak at 240° also indicates decomposition as opposed to the characteristic sharpness of a melting point peak. The difference in decomposition peaks for the dimethyl and diethyl complexes indicates that a different initial decomposition process occurs. Other DTA peaks for $Cu(Me_2Dtc)$ in air occur at 320°, 375° and 430° (all exothermic) and 760°

(endothermic). These correspond to similar peaks for the diethyl complex and are due to oxidation of Cu_2S to CuO and $CuSO_4$, and final decomposition $CuSO_4$ to CuO.

The combined GC-MS analysis of the thermal decomposition of $Cu(Me_2Dtc)_2$ gave a total ion-monitor output as shown in Fig. 7. Peak A was identified as CS_2 but peak B was not listed in the literature. From mass spectrometric considerations however, the compound is most likely to be tetramethylthiourea — $(CH_3)_2N.CS.N(CH_3)_2$. Although there was no standard to compare the spectrum with, all of the main peaks could be explained by simple fragmentation of tetramethylthiourea. Mass spectral analysis of the volatile decomposition products indicates a different thermal decomposition process to that of the diethyl complex. To account for the products formed, the decomposition process shown in Fig. 8 is proposed. This is a relatively simple decomposition process and the molecule does not have to be considered in the dimeric form as was the case with the diethyl complex. From the total ion output (Fig. 7) it can also be seen that the amounts of CS_2 and tetramethylthiourea produced are approximately the same, which agrees with the decomposition process schematically represented in Fig. 8. It is interesting to note that the Cu atom is not reduced in this process, whereas it was for the diethyl complex. According to Duval [12], CuS loses sulphur from 195—300° and is reduced to Cu_2S. The decomposition process for $Cu(Me_2Dtc)_2$ occurs between 200—320°; consequently, as the CuS is formed, it is immediately reduced to Cu_2S. At the end of the decomposition step, the mass loss obtained corresponds to Cu_2S as the residue. The DTA curves show two peaks for the main decomposition process (Fig. 6). One of these is most probably due to the decomposition of the molecule and the other to reduction of CuS to Cu_2S.

Conclusion

The results reported in this paper show that although the TG curves are similar for the copper dithiocarbamates, the thermal decomposition process varies remarkably with a change in the terminal R-group attached to the dithiocarbamate moiety. For $Cu(Me_2Dtc)_2$ the process is relatively simple with CS_2 and tetramethylthiourea being produced as the main decomposition products but for $Cu(Et_2Dtc)_2$ the main products are CS_2 and diethylamine with tetraethylthiourea being formed as a minor product.

For some years, the dithiocarbamates of sodium, zinc, manganese, iron and copper have been known to exhibit antifungal activity [13]. Van der Kerk and Klopping [14] showed that the activity varies with a change in R-group. For the sodium dialkyldithiocarbamates, NaR_2Dtc, the largest anti-fungal activity occurs when R = Me and Et, with the dimethyl salt more potent than the diethyl. Many theories have been advanced for the mode of fungicidal action of the dithiocarbamates [13] and at present the correct mode of action is unknown. A recent work by Zielinski [15] indicates that the thiourea breakdown product is an important

intermediate in the anti-fungal process. The thiourea is thought to decompose in the soil by acid hydrolysis to give carbonyl sulphide and the amine. Moje et al. [16], described carbonyl sulphide as the volatile fungitoxicant from sodium ethylene bisdithiocarbamate (Nabam) in soil.

In the thermal decomposition of $Cu(Me_2Dtc)_2$, the tetramethylthiourea is formed in greater quantities than the corresponding tetraethylthiourea from $Cu(Et_2Dtc)_2$. If the dithiocarbamates decomposed in a similar fashion in soil, this would enable more carbonyl sulphide to be formed by the acid hydrolysis thus explaining the greater fungicidal activity of the dimethyl dithiocarbamates.

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RÉSUMÉ — Emploi d'une technique qui associe la chromatographie en phase gazeuse et la spectrométrie de masse pour l'analyse semi-quantitative des produits de la décomposition thermique du diméthyldithiocarbamate et du diéthyldithiocarbamate de cuivre. Des mécanismes de décomposition thermique sont proposés pour ces deux complexes. Le processus de la fragmentation est fortement influencé par la nature du groupe alkyle terminal lié au groupe dithiocarbamate.

ZUSAMMENFASSUNG — Die thermischen Zersetzungsprodukte von Kupfer-Dimethyldithio-karbamat und Kupfer-Diäthyldithiokarbamat wurden unter Verwendung einer halbquantitativ analysiert und thermische Zersetzungsmechanismen für beide Komplexe vorgeschlagen. Der Fragmentierungsweg wird durch die Beschaffenheit der an den Dithiokarbamat-Teil gebundenen terminalen Alkylgruppe stark beeinflusst.

Резюме — Полуколичественно проанализированы продукты термического разложения диметил- и диэтилдитиокарбаматов меди с помощью комбинационной техники газ-хроматография — масс-спектрометрия. Для обоих комплексов предложен механизм термического разложения. Иуть фрагментации сильно зависит от природы концевых алкильных групп, присоединенных к дитиокарбаматому остову.