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SIMULTANEOUS TG-DTG-DTA-MS INVESTIGATIONS OF COPPER(II)-COMPLEXES WITH MIXED LIGANDS (ORGANIC NITROGEN BASES)

G. RADHOFF, K.-H. OHRBACH and A. KETTRUP
University GH Paderborn, FB 13, Applied Chemistry, P.O.Box 1621, D-4790 Paderborn, F.R.G.

ABSTRACT

Copper(II)complexes with the general formula CuL_nX_2 (X=Cl or Br, n=1 or 2 and L= pyridine-N-oxide, 2-picoline-N-oxide, 3-picoline-N-oxide, 4-picoline-N-oxide, 4-chloropyridine-N-oxide, 4-methoxy-pyridine-N-oxide or 4-nitropyridine-N-oxide) have been prepared. The TG-DTG-DTA-MS data have been recorded simultaneously using a Netzsch STA 429 thermal analyzer combined with Balzers QMG 511 mass spectrometer. Thermal stability of the compounds dependsonthe basicity of the organic ligands as well as on the electronegativity of the halogen atom. The decomposition of the complexes has been determined as a two-stage degradation process corresponding with the cleavage and fragmentation of the organic bases first, followed by the release of the halogen atoms.

INTRODUCTION

Complexes of divalent transition metals and organic ligands have become of great interest in heterogenous catalysis. In order to investigate thermal behaviour and especially the influence of the ligand on the thermal stability of metal complexes we prepared a series of Copper(II)complexes with various subatituted pyridine-N-oxides and chlorine or bromine as ligands. Thermal degradation has been studied by use of a TG-DTG-DTA-MS coupling system. We have demonstrated this equipment to be well suited for these investigations as reported previously (ref. 1-3).

METHODS

The experiments were carried out using a coupling system Netzsch thermal analyzer STA 429 and Balzers quadrupole mass spectrometer QMG 511. A new gas inlet system as pressure reduction - consisting of quartz glass tubes instead of Al_2O_3-tubes - has been applied successfully for the first time. The final working temperature of the quartz tubes is limited to nearly 900°C, sufficient for our main subjects of investigation. Other aspects for using the quartz glass tubes are their low costs and easy handling especially with

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regard to the cleaning procedure.

All metal complexes were prepared by well known methods (re. 4) and identified by elemental analysis and spectroscopic methods.

RESULTS AND DISCUSSION

The TG curves of all complexes exhibit a two stage mass loss. The first stage corresponds quantitatively with the loss of the organic ligands while the second mass loss is due to the elimination of the halogen atoms.

A typical TG-DTG-DTA run (see Fig. 1) shows the elimination of both ligands from Cu(3-picoline-N-oxide)$_2$Br$_2$ at temperatures of 486 K and 561 K followed by the cleavage of the bromine atoms at 896 K (DTG maxima). The DTA curve exhibits a small endotherm at 417 K indicating the melting of the complex and a large exotherm in the temperature range of the first mass loss, corresponding to elimination and oxidative decomposition of the organic bases.

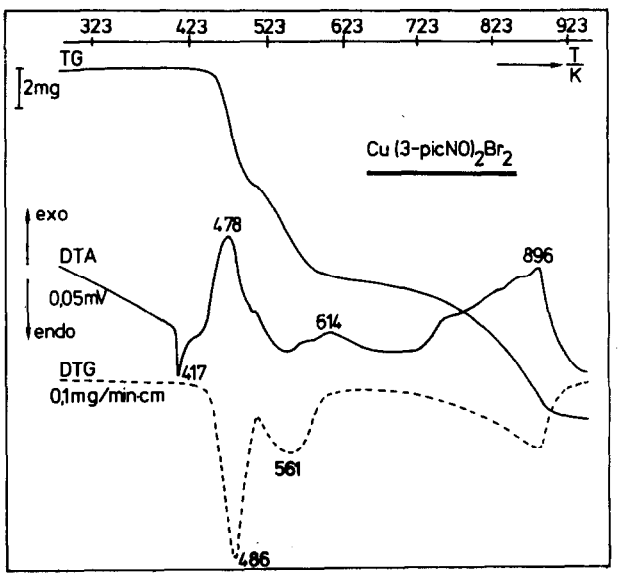

Fig. 1. TG-DTG-DTA curves of Cu(3-picoline-N-oxide)$_2$Br$_2$

The mass spectra were recorded simultaneously to the TG-DTG-DTA measurements, affirming the decomposition steps we proposed based on the TG-DTG-DTA data. An autocontrol spectrum of Cu(3-picoline-N-oxide)$_2$Br$_2$ is given in Fig. 2 showing increasing intensities of the ligand and typical ligand fragments such as m/z = 93 and 66 due to consecutive elimination of oxygen and hydrogen cyanide, or m/z = 51 and 78 due to loss of a methyl group from m/z = 66 and 93 as well as ion currents of the halogen Br$_2$ at m/z = 158, 160 and 162. In a mass scan of the complex we recorded the intensities of Br and Br$_2$ according to their natural relative isotopic abundance.

The ion currents of mass numbers due to the ligand fragmentation exhibit a maximum in intensity at 496 K and 578 K while the maximum intensity of bromine is at 886 K. All maxima correspond well with thermal respectively with mass loss data taken from the DTA and DTG curves.

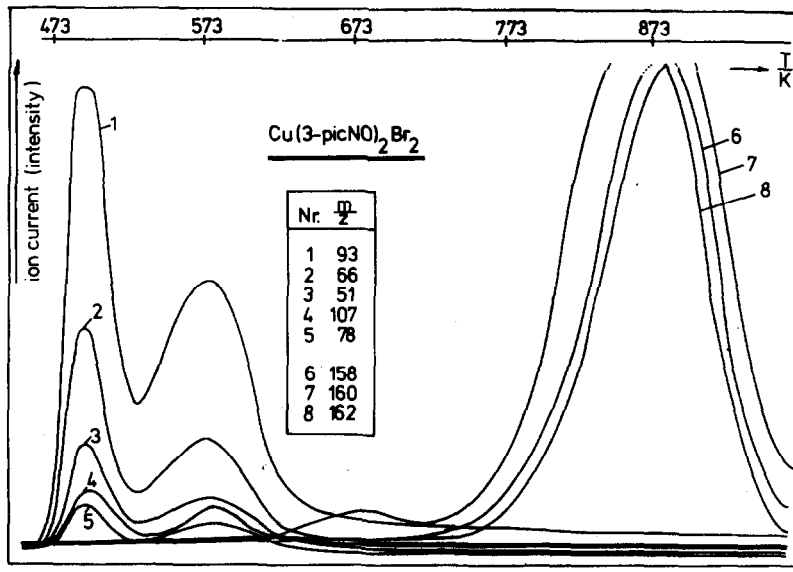

Fig. 2. Autocontrol spectrum of Cu(3-picoline-N-oxide)$_2$Br$_2$

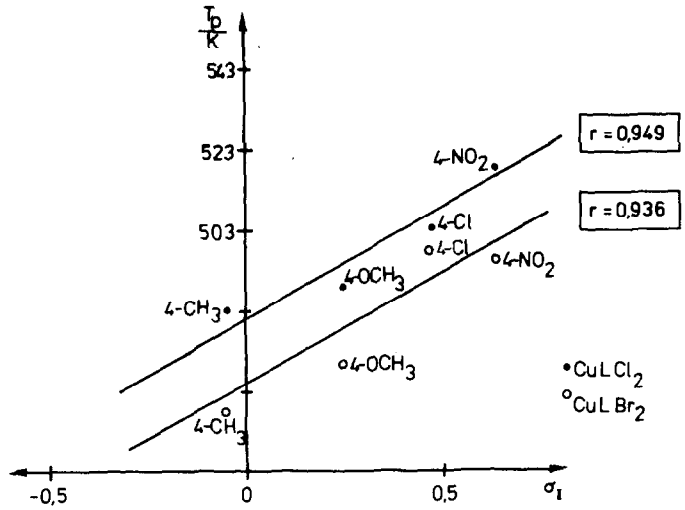

Fig. 3. Diagramm showing relationship between the Hammett σ_I-values and the temperature of the first exothermic DTA peak (T_p)

The influence of ligand substituents and the halogens on the thermal stability of the complexes is illustrated in Fig. 3. A plot of the maximum temperatures of the first DTA exotherm vs. the Hammett σ_I-values shows increasing decomposition temperatures following the order

4-picoline-N-oxide < 4-methoxypyridine-N-oxide < 4-chloropyridine-N-oxide < 4-nitropyridine-N-oxide.

The two parallel straights reveal the complexes with bromine to be less stable than those containing chlorine.

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