Thermochimica Acta, 67 (1983) 197–203
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

TG–DTA–MS INVESTIGATIONS OF COPPER CHELATES WITH VARIOUS β-DIKETONES AS LIGANDS

KARL-HEINZ OHRBACH, GABRIELE RADHOFF and ANTONIUS KETTRUP *
Applied Chemistry Department, University-GH Paderborn, D-4790 Paderborn (F.R.G.)

(Received 10 February 1983)

ABSTRACT

The complex stability of copper-β-diketonates is influenced by the donor strengh of the ligand. The thermal properties of the compounds are related to mass spectral data and correlated with σ^* constants of the Hammett equation. The connection between electron releasing-withdrawing forces of ligand substituents on endothermic as well as exothermic effects in the DTA curve are discussed. Endotherms arise from electron-withdrawing substituents, while the exotherms are attributed to electron-releasing substituents. Our thermoanalytical data are correlated on the one hand with the stability constants of the complexes (pK_{av}) and on the other, with the dissociation constants (pK_D) of the chelating agents [1].

INTRODUCTION

The present work is a continuation of the work in the field of the application of a combined system (TG–DTA–MS apparatus) to yield more information about the thermal behaviour and thermal degradation process of metal complexes. This technique is presently being employed in our laboratory to examine structure–stability relationships of metal complexes as described previously [4,7].

We have shown that the thermal stability of metal complexes varies systematically with the acceptor ability of transition metals [4]. On the basis of these measurements interest was focused on the influence of different substituents in the ligand molecules on the thermal stability of several copper-β-diketonates.

EXPERIMENTAL

Apparatus

The working procedure and detailed information about the Netzsch STA 429 simultaneous thermoanalyzer and Balzers QMG 511 quadrupole mass

---

* To whom correspondence should be addressed.

0040-6031/83/$03.00

TABLE 1

Series of copper-β-diketonates and abbreviations used in the text

Compound	Abbreviation
Bis(acetylacetonato)copper(II)	$Cu(acac)_2$
Bis(trifluoroacetylacetonato)copper(II)	$Cu(tfacac)_2$
Bis(hexafluoroacetylacetonato)copper(II)	$Cu(hfacac)_2$
Bis(benzoyltrifluoroacetyl acetonato)copper(II)	$Cu(benztfac)_2$
Bis(thenoyltrifluoroacetyl-acetonato)copper(II)	$Cu(tta)_2$
Bis(benzoylacetonato)copper(II)	$Cu(benzac)_2$
Bis(dibenzoylmethanato)copper(II)	$Cu(dbzm)_2$

spectrometer TG–DTA–MS equipment has been reported previously [2–4]. Some experimental conditions are given in the text.

Materials

The copper-β-diketonates listed in Table 1 were prepared and purified in our laboratory by well-known methods [5,6].

RESULTS AND DISCUSSION

TG–DTA investigations

The influence of various substituents in metal-β-diketonates on their thermal stability and volatility has been investigated by means of thermogravimetry [8]. The TG–DTA curves of all copper-β-diketonates illustrate clearly different thermal behaviour related to the nature of the electron structure and chemical environment. The TG–DTA data are not easy to correlate with other parameters because several curves show a lot of asymmetric peaks and complicated decomposition routes.

The DTA curve of $Cu(dbzm)_2$ shows only an exothermic course, in contrast with that of $Cu(hfacac)_2$ which exhibits two endotherms. The remaining compounds indicate both of the thermal effects, as a result of different electronic forces at the reaction centres in the ligand molecules. The TG–DTA curves of $Cu(hfacac)_2$ and $Cu(dbzm)_2$ are shown in Figs. 1 and 2. The first endothermic peak in the DTA curve of $Cu(hfacac)_2$ is due to melting of the compound while the second peak corresponds to vaporization of the metal complex, as detected by our simultaneous mass spectrometric experiments in the temperature range 373–428 K.

Typical mass fragments shown in Table 2 arise from the degradation of

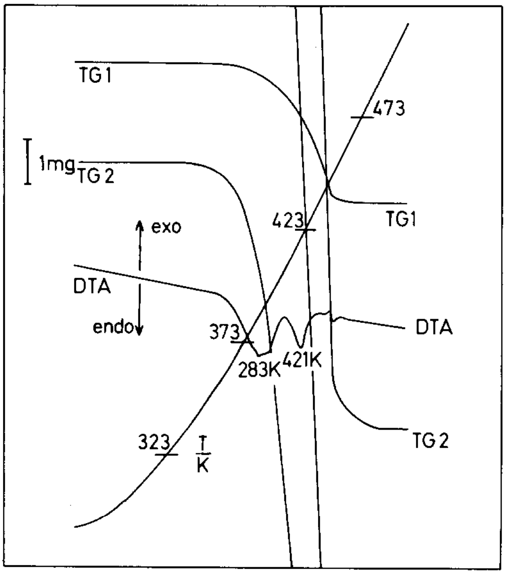

Fig. 1. TG–DTA curve of $Cu(hfacac)_2$.

$Cu(hfacac)_2$. The small temperature range of vaporization of $Cu(hfacac)_2$ is in contrast with the wide range of temperature-dependent decomposition routes of $Cu(dbzm)_2$. This is in agreement with previous investigations [9–11] showing that increasing volatility occurs by substitution of fluorine-containing groups in contrast to other compounds which decompose rapidly

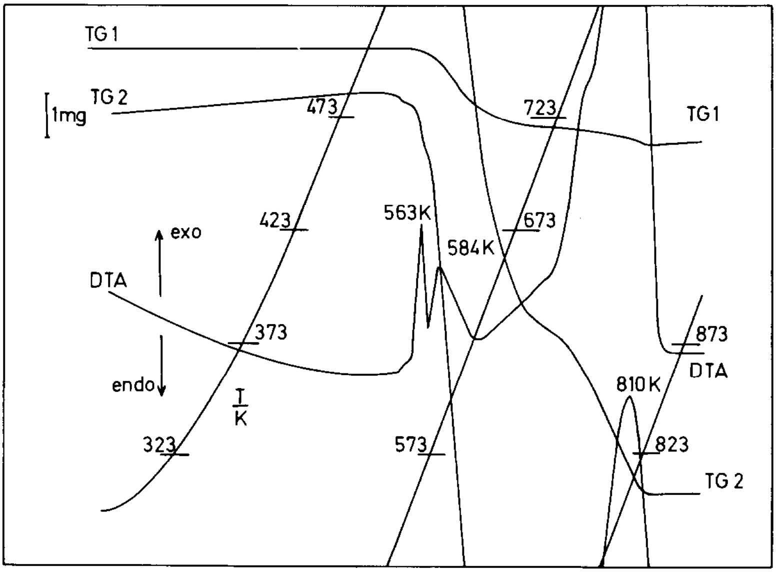

Fig. 2. TG–DTA curve of $Cu(dbzm)_2$.

TABLE 2

Typical mass fragments arising from the degradation of Cu(hfacac)$_2$

m/z	Fragment
69	CF_3
97	CF_3CO
110	CF_3COCH
138	$CF_3COCHCO$
208	$CF_3COCHCOCF_3$

in a three-stage degradation process in an oxidative atmosphere. This is indicated by three characteristic exothermic peaks in the DTA curve during the main mass loss of the sample.

Different substituents in the ligand molecules reduce the bonding strength of the metal–oxygen bond in the metal complexes induced by electron removal or release of the substituent. These facts are confirmed by correlation of the temperature interval of decomposition taken from the DTA

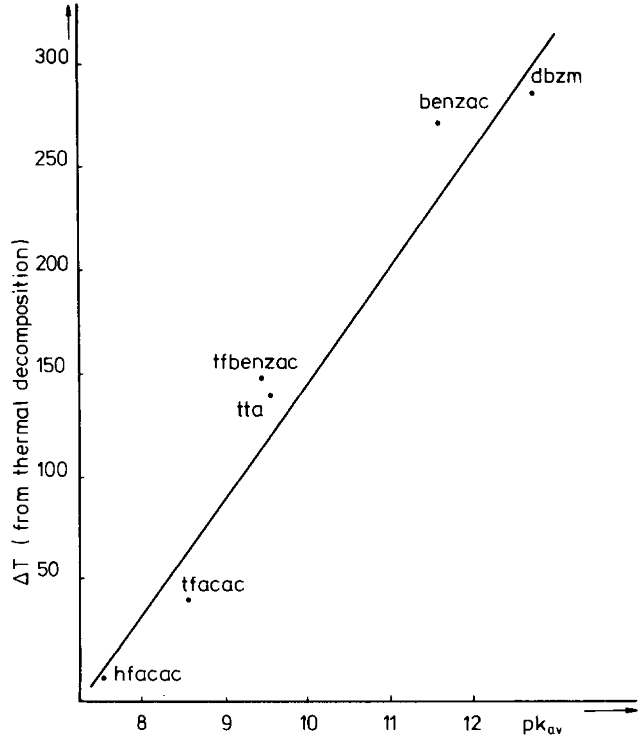

Fig. 3. Correlation of ΔT from thermal decomposition with the average stability constants of the copper-β-diketonates.

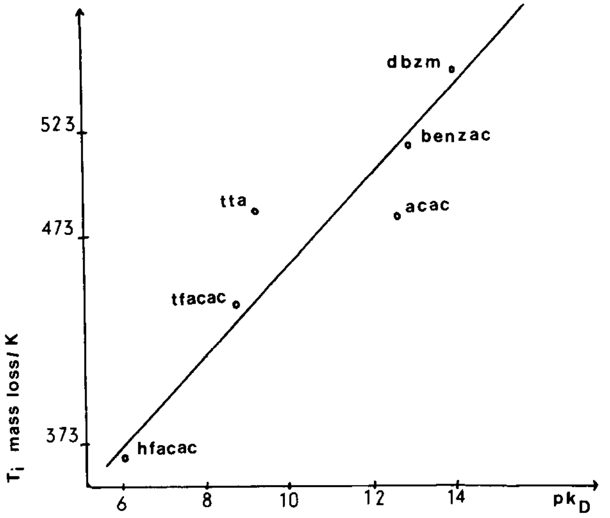

Fig. 4. Correlation of temperatures of initial mass loss with the average dissociation constants of the β-diketones.

curves or the temperatures of initial mass loss with the average stability constants of the copper-β-diketonates and the dissociation constants of the ligands, as shown in Figs. 3 and 4. In all cases the thermal stability of the metal complexes follows the order: hfacac < tfacac < benztfac < tta < acac < benzac < dbzm, corresponding to the more negative inductive effects of

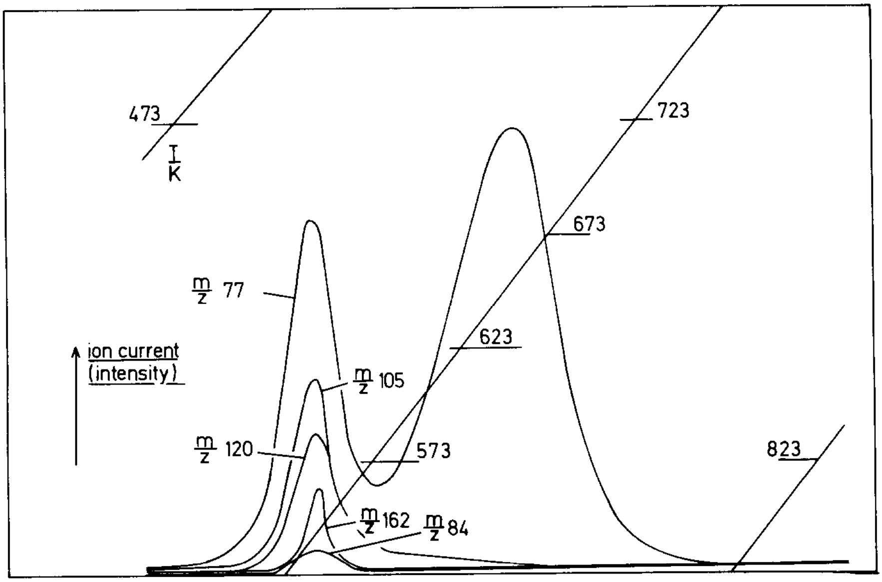

Fig. 5. Intensities of selected ion currents of mass fragments of $Cu(benzac)_2$ listed in Table 3.

TABLE 3

Mass fragments of Cu(benzac)$_2$

m/z	Fragment
77	ph
84	$CH_3COCHCO$
105	phCO
120	CH_3COCH-Cu
162	ligand

the substituents. The greater the stability of the complexes the more energy is required for thermal decomposition.

MS investigations

The composition of the volatile release was studied as a function of temperature and mass loss. It is important to note that degradation of the copper-β-diketonates is a multi-step process, with first elimination of substituent groups and not by removal of the complete ligand molecules. Figure 5 shows the temperature-dependent spectrum of the intensities of several mass units (mass ranges) listed in Table 3.

Figure 6 shows a mass spectrum in the temperature range 513–543 K with a continuously repeated mass scan from $m/z = 160$ to $m/z = 163$. This

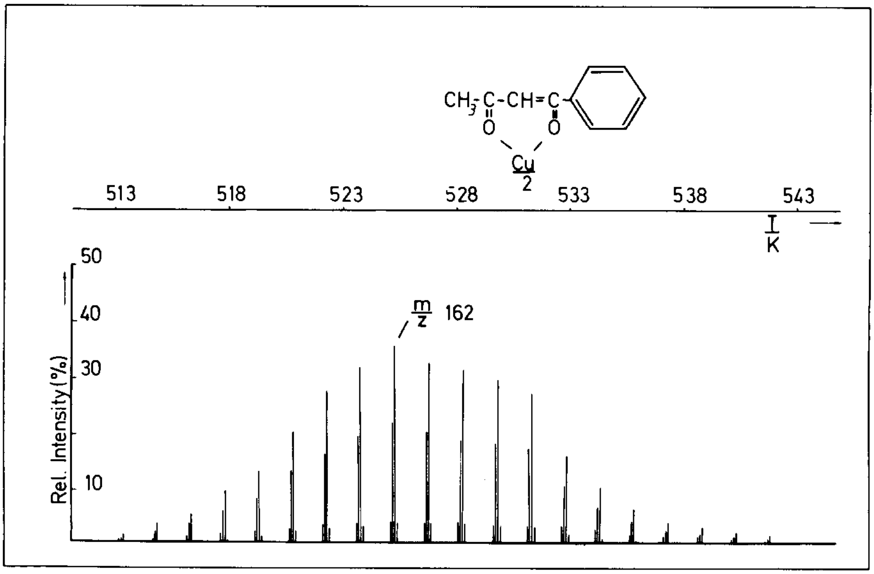

Fig. 6. Elimination of benzac from Cu(benzac)$_2$ in the temperature range 513–543 K.

TABLE 4

Metal-free fragments from the fragmentation pattern of copper-β-diketonates

Compound	Fragments			
Cu(II)-acac	CH_3	CH_3CO	CH_3COCH	$CH_3COCHCO$
Cu(II)-tfacac	CH_3	CH_3CO	CH_3COCH	$CH_3COCHCO$
	CF_3	CF_3CO		$CF_3COCHCO$
Cu(II)-hfacac	CF_3	CF_3CO	CF_3COCH	$CF_3COCHCO$
Cu(II)-benzac	CH_3	CH_3CO	CH_3COCH	$CH_3COCHCO$
	Ph	Ph-CO	Ph-COCH	Ph-COCHCO
Cu(II)-benztfac	CF_3	CF_3CO		$CF_3COCHCO$
	Ph	Ph-CO	Ph-COCH	Ph-COCHCO
Cu(II)-tta	CF_3	CF_3CO	CF_3COCH	$CF_3COCHCO$
	Th	Th-CO	Th-COCH	Th-COCHCO
Cu(II)-dbzm	Ph	Ph-CO	Ph-COCH	Ph-COCHCO

example shows the particular removal of ligand molecules of benzac with a maximum at about 525 K. The predominant volatization of fluorine-containing metal complexes depends on the nature of these substituents. Nearly all fragments we recorded were metal-free products, in contrast to the other compounds we examined. The results are summarized in Table 4.

ACKNOWLEDGEMENTS

The financial support of Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is gratefully acknowledged.

REFERENCES

1 G. LeGrand Van Uitert, W.G. Fernelius and B.E. Douglas, J. Am. Chem. Soc., 75 (1953) 457.

2 W.D. Emmerich and E. Kaisersberger. J. Therm. Anal., 17 (1979) 197.

3 K.-H. Ohrbach, G. Radhoff and A. Kettrup, Thermochim. Acta, 67 (1983) 189.

4 K.-H. Ohrbach, G. Radhoff and A. Kettrup, Z. Anal. Chem., 314 (1983) 398.

5 R.L. Belford and A.E. Martell, J. Inorg. Nucl. Chem., 2 (1956) 11.

6 H. Holtzclaw, Jr. and J.P. Collman, J. Am. Chem. Soc., 79 (1957) 3318.

7 A. Kettrup and K.-H. Ohrbach, in E. Marti, H.R. Oswald, H.G. Wiedemann (Eds.), Angewandte Chemische Thermodynamik, Birkhäuser, Basel, 1979, p. 103.

8 K.J. Eisentraut and R.E. Sievers, J. Inorg. Nucl. Chem., 29 (1967) 1931.

9 A.L. Henne, M.S. Newman, L.L. Quill and R.A. Staniforth, J. Am. Chem. Soc., 69 (1947) 1819.

10 R.N. Haszeldine, W.K.R. Musgrave, F. Smith and L.M. Turtan, J. Chem. Soc., (1951) 609.

11 H. Gilman, R.G. Jones, E. Buschadler, D. Blume, G. Karmas, G.A. Martin, J.F. Nobis, J.R. Thirtle, H.L. Yale and F.A. Yoeman, J. Am. Chem. Soc., 78 (1956) 2790.