THE THERMAL DISSOCIATION OF SOME METAL CUPFERRATE CHELATES

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The use of cupferron (ammonium salt of N-nitrosophenylhydroxylamine) as an organic precipitant for copper(II) and iron(III) ions was first proposed by BAUDISCH[1] in 1909. Since that time, much work has been done using the reagent for the determination of these 2 metal ions and other ions[2] as well.

Perhaps the least studied physical parameter of these metal cupferrates has been their thermal properties. Previous studies on this subject have consisted mainly of weight-loss determinations on the thermobalance[3,4]. Normally, the precipitated complexes are contaminated with excess cupferron or are of such low thermal stability that they cannot be weighed as metal complexes but must be ignited and weighed as metal oxides. Only the copper(II) and iron(III) complexes show any possibility of being weighed as the $Cu(Cup)_2$ and $Fe(Cup)_3$ (Cup = cupferrate ion) complexes, respectively, on the basis of their thermal stability[3]. The rare earth cupferrates also appear to possess excellent thermal stability properties although they are usually ignited to the metal oxides and weighed as such[4].

Very little is known concerning the fate of the organic ligand on ignition of the metal cupferrates in the solid state. In solution, cupferron is said to decompose to nitrosobenzene on heating[5]. Likewise, the sodium salt of *p*-nitrocupferron decomposes to *p*-nitrosonitrobenzene while the silver salt gives free silver and nitrosobenzene in boiling solutions[6]. It was thus the object of this study to investigate the thermal dissociation of several of the metal cupferrates by differential thermal analysis and mass spectrometric analysis of the pyrolysis decomposition products.

EXPERIMENTAL

Preparation of complexes

Most of the metal cupferrates were prepared according to previous procedures[2]. The rare earth cupferrates were prepared as previously described[7]. All of the precipitated complexes were washed with water and alcohol and air-dried for at least 24 h at room temperature. The complexes were analyzed for metal content by ignition of the air-dried complexes to the metal oxide at the temperatures previously recommended[3]. The metal contents of the complexes are given in Table I.

TABLE I

METAL CONTENTS OF CUPFERRON METAL CHELATES

Metal cupferrate	*Per cent Metal*	
	Theoretical	*Found*
$Cu(Cup)_2$[a]	18.81	18.7
$Ni(Cup)_2$	17.63	18.1
$Co(Cup)_2$	17.69	17.8
$Zn(Cup)_2$	19.25	19.0
$Cd(Cup)_2$	29.07	28.9
$Mn(Cup)_2$	16.69	16.5
$Hg(Cup)_2$	42.24	42.0
$Mg(Cup)_2$	8.14	8.06
$Cu(Cup)_2 \cdot 2H_2O$	11.44	11.5
$Ba(Cup)_2 \cdot 3H_2O$	29.49	29.5
$Sr(Cup)_2 \cdot 2H_2O$	22.02	22.1
$Al(Cup)_3$	6.15	6.03
$Fe(Cup)_3$	11.95	12.0
$Ce(Cup)_3$	25.40	25.3
$La(Cup)_3$	25.24	25.1
$Nd(Cup)_3$	25.97	25.4

[a] Cup = cupferrate ion, $C_6H_5N(NO)O^-$.

Differential thermal analysis apparatus

The apparatus employed has previously been described[8]. The samples were decomposed in either a vacuum, less than 1 mm Hg pressure, or in a static atmosphere of argon. In the latter case, the air was first removed from the system by evacuation to less than 1 mm Hg, then filled with argon to atmospheric pressure. Sample sizes ranged in weight from 60 to 80 mg and were pyrolyzed at a heating rate of 10°/min. Excellent agreement was found between duplicate and triplicate runs on the same sample.

Pyrolysis studies

The pyrolysis decomposition products were introduced into a Consolidated Engineering Corp. Model 21-602 mass spectrometer by means of an "L"-shaped pyrolysis tube connected directly to the sample inlet chamber of the mass spectrometer. The pyrolysis tube contained a small Nichrome wire wound furnace, 1.5 cm in diameter by 10 cm in length, into which was placed a small porcelain boat containing 1–10 mg of sample. After evacuation to less than 1-micron pressure, the furnace and sample were slowly heated to about 300°. The resulting pyrolysis products were then analyzed by mass spectrometry.

To determine the temperature at which certain pyrolysis products were evolved, the samples were heated at about 5°/min and the various m/e peaks were scanned at periodic intervals. From the intensity increase of the various peaks, the amount of decomposition product could be ascertained as a function of temperature.

The temperature of the pyrolysis furnace was detected by a Chromel–Alumel thermocouple located between the furnace windings and the glass wall of the pyrolysis tube. The voltage output from the thermocouple and the reference 0° thermocouple was recorded on a Varian Model G-10 strip-chart recorder.

RESULTS AND DISCUSSION

The differential thermal analysis (DTA) curves of the metal cupferrates, in argon, are given in Figs. 1–3.

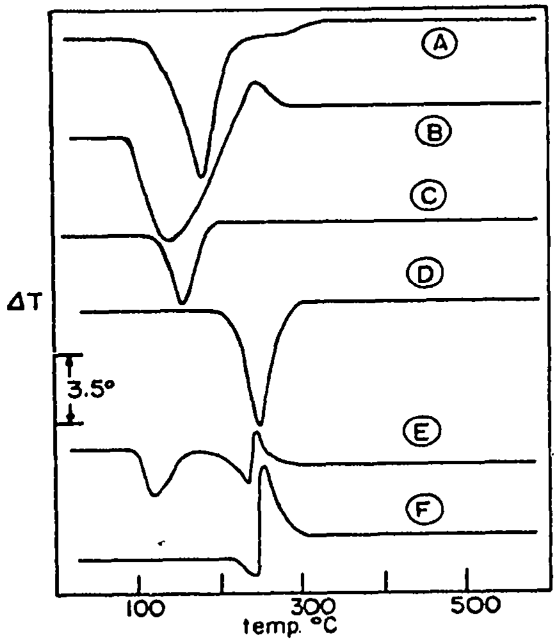


Fig. 1. DTA curves of cupferron and metal cupferrates (argon). A, cupferron; B, $Ni(Cup)_2$; C, $Co(Cup)_2$; D, $Cu(Cup)_2$; E, $Zn(Cup)_2$; F, $Mn(Cup)_2$.

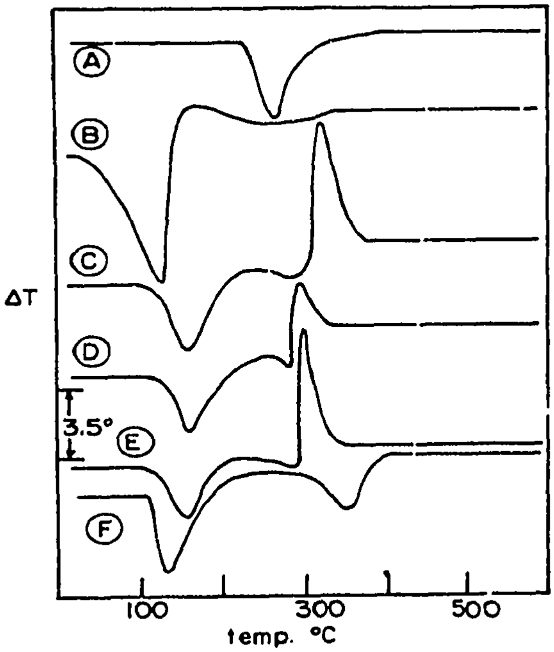


Fig. 2

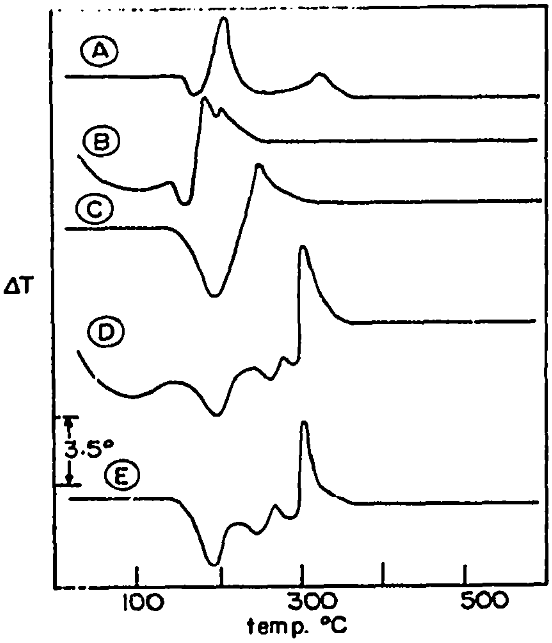


Fig. 3

In general, the DTA curves consisted mainly of endothermic peaks but a number of them also contained exothermic peaks. Since the complexes were studied in an argon atmosphere or vacuum, the origin of the exothermic peaks must be due to the exothermic decomposition of the compounds and not to air-oxidation reactions of the pyrolysis intermediates. Although it is not possible to characterize each peak as a specific decomposition or dissociation reaction, the endothermic peaks must be the result of heat-absorbing bond-breaking reactions. This initial DTA peak was then followed by other endothermic or exothermic peaks which must be due to reactions involving pyrolysis intermediates.

The DTA curve for cupferron contained but a single endothermic peak with a peak maximum temperature of 185°. Since the peak began or deviated from the base line at about 130°, there must have been considerable decomposition before the fusion temperature[5] of 163–164° was reached.

The DTA curves for the cobalt(II), copper(II), mercury(II), and cadmium(II) cupferrates consisted of a single endothermic peak at temperatures of 155°, 250°, 130°, and 260°, respectively. Based upon the temperature at which the curve deviated from the base line, the cadmium complex appeared to be the most stable.

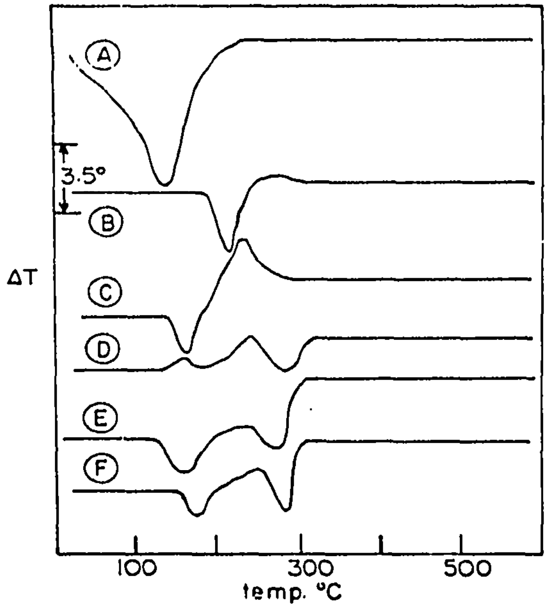


Fig. 4

For the nickel(II), manganese(II), aluminum, and iron(III) cupferrates, the DTA curves consisted of an endothermic peak followed by an exothermic peak or peaks. Generally, the reaction which was responsible for the exothermic peak started as an endothermic one and then changed to exothermic as the reaction progressed. The exact dissociation sequence cannot be determined from the DTA curve itself.

The DTA curves for the calcium, strontium, and barium cupferrates were all quite similar. In contrast, the curve for magnesium cupferrate was different because the exothermic peak was absent. The peak temperatures for the first endothermic peak were: Mg, 130°; Ca, Sr, and Ba, 155°; and for the exothermic peak, Sr and Ba, 300°; Ca, 320°. Because water of hydration occurs with these complexes, it is probable that the first endothermic peak is related to the dehydration reaction.

For the rare earth cupferrates, the DTA curves for lanthanum and neodymium were quite similar. The lanthanum cupferrate curve had endothermic peaks at 200°, 270°, and 300° with an exothermic peak at 310°. Similarly for neodymium, the peak temperatures were 195°, 250°, 295°, and 305°, respectively. Cerium(III) cupferrate exhibited a curve with a single endothermic peak at 200° followed by an exothermic peak at 250°. This anomaly might be expected because of the different oxides obtained, CeO_2, compared to La_2O_3 for the lanthanum complex.

The DTA curves of the metal complexes *in vacuo* are shown in Fig. 4. The most pronounced differences between the vacuum and argon curves were the change in peak maxima temperatures and the decrease in intensity of the endothermic and exothermic peaks. For example, the endothermic peak maximum for cupferron shifted from 185° in argon to 140° in vacuum. Normally, a phase transition should not be pressure-dependent, as was illustrated previously with sodium nitrate[8]. Thus, the curve for cupferron must involve decomposition as well as fusion, which would explain the pressure dependency.

The vacuum DTA curves for the lanthanum and neodymium cupferrates showed only 2 endothermic peaks. The peak maxima were 160° and 280° for lanthanum and 175° and 290° for neodymium. As seen previously, the argon DTA curves contained 3 endothermic peaks followed by an exothermic peak. The endothermic peak maximum for copper(II) cupferrate shifted from 250° in argon to 220° *in vacuo*.

Pyrolysis studies

The results of the pyrolysis studies are shown in Figs. 5–8.

The total mass spectra of the pyrolysis products of cupferron and the copper(II) and iron(II) cupferrates are given in Fig. 5. The spectrum for cupferron indicated

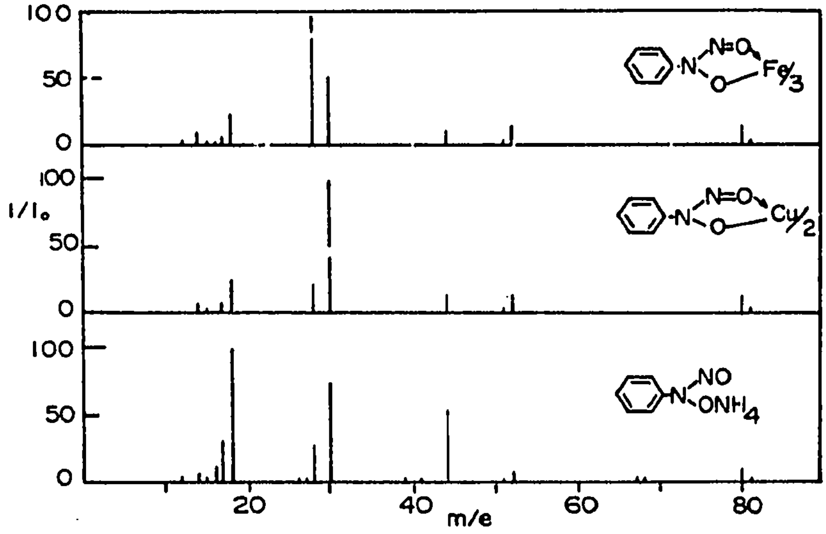


Fig. 5

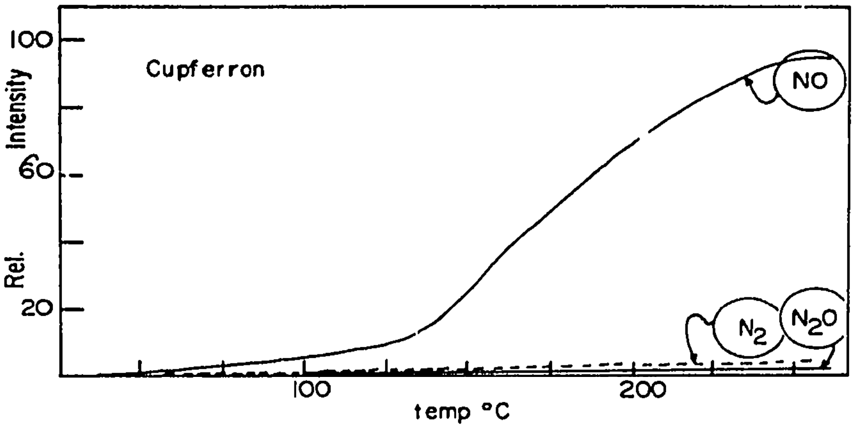


Fig. 6

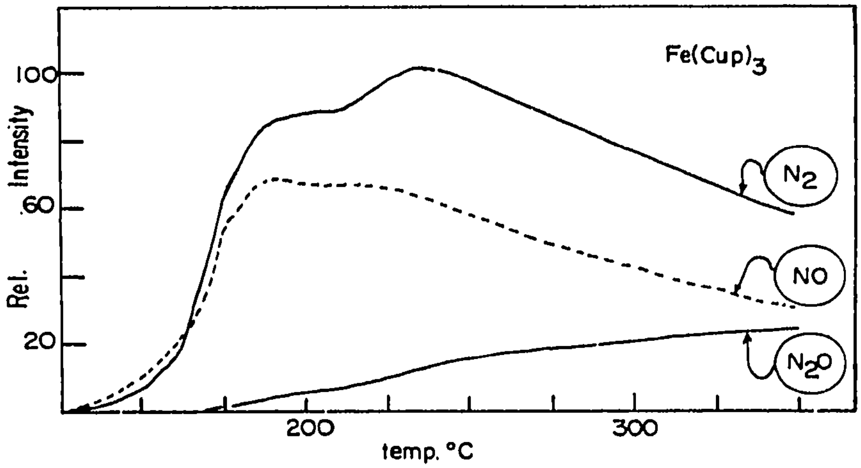


Fig. 7

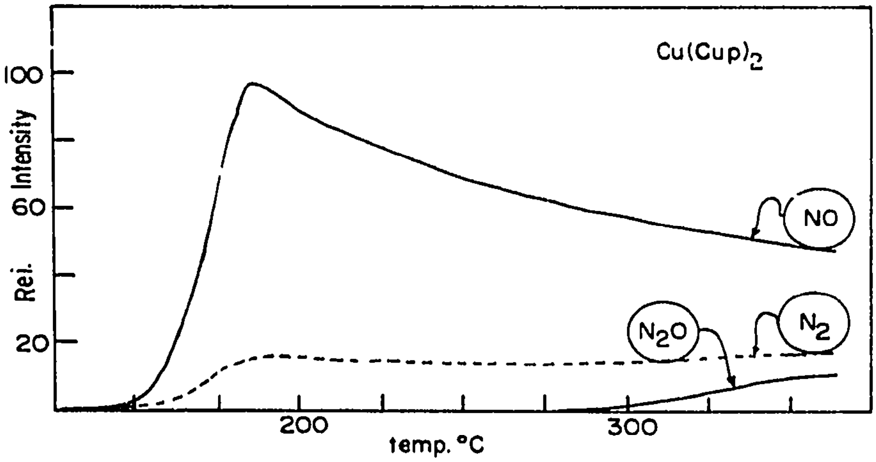
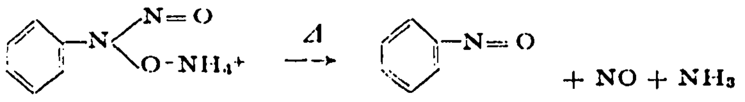


Fig. 8

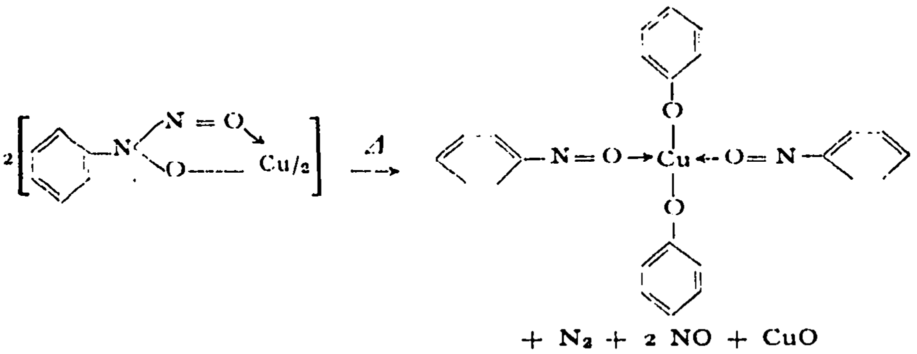
the presence of ammonia, water, nitrogen(II) oxide, nitrogen, nitrogen(I) oxide, and a hydrocarbon entity with a maximum peak intensity at m/e of 80. The 100% I/I_0 peak was positioned at a m/e of 18 for water. For the metal cupferrates, the mass spectra contained similar peaks except for the absence of ammonia. The 100% peaks were different; NO for copper(II) and N_2 for the iron(II) complex.

The curves obtained by oscillating over the 100% m/e peaks for N_2O, NO, and N_2 are given in Figs. 6–8. For cupferron, the curves indicated that NO was detectable at temperatures slightly above ambient. The compound was unstable under conditions of high vacuum with respect to the evolution of nitrogen(II) oxide. Although not shown on the curve, ammonia and water were also evolved at these low temperatures. Most of the water probably came from adsorption and not necessarily from pyrolysis since the amount evolved was dependent on how long the material was contained within the high vacuum system. Thus, the initial decomposition probably involved the reaction:



Only at temperatures greater than 100° were appreciable amounts of nitrogen and nitrogen(I) oxide detected in the pyrolysis products. These gases could result from further decomposition of the cupferron and/or from hot-tube reactions involving nitrosobenzene, nitrogen(II) oxide, and other products.

The situation was similar for the pyrolysis of the copper(II) cupferrate chelate. The decomposition gases, NO and N_2, were detectable at about 150° with the maximum intensities for the gas evolution being obtained at about 185°. Nitrogen(II) oxide was present in the largest amount followed by nitrogen and then nitrogen(I) oxide. A mechanism which could explain this behavior is as follows:



According to this mechanism, additional nitrogen(II) oxide could be evolved at still higher temperatures as well as a hydrocarbon entity and CuO. An alternative mechanism at higher temperatures could possibly involve the evolution of N_2O instead of N_2 from the organic ligand.

The mass spectra curves for the pyrolysis of iron(III) cupferrate revealed an interesting feature. The evolution of N_2 and NO began at about 125°, giving a break in the curve at 185°. Then, at temperatures near 210°, additional N_2 and NO were evolved. From the DTA curve, *in vacuo*, it is seen that the curve contained an endothermic peak at 170° followed by an exothermic peak near 245°. The endothermic reaction evolved NO and N_2 as was found with copper cupferrate, while the exothermic peak reaction evolved still more N_2 and NO as well as N_2O. The difference in the amount of nitrogen compared to NO in the pyrolysis gases may be due to the greater stability of iron(III) oxide compared to copper(II) oxide. Thus, the C–N and N–O bonds would be broken more easily than the Fe–O bonds.

The mass spectra curves for several of the other metal cupferrates revealed similar results. All involved only the gaseous products given off by the two examples presented here.

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SUMMARY

The thermal dissociation of the cupferron complexes with Cu(II), Ni, Co(II), Zn, Cd, Mn(II), Hg(II), Mg, Ca, Ba, Sr, Al, Fe(III), Ce(III), La, and Nd was studied by differential thermal analysis (DTA) and by pyrolysis into a mass spectrometer. The DTA curves consisted mainly of endothermic peaks although some contained exothermic peaks as well. The mass spectrometer showed that cupferron decomposes slightly above room temperature, giving off N_2, NO, N_2O, NH_3 and H_2O. A mechanism for the thermal dissociation of the copper(II) cupferrate is proposed.

RÉSUMÉ

Les auteurs ont examiné la dissociation thermique des complexes du cupferron avec Cu, Ni, Co, Zn, Cd, Mn, Hg(II), Mg, Ca, Ba, Sr, Al, Fe(III), Ce(III), La et Nd, par analyse thermique différentielle et par pyrolyse dans un spectromètre de masse. On constate que le cupferron se décompose légèrement, au-dessus de la température ordinaire, en donnant N_2, NO, N_2O, NH_3 et H_2O. Un mécanisme de dissociation thermique du cupferrate de cuivre est proposé.

ZUSAMMENFASSUNG

Die thermische Dissoziation von Cupferron-Komplexen mit Cu(II), Ni, Co(II), Zn, Cd, Mn(II), Hg(II), Mg, Ca, Ba, Sr, Al, Fe(III), Ce, La, und Nd wurde mittels der Differentialthermoanalyse (DTA) und durch Pyrolyse in einem Massenspektrometer untersucht. Die DTA-Kurven besitzen neben einigen exothermen Maxima hauptsächlich endotherme Maxima. Die massenspektrometrischen Untersuchungen zeigten, dass Cupferron sich oberhalb der Raumtemperatur leicht zersetzt unter Abgabe von N_2, NO, N_2O, NH_3 und H_2O. Es wird ein Mechanismus für die thermische Dissoziation des Kupfer-Komplexes vorgeschlagen.

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