Reduction of Copper(II) Acetate with Copper Metal in Heterogeneous Systems

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The thermal decomposition of copper(II) acetate has been proposed by several workers as a useful method for the synthesis of pure copper(I) acetate [1–3]. This method, however, suffers from several drawbacks. The major products of the decomposition are cuprous oxide and acetic acid; in contrast, the copper(I) acetate is obtained in low yields ($< 5\%$) together with some acetone and carbon dioxide. Under oxygen free conditions and in solvents that are capable of solvating copper(I) more effectively than water, copper(II) can be reduced to copper(I) with copper metal. Copper(I) acetate was synthesized in this manner and isolated from a pyridine solution [4]. Single crystals of copper(I) acetate that were suitable for an X-ray structure determination were obtained when dry acetonitrile was used as a solvent instead of pyridine. Copper(II) acetate has been reduced in a homogeneous system by employing hydrazine hydrate and hydroxylamine acetate as reducing agents [3].

All the synthetic methods described above give products that require extensive purification. Moreover, the copper(I) acetate often undergoes rapid oxidation on exposure to the atmosphere because any solvent in contact with the copper(I) acetate absorbs water vapor which promotes the conversion of copper(I) to copper(II) acetate in air.

A simple heterogeneous gas phase reaction for the synthesis of extremely pure copper(I) acetate in high yields is described below. No solvents are required in the synthetic procedure and the product is relatively stable in air. A mechanism for the reduction of copper(II) to copper(I) with copper metal in heterogeneous systems has also been proposed.

Experimental

Synthesis of Copper(I) Acetate

Cupric acetate hydrate, [$Cu_2(CH_3COO)_4 \cdot 2H_2O$, Mallinckrodt A.R.], (0.25 g) was mixed with electrolytic copper dust (Fisher purified), (0.50 g) and finely ground with the aid of a mortar and pestle. The mixture was placed in a sublimation apparatus in which sublimation could be carried out at reduced pressures and elevated temperatures. The apparatus was evacuated and its temperature slowly increased to 100 °C with a paraffin wax bath. The cupric acetate was dehydrated in approximately 15 minutes. The temperature was then raised rapidly and maintained at 180–190 °C for several hours. Copper(I) acetate, $Cu_2(CH_3COO)_2$, collected on the 'cold finger' in the form of a white solid (0.20 g).

Synthesis of Copper(I) Acetate Labeled with Radioactive ^{64}Cu

Two samples of copper dust (0.5 g) in polyethylene vials were irradiated for 30 minutes at 100 kw in a Triga Mark I reactor. The samples were cooled for 30 minutes and one of the samples was used to make up seven standards. The second sample was mixed with copper(II) acetate, finely ground and sublimed at 180–190 °C under reduced pressure as described above. The product that collected on the 'cold finger' was weighed and the emitted radiation was counted with a Ge–Li detector (Nuclear Diodes Model LGCC 9-6-2.0). Count rates for the sample and standards were obtained directly from an Omega-1 multichannel analyzer (Canberra Industries Model 4100). Peak areas were calculated and corrected for background for the 0.511 Mev positron annihilation peak in the decay of ^{64}Cu($t_{1/2}$ = 12.9 h). The amount of ^{64}Cu from the copper metal that was incorporated in the copper(I) acetate was calculated from the linear plot of count rate *versus* weight of the ^{64}Cu standards that bracketed the sample (Figure 1).
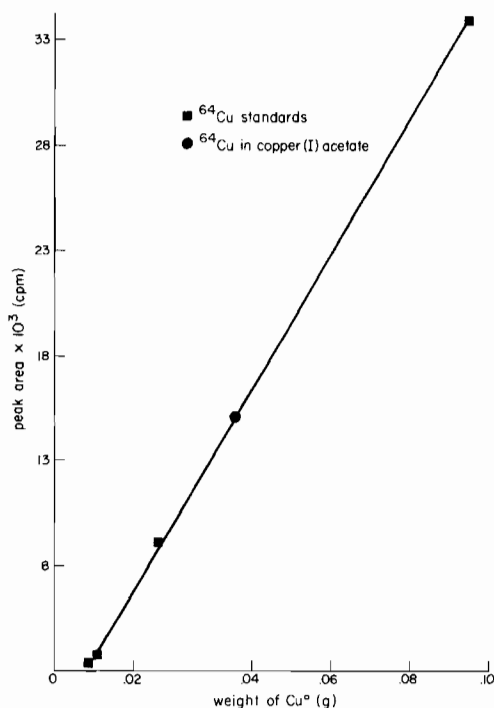

Fig. 1. Calibration curve for the determination of radioactive ^{64}Cu incorporated into copper(I) acetate.

TABLE I. Fractional ^{63}Cu Content in Copper Acetates.

Ion	Non-enriched	Enriched	Reaction Product	Per Cent Incorporation of Copper from Copper Metal
$Cu_2(CH_3CO_2)_2^+$	0.692	0.937	0.838	45
$Cu_2(CH_3CO_2)CO_2^+$	0.686	0.933	0.829	42
$Cu_2(CH_3CO_2)^+$	0.683	0.941	0.832	42
Cu_2^+	0.688	0.932	0.829	42
Cu^+	0.679	0.933	0.820	44

Synthesis of Copper(I) Acetate Enriched with the ^{63}Cu Isotope

Isotopically enriched copper(II) acetate was synthesized by heating 55 mg of ^{63}CuO in 400 mg of acetic acid and 3 ml of water to 80 °C. The blue product that was obtained after 48 hours was dried *in vacuo* and recrystallized from acetonitrile. The isotopically enriched copper(II) acetate was dissolved in pyridine and reduced with copper metal [4] to give copper(I) acetate that was enriched with the ^{63}Cu isotope.

Mass spectra of copper(II) acetate, isotopically enriched copper(II) acetate, and isotopically enriched copper(I) acetate were obtained with a Hitachi Perkin Elmer RMU-6E double-focussing mass spectrometer with an electron energy of 70 eV and an ionizing current of 80 μamp. The compounds were introduced into the ionization chamber by the direct insertion method and temperatures varying between 100° and 150 °C were used to obtain the spectra.
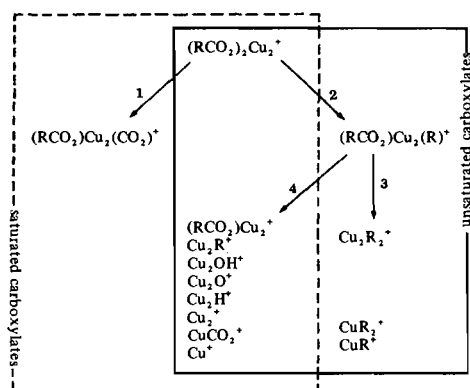

Fig. 2. Fragmentation pattern of copper carboxylates.

Results and Discussion

The fragmentation pattern of copper carboxylates is shown in Figure 2. The natural abundances of ^{63}Cu and ^{65}Cu are in the fractional ratio of about 0.691:

0.309. A fragment that contains one copper atom will have a doublet in which the M:(M + 2) intensity is 0.691:0.309. If the fragment contains two copper atoms, three peaks will be found in which the M: (M + 2):(M + 4) intensities are 0.477:0.427:0.096. These intensity ratios can be obtained from the binomial expansion, $(p + q)^n$, where p and q are the fractions of ^{63}Cu and ^{65}Cu present and n the number of copper atoms in the fragment. For the non-enriched copper, $p = 0.691$ and $q = 0.096$.

The fractional intensities of the three peaks that were obtained in the mass spectra of the isotopically enriched copper(II) acetate and the isotopically enriched copper(I) acetate were measured, and the abundances of the ^{63}Cu and ^{65}Cu isotopes in each of the prominent mass fragments were obtained. From these values it was possible to calculate the amount of copper metal that was incorporated in the copper(I) acetate by the reduction of the isotopically enriched copper(II) acetate in pyridine solution with copper metal (Table I).

The calculated values in Table I show that a large percentage of copper metal has been incorporated in the copper(I) acetate which was the reaction product that was isolated from the pyridine solution. The copper(II) species in the pyridine solution is brought into contact with the surface of the copper metal, thereby promoting the reduction reaction, which is the reverse of the reaction in which the disproportionation of the copper(I) species occurs.

$$2Cu(I) \xrightleftharpoons[]{Pyridine} Cu(II) + Cu^0$$
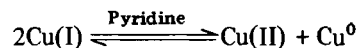
The pyridine solvates the copper(I) species that is formed and effectively stabilizes it.

When copper(I) acetate was synthesized in about 65% yield from copper(II) acetate and radiolabeled copper metal in the absence of any solvent or water of hydration, approximately 50% of the radiolabeled copper metal was incorporated in the copper(I) acetate. The mechanism for this reaction is quite different from that described by Angel [2], in which copper(I) acetate was synthesized by the thermal decomposition of copper(II) acetate. It is inconceivable that the reaction between the anhydrous solid copper

(II) acetate and solid copper metal can give such a high yield of copper(I) acetate. A gas-solid reaction however, can result in the formation of copper(I) acetate in high yield. The reaction pathway is essentially the reverse of the disproportionation reaction of copper(I). Anhydrous copper(II) acetate has a considerable vapor pressure at elevated temperatures and can abstract radioactive ^{64}Cu atoms by reaction with the surface of the radiolabeled copper metal. Copper–copper bonds are formed *via* an electron transfer reaction between the ^{64}Cu atoms in the copper metal and the copper atoms in the copper(II) acetate thereby resulting in the disruption of the copper–copper bond and some of the copper–copper bonds in the copper(II) acetate. The resulting product is a highly volatile dimeric copper(I) acetate in which half the copper atoms are radioactive ^{64}Cu. This product condenses on the cold finger of the sublimation apparatus and forms a colorless polymeric solid. The unreacted anhydrous copper(II) acetate, which is much less volatile than the copper(I) acetate, forms a blue ring just above the reaction mixture in the sublimation apparatus. The copper(I) acetate prepared in this manner is extremely pure and relatively stable. It decomposes slowly in air over a period of several days.

References

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