Transition Met. Chem. 3, 342–344 (1978)
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Pt : I ratio of 1 : 1. The solution was stirred for 2 h at room temperature and then filtered, and the residue was repeatedly washed with mother liquor. Washing with EtOH, MeOH, Me_2CO, Et_2O, CCl_4, $CHCl_3$, CH_2Cl_2 or DMF gave solutions of iodine, leading ultimately to the regeneration of the starting material from the residue. Attempts to recrystallise the product therefore failed, and the residues were analysed after air-drying (see Table). Iodine uptake was measured by titration with thiosulphate.

All the compounds are bronze in colour, strongly reflecting and microcrystalline, but the crystals were not suitable for single crystal x-ray structure determination. Crystals of $Pt(N{-}N)X_2$ suitable for x-ray structural analysis were used as starting material in an attempt to obtain products suitable for crystallographic examination but without success. Infrared spectra were measured in nujol mulls on CsI discs using a Perkin Elmer 437 spectrophotometer.

Acknowledgements

Dr. L. Hullet of Cape Town University and Dr. J. A. van Wyk of Witwatersrand University, Johannesburg are thanked for their assistance with the magnetic susceptibility and e.p.r. measurements respectively.

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Copper(I) Nitrile Complexes, Part IV*. Mechanism of Copper(II) Acetate and Trifluoroacetate Reduction by Copper in Acetonitrile in the Presence of Free Carboxylic Acid

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(Received April 24th, 1978)

Summary

Copper(II) carboxylates, $Cu(O_2CR)_2$, R = Me or CF_3, in acetonitrile are reduced to copper(I) complexes by copper metal in the presence of RCO_2H. No reduction however, was observed in the absence of the acid. The CuO_2CMe, $Cu(O_2CCF_3)(MeCN)$ and $Cu(O_2CCF_3)(CF_3CO_2H)_2 \cdot (MeCN)_4$ complexes were isolated from the reaction mixture. Copper(I) species are stabilized by coordination of diacetamide or isoamide, a reaction product of the free acid and nitrile. Copper(I) carboxylate is obtained after decomposition of the coordinated species to the original acid and nitrile.

Introduction

Aquated copper(I) ion disproportionates into copper(II) and copper metal, however ligands such as alkenes however, drive the reaction in the direction of the copper(I) ion(1). The relative stabilization effect of a ligand on copper ions is recognized easily by the appearance or disappearence of the blue aquated copper(II)(1–4).

Copper(II) acetate is reduced to copper(I) acetate in acetonitrile by copper metal in the presence of acetic acid(5, 6). In the absence of the acid, no reduction is detectable. On the other hand, copper(I) acetate thus formed disproportionates into the starting materials in acetonitrile or in acetic acid. This unusual behavior of the complexes is the subject of this investigation.

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* Part III: R. J. Hurtado, R. V. Casillas and T. Ogura, *Transition Met. Chem.*, *2*, 91 (1977).

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Experimental

Materials

AcOH, trifluoroacetic acid (TfOH) and MeCN were dried over P_4O_{10} and distilled *in vacuo* before use. $Cu(OAc)_2$ and $Cu(OTf)_2$ were prepared and purified as described previously(6).

Since all the investigated copper(I) complexes reacted readily with oxygen and atmospheric moisture, all the reactions were performed *in vacuo*.

Attempted reduction of $Cu(OAc)_2$ in the presence of NaOAc

Dehydrated $Cu(OAc)_2$ (2.0 mmol) and NaOAc (2.0 mmol) in MeCN were stirred with an excess of copper for one week. The resultant mixture was decanted from the copper metal into iron(III) in order to determine the amount of copper(I) present by the ferrous-ceric titration; however, no copper(I) was detected.

Reduction of $Cu(OAc)_2$ in MeCN

A MeCN solution of $Cu(OAc)_2$ was stirred in the presence of copper metal for 70 h at room temperature, but no reaction was observed. However, $Cu(OAc)_2$ (0.6 g) dissolved in a mixture of AcOH (1 cm^3) and MeCN (5 cm^3) was reduced by copper within 2 h. The resultant mixture was filtered through a sintered glass frit, and the solvent was evaporated from the filtrate and condensed in a dry ice : Me_2CO cold trap. A powdery crystalline product was obtained. (Found: Cu, 51.3. $C_2H_3CuO_2$ calcd.: 51.8%.) It was confirmed that MeCN does not coordinate to solid CuOAc; thus a small amount of MeCN was introduced to CuOAc, but no vapor pressure depression of MeCN was observed.

Reduction of $Cu(OTf)_2$ in MeCN

Although $Cu(OTf)_2$ did not react with copper metal, it was reduced in the presence of free TfOH. A mixture of $Cu(OTf)_2$ (1 g), TfOH (1 cm^3), MeCN (10 cm^3) and an excess of copper was stirred until the blue of copper(II) disappeared (1-3 h). The reaction mixture was treated as described above for the $Cu(OAc)_2$: Cu system. The filtrate was maintained at 25° while the excess of solvent was transferred into a cold trap maintained at 0°, by vacuum distillation during 50 h. The remaining complex showed an equilibrium ligand vapor pressure. Hence, some of the ligands in the coordination sphere of the complex were freed by condensing the vapor phase in a dry ice : Me_2CO cold trap. The spectrum of the condensate was consistent with a mixture of MeCN and TfOH. The complex was analyzed titrimetrically (Found: Cu, 10.9; TfOH, 38.7. CuOTf · 4 MeCN · 2 TfOH calcd; Cu, 11.2; TfOH, 40.1%). A powdery white complex remained (Found: Cu, 29.2. $CuCO_2CF_3$ · MeCN calcd.: Cu, 31.0%).

Reduction of $Cu(OAc)_2$ in the presence of diacetamide

Diacetamide (0.350 mmol) in MeCN (4 cm^3) was added to a mixture of $Cu(OAc)_2$ (2.00 mmol) and copper (5 mmol) and the mixture was stirred overnight, and then filtered through a sintered glass filter. The copper metal remaining on the filter was washed thoroughly with the solvent, the excess of solvent was removed *in vacuo*, the copper metal weighed and the copper which dissolved during the reaction determined by difference (Found: 11.4 mg, 0.179 mmol). In a duplicate experiment: diacetamide (1.011 mmol) caused oxidation of copper (0.553 mmol).

Results and Discussion

We have demonstrated that copper(II) acetate and trifluoroacetate in acetonitrile do not react with copper metal and that the addition of free carboxylic acid to the reaction mixture causes stoichiometric reduction to the corresponding copper(I) carboxylate. Hence, it is of interest to elucidate the role of the carboxylic acids.

Copper(II) acetate in acetic acid has been studied widely(7–12). The dimeric structure found in the solid state persists in acetic acid as well as in nonaqueous solvents. $Cu_2(OAc)_4$ in acetic acid reacts with the acetate anion according to Equations (1) and (2):

$$Cu_2(OAc)_4 + 2\ LiOAc \rightleftharpoons Li_2Cu_2(OAc)_6 \quad (1)$$

$$Cu_2(OAc)_4 + 4\ LiOAc \rightleftharpoons 2\ Li_2Cu(OAc)_4 \quad (2)$$

The equilibrium constants for reactions (1) and (2) at room temperature were $10^{0.9}$ and $10^{-0.4}$, respectively(9). In order to examine the possible participation of the species produced *via* reactions (1) and (2), sodium acetate was added to a reaction mixture of copper(II) acetate and copper metal in acetonitrile, however, such species did not cause any reduction of copper(II) acetate.

Hydrochloric and perchloric acids also react with copper(II) acetate in acetic acid forming a monomeric species according to (3):

$$Cu_2(OAc)_4 + 2\ HX \rightleftharpoons 2\ Cu(OAc)X + 2\ AcOH \quad (3)$$

The equilibrium constant for reaction (3) has been reported as $10^{3.5}$ ($X = ClO_4$) and $10^{4.7}$ (X = Cl) at room temperature(10). A similar reaction might be expected to occur in our experiments; a carboxylic acid in acetonitrile dissociates partially and the resultant hydrogen ion may attack the carboxylate moiety of the copper(II) carboxylate dimer forming monomeric species, which may be attacked subsequently by copper metal(12).

Copper(I) acetate disproportionates to copper metal and copper(II) acetate in acetic acid slowly at room temperature and rapidly at elevated temperature. Acetonitrile also catalyzes the disproportionation. Crystalline copper(I) acetate precipitates copper metal on heating to 150°. These findings show that copper(I) acetate, even though it is present in an acetic acid or acetonitrile medium, is less stable than a system consisting of copper(II) and metal. Hence, copper(I) acetate is the thermodynamically unfavorable state; it exists as a metastable state in the crystalline form.

Why can we isolate the copper(I) carboxylates from the reaction system? The crystalline product of copper(I) trifluoroacetate, CuOTf · 2 TfOH · 4 MeCN, suggests a possible answer to the question. This complex has some remarkable features: (a) there are six neutral organic molecules and one carboxylate anion per copper atom, (b) the complex has an equilibrium vapor pressure of trifluoroacetic acid and acetonitrile, (c) removal of the vapor phase at 40° *in vacuo* leaves the complex, CuOTf · MeCN, and further heating at a higher temperature results in the formation of copper(I) trifluoroacetate. Disproportionation of the final trifluoroacetate is accelerated by the presence of free acid or of nitrile, or by increasing the temperature, as seen with the acetate.

Copper(I) trifluoroacetate is less stable than a mixture of the copper(II) compound and copper metal. The former however, is stabilized by coordination of a ligand, L, consisting of the acid and the nitrile, since neither the acid nor the nitrile, separately, stabilizes the copper(I) state relative to the mixture of Cu + $Cu(OAc)_2$. The ligand, L, decomposes partially to the volatile starting materials which are removed *in vacuo*.

Thus, copper(I) acetate in a mixture of acetonitrile and acetic acid must be stabilized by a special ligand. Diacetamide was isolated from a reaction mixture of acetonitrile and acetic acid at room temperature catalyzed by hydrogen chloride or copper(I) acetate. A similar product was detected with trifluoroacetic acid by its i.r. spectrum. (NH stretch, 3300–3500 cm^{-1}) and its electronic spectrum (230 nm, ϵ = *ca.* 10^2) but it was not isolated.

One mole of diacetamide causes reduction of a half mole of $Cu(OAc)_2$ with copper metal, however, the isolated product was copper(I) acetate contaminated with a small amount of copper(II) acetate and copper. The stoichiometry of the reaction is:

$$\mathrm{Cu(OAc)_2 + Cu + 2\ MeCN \cdot AcOH}$$

$$\downarrow$$

$$\mathrm{2\ CuOAc(MeCN \cdot AcOH)\ (in\ solution)}$$

$$\downarrow$$

$$\mathrm{2\ CuOAc + 2\ MeCN + 2\ AcOH}$$

However, we believe that the rate of reduction of copper(II) ion in the presence of the amide is almost the same as in the acetonitrile : acetic acid system. Thus, we can not discard the possible participation of the *c*-acetoxyimine, MeC(NH)OAc, which has been frequently cited as an intermediate in the formation of diacetamide from acetonitrile and acetic acid but has yet to be isolated(13). These findings must be verified by an x-ray structure determination of CuOTf · 2 TfOH · 4 MeCN.

Acknowledgements

We thank Dr. Q. Fernando, University of Arizona, for valuable discussions.

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