Mechanism of Decomposition of Cuprous Cyanide. Infrared and Thermal Evidence

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The thermal decomposition behavior of cuprous cyanide, which has been used to synthesize ceramic superconductors, is studied using Fourier transform infrared spectroscopy, thermogravimetry, and differential thermal analysis. The results are best understood by assuming that cuprous cyanide polymerizes to various cyclized products upon heating which differ in structure somewhat. The melting point of 470 °C assigned previously to cuprous cyanide is actually that of these cyclized products. Upon continued heating these polymerized products decompose to Cu metal at ~850 °C in N_2 atmosphere and to oxides of copper at 380 °C in air atmosphere besides liberating cyanogen gas in both cases. The polymerization seems to convert $Cu_2(CN)_2$ to a higher energy state which, probably, is the reason for its efficient reaction with Ba and Y compounds responsible for better quality ceramic superconductors.

Introduction

Since the discovery of bulk superconductivity in layered cuprates, such as $YBa_2Cu_3O_{7-x}$[1] and $YBA_2Cu_4O_8$,[2] it has been realized that copper in these compounds plays the most important role in determining superconductivity. Extensive studies of these compounds have led to the conclusion that superconductivity probably originates in the copper oxygen planes.[3] The valence state of copper responsible for determining superconductivity has been controversial for quite some time.[4] The optimal valence state of copper for superconductivity is still unknown, and it is believed that a mixed valence state of copper is the source of superconductivity.[5]

For the synthesis of $YBa_2Cu_3O_{7-x}$ mostly CuO has been used. It is a relatively high melting point (~980 °C) copper compound and takes a rather long time for the solid-state reaction with other constituents (such as Y_2O_3, $BaCO_3$) to be completed. We have recently prepared $YBa_2Cu_3O_{7-x}$ superconductor[6] from $Cu_2(CN)_2$ with a degree of higher homogeneity than the same compound prepared from CuO. Cuprous cyanide is a low melting point (473 °C) material[7] and copper in this compound is in the Cu^+ oxidation state. The motivation for using $Cu_2(CN)_2$ in this preparation was, partly, to use the highly reactive state Cu^+ that was expected to be liberated upon its decomposition, to facilitate the chemical reaction. The successful preparation of the single-phase $YBa_2Cu_3O_{7-x}$ material[6] using $Cu_2(CN)_2$ made it interesting to study the decomposition behavior of $Cu_2(CN)_2$.

The synthesis of $YBa_2Cu_4O_8$ has from the beginning, proved to be much more difficult. Initially it was prepared at high oxygen pressure.[2] Its synthesis at atmospheric oxygen pressure takes extremely long, and reaction rate enhancers have to be added to synthesize it in a reasonably short time (for details see ref 8 and references therein). We found that the use of $Cu_2(CN)_2$ makes it possible to simplify the preparation of $YBa_2Cu_4O_8$ at atmospheric oxygen pressure,[8] without the requirement of any reaction rate enhancer. This breakthrough in the synthesis of $YBa_2Cu_4O_8$ further enhances the interest in studying the thermal decomposition behavior of $Cu_2(CN)_2$.

The purpose of this paper is to report the results of a detailed study of the decomposition of cuprous cyanide using thermogravimetry (TG), differential thermal analysis (DTA), and Fourier transform infrared (FTIR) spectroscopy techniques. The analysis of the data obtained from these experiments was carried out primarily to attain an understanding of the chemistry of decomposition of $Cu_2(CN)_2$ with a view to understand the influence on the physical characteristics of our $Cu_2(CN)_2$-based 1-2-3 and 1-2-4 superconductors. The results obtained have, however, provided new insight into the compositional changes brought about in $Cu_2(CN)_2$ upon heat treatment and suggest a complete reevaluation of the understanding of the thermal decomposition behavior of this compound irrespective of its use in the synthesis of layered cuprate superconductors.

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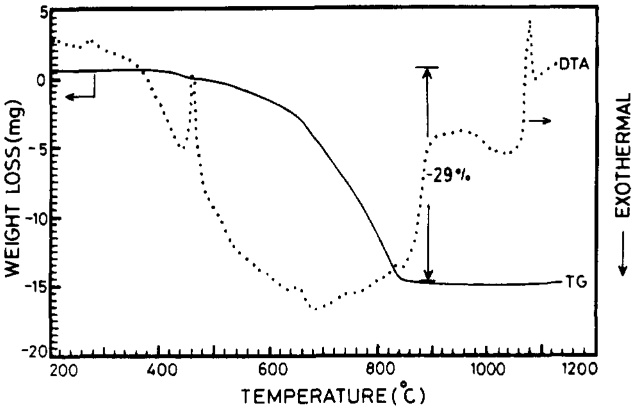

Figure 1. TG and DTA curves of $Cu_2(CN)_2$ under atmosphere of dry N_2 gas: 52.4 mg of sample was used, heating rate = 10 °C/min.

Experimental Section

(a) TG/DTA Measurements. Cuprous cyanide ($Cu_2(CN)_2$) of purity 99.9% from Fluka was used in our study. TG/DTA measurements were made using computer-assisted NETZSCH simultaneous thermal analyzer STA 429, using Kaoline as reference. Samples of $Cu_2(CN)_2$ were heated with constant heating rate of 10 °C/min from room temperature to 1140 °C under ambient of nitrogen gas. The activation energy of the decomposition reactions have been calculated from the thermograms using the Arrhenius equation:

$$A = W \exp(-E/RT) \qquad (1)$$

where E is the activation energy, R the molar gas constant, and A the local slope of the thermogram at any temperature T. The preexponential factor W is related to the total weight of the material used.

(b) Optical Measurements. For optical studies, the samples were prepared in the following manner. Approximately 1 g $Cu_2(CN)_2$ was taken in an alumina crucible and heated in air in a muffle furnace at successively increasing temperatures for about 15 min each. After each heat treatment a small quantity of the material was taken out for optical absorption study. The maximum temperature at which heat treatment was performed was 400 °C.

For FTIR absorption spectroscopy, 2.5 mg of the sample was ground and mixed with 200 mg of dry KBr in an agate mortar and pestle. Pellets of about 0.45-mm thickness were obtained from this powder. Pure KBr pellets were used as reference for obtaining the infrared absorption characteristics for our samples. Room-temperature spectra were measured using Nicolet 20DX Fourier transform infrared (FTIR) spectrometer. All the spectra were obtained at the resolution of 4 cm^{-1} between the wavenumbers 3000 and 400 cm^{-1} after thoroughly purging the spectrometer with dry compressed air.

Results and Discussion

The TG and DTA curves of $Cu_2(CN)_2$ heated in N_2 ambient are shown in Figure 1. The thermogram shows loss of weight starting around 400 °C and leveling off around 850 °C. The total loss of weight in this process is about 29%. This loss in weight corresponds to complete decomposition of $Cu_2(CN)_2$ to $(CN)_2$ and Cu according to the chemical reaction

$$Cu_2(CN)_2 \rightarrow 2Cu + (CN)_2 \qquad (2)$$

for which the calculated weight loss is 29.05%, agreeing well with the experimental value. A graph between the local slope (A) of the thermogram and reciprocal temperature ($1/T$) is shown in Figure 2. The curve seems to follow the Arrhenius behaviour (eq 1) in two regions covering major part of the weight-loss temperature regime. This indicates that the decomposition process consists of two main steps—the first step starting around 480 °C and extending to 640 °C with an activation energy of decomposition 3.8 kcal/mol, while the second step occurs at 660 °C, being completed at 820 °C with an activation energy 4.1 kcal/mol.

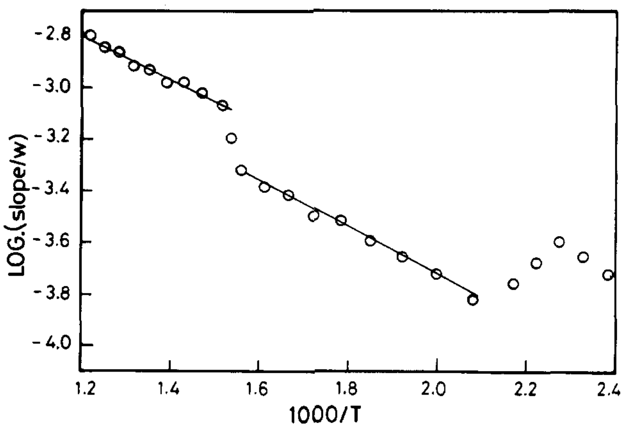

Figure 2. Arrhenius plot of the thermal decomposition of $Cu_2(CN)_2$ in N_2 atmosphere obtained from the local slope of the TG curve of Figure 1.

The DTA curve has two sharp endothermic peaks at 470 and 1083 °C. There is, in addition, a very broad exotherm starting around 300 °C going all the way to about 900 °C with a few abrupt but not very sharp features.

These TG and DTA data show, in the least, that the thermal decomposition of $Cu_2(CN)_2$ is not a simple process as suggested by the chemical reaction 2. The melting point of Cu is 1083 °C.[9] Thus the endothermic peak at this temperature shows that the end product of decomposition is indeed Cu. The melting point of $Cu_2(CN)_2$ is reported to be 473 °C[7] so that the endothermic peak at this temperature is due to melting of the starting material. However, the start of the exotherm at temperature much lower than 470 °C indicates that some morphological changes start to occur before this melting. A few points in Figure 2 at temperature much lower than 470 °C not lying on the straight line also suggest such behavior. To explain these results we suggest that $Cu_2(CN)_2$ polymerizes to ring structures which keep on changing slightly during heating. The melting point of 480 °C is not that of $Cu_2(CN)_2$ itself but that of the mixture of the polymerized products obtained as a result of cyclization of $Cu_2(CN)_2$. There is indication of at least two distinct cyclic products being decomposed, represented by the two straight lines in Figure 2 but the lower temperature points in this figure and the broad exotherm in DTA curve of Figure 1 indicate many changes in the structure of the cyclized product. The similar value of activation energy of decomposition corresponding to the two straight lines in Figure 2 suggests a similar structure for the two cyclic intermediates. This is in agreement with the above proposal that the structure of the cyclized product changes somewhat upon heating.

The infrared absorption spectra of $Cu_2(CN)_2$, heated in air, according to the schedule described in the previous section reveals interesting aspects leading support to this suggestion regarding the cyclization of the compound. $Cu_2(CN)_2$ contains triply bonded $C\equiv N$. This bond has been reported to give the characteristic absorption in cuprous

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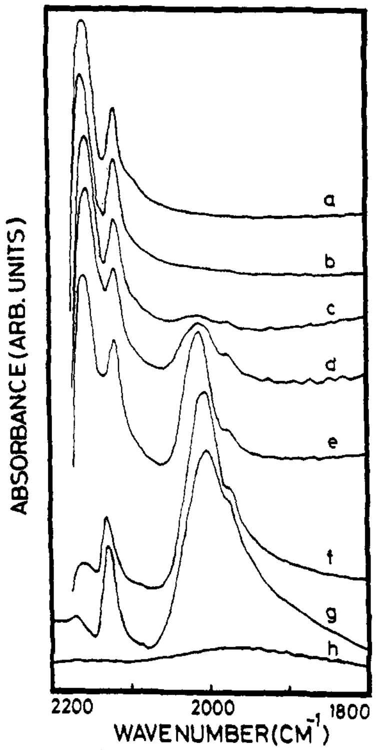

Figure 3. Infrared absorption spectra of the $Cu_2(CN)_2$ at room temperature (a), heated for 15 min at 250 (b), 270 (c), 290 (d), 300 (e), 350 (f), 370 (g) and at 380 °C (h), all in an air atmosphere.

cyanide at[10] ν_{asym} = 2160 cm^{-1} (2172 cm^{-1} is also reported[11]). We find the dominant IR peak at 2160 cm^{-1} in the spectra of $Cu_2(CN)_2$ which is not heat treated and we assign this to the ν_{asym} vibration of $Cu_2(CN)_2$. Another peak in non-heat-treated material appears at 2120 cm^{-1}, the origin of which is not known. The most interesting feature of our spectra obtained from the heated $Cu_2(CN)_2$ samples is a peak appearing around 2010 cm^{-1} with a shoulder around 1977 cm^{-1}. This is seen in Figure 3, which shows the absorption spectra from 1800 to 2200 cm^{-1} of $Cu_2(CN)_2$ heated at different temperatures. As seen in the figure there is no change in the spectrum upto 250 °C. In the temperature range 260–270 °C, a feature starts to appear around 2000 cm^{-1} and becomes a clear cut peak at 2014 cm^{-1} with a shoulder at 1978 cm^{-1} at 290 °C. Further heating increases the intensity of this peak compared with the ν_{asym} peak of C≡N. Beyond 300 °C the lower wavenumber side of the new peak broadens considerably along with increase in its intensity. These peaks disappear at 380 °C altogether.

The appearance of new IR peaks and relative diminishing of ν_{asym} peak of $Cu_2(CN)_2$ clearly show that beyond 280 °C certain morphological changes are taking place in the structure of $Cu_2(CN)_2$. There is a clear difference of about 150 cm^{-1} between the ν_{asym} peak of $Cu_2(CN)_2$ and the peak position of the new absorption feature. To identify the origin of these heat-induced IR absorption peaks it is pointed out that heat treatment of compounds containing the C≡N group is known to result in polymerization/cyclization converting it to C=N (for example fumaronitrile, maleonitrile,[12] and poly(acrylonitrile)[13]). In the case of fumaronitrile and maleonitrile it was reported[12] that upon polymerization the C≡N absorption at 2250 cm^{-1} vanished and a new characteristic peak at 2190–2195 cm^{-1} was observed which was attributed to conjugated C=N system. In the case of poly(acrylonitrile) also, upon thermal degradation, an IR peak at 2185 cm^{-1} was observed[14] for which a possible assignment to conjugated carbon–nitrogen system was indicated.

In our measurements, the appearance of the new peaks at lower frequencies indicates the reduced order of the bond. We, therefore, assign the new features to C=N vibration in the polymerized ring structure produced by the heating of $Cu_2(CN)_2$. The main peak of this structure lies between 2004 and 2017 cm^{-1}. As the material is heated beyond 290 °C the relative abundance of C≡N decreases and C=N increases because of increase in the amount of cyclized product. From the relative peak intensities of the ν_{asym} of C≡N and C=N, the relative amount of the cyclized product and the parent compound can be estimated. These estimates give an amount of about 20% at 290 °C, 40% at 300 °C, and 90–95% at 350–370 °C. The presence of the shoulder at 1974–1978 cm^{-1} and the broadening of the low-wavenumber side of the new peak shows that there can be several cyclic products of different chain lengths and molecular weights differing from one another slightly in these respects.

The earlier mentioned unidentified peak at 2120 cm^{-1}, as seen in Figure 3, seems to remain uneffected upto a temperature of 370 °C while it also vanishes at 380 °C. It could, therefore, belong to some unknown impurity which oxidizes at 380 °C.

A close inspection of the IR absorption spectra in the range 400–650 cm^{-1} reveals that a peak around 525 cm^{-1} in the non-heat-treated material persists to about 350 °C and vanishes on further heat treatment. We assign this to the Cu–C peak which vanishes at the complete decomposition of the cyclized products (metal–carbon IR absorption lies in this region in cyanides[15]). Another peak in this region at 614–625 cm^{-1} appears at 260 °C and persists at higher temperatures. This is the Cu_2O peak.[16,17] A feature corresponding to CuO at[18] 500 cm^{-1} is also found at highest temperatures of treatment.

Thus we conclude that when $Cu_2(CN)_2$ is heated, it decomposes into several cyclic products which, upon continued heating, keep on changing slightly in structure etc. This process of cyclization is accompanied by the liberation of cyanogen gas. In nitrogen atmosphere this process goes until about 850 °C, terminating in the end product of pure Cu, while in an air atmosphere the cyclization process is terminated at 380 °C by oxidation into oxides of copper. The evidence in the case of air atmosphere is very strong, while for nitrogen atmosphere the evidence is only circumstantial. We conclude, therefore, on the basis of these observations that the thermal decomposition process of $Cu_2(CN)_2$ can probably be represented as follows:

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$$Cu_2(CN)_2 \xrightarrow{N_2} \text{cyclic products} \xrightarrow{N_2} 2Cu + (CN)_2 \quad (3)$$

$$2Cu_2(CN)_2 \xrightarrow{air} \text{cyclic products} \xrightarrow{air} 2(CN)_2 + 2CuO + Cu_2O \quad (4)$$

Coming back to the original motivation of this work, i.e., to probe why the use of $Cu_2(CN)_2$ as the starting copper compound for the synthesis of $YBa_2Cu_3O_{7-x}$ and $YBa_2Cu_4O_8$ results in better quality superconductors, the key to the issue seems to be the enhanced reactivity of the starting compounds in addition to their thorough mixing achieved by the melting of $Cu_2(CN)_2$ in whatever form it exists at elevated temperatures. The polymerization of $Cu_2(CN)_2$ evidenced in the present study might be resulting in the enhanced reactivity of this material with other compounds used for the synthesis of the two superconductors. This is indicated clearly in the case of the preparation of $YBa_2Cu_4O_8$ where the slow rate of reaction had been a problem in the earlier recepies. It was also observed[19] that $Cu_2(CN)_2$ based preparation of $YBa_2Cu_3O_{7-x}$ results in strong reaction of the fired material with the alumina boats which is not the case with CuO-based preparation, which again points to an enhanced reactivity. Looking at Figure 3, it can be seen that going from curve g to h, an increase of only 10 °C in temperature results in sudden complete oxidation of the material. This shows that the process of polymerization converts $Cu_2(CN)_2$ to a higher energy state which, then, requires a very small additional energy to react strongly with oxygen.

It is not possible, on the basis of the present study alone, to exactly describe the reactions taking place during the high-temperature (835–900 °C) synthesis of the superconductors when $Cu_2(CN)_2$ is premixed with compounds of Ba and Y in the presence of oxygen. However, the present results indicate that the polymerization of $Cu_2(CN)_2$ might enhance reactivity of the starting compounds facilitating the chemical reactions taking place.

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