

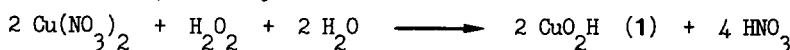
# A NEW OXIDIZING COPPER REAGENT : $\text{CuO}_2\text{H}$ PREPARATION AND PRELIMINARY STUDY OF REACTIVITY

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**Abstract :** Copper(II) ion and  $\text{H}_2\text{O}_2$  in slightly acidic water give rise to an insoluble copper derivative 1 (raw formula  $\text{CuO}_2\text{H}$ ), new oxidizing reagent for e.g. alcohols, phenylacetic acids, primary amines, triphenylphosphine, and toluene .

The reaction between cupric acetate and dilute hydrogen peroxide has been claimed<sup>1</sup> to afford  $\left\{ \left[ \text{Cu}^{\text{II}}(\text{OH}) \right]_2 (\text{OOH})(\text{OAc}) \right\}_n$  (the only reported stable hydroperoxy copper(II) compound), on the basis of the copper content of the air-dried product. This EPR silent compound presents, in fact, the raw formula :  $\text{CuO}_2\text{H}$  (1), once thoroughly vacuum-dried over phosphorus pentoxide ; the acetate anion is absent, like with other carboxylates we have tried. Moreover, the same compound is obtained from various inorganic copper salts, e.g. copper(II) nitrate<sup>2</sup>, in 80% yield:



Nitric acid must be neutralized by added  $\text{KHCO}_3$  to maintain  $\text{pH} \approx 5$ .

This new copper compound 1 may be formulated either as a trivalent copper oxo-hydroxide with a monomeric :  $\text{Cu}(\text{III})(\text{O})\text{OH}$  or with a polymeric structure :  $\left[ \text{O}-\text{Cu}(\text{III})(\text{OH})- \right]_n$  or as a peroxyhydroxide binuclear copper(II) compound :  $\text{HO}-\text{Cu}(\text{II})-\text{O}-\text{O}-\text{Cu}(\text{II})-\text{OH}$ . Recently,  $\text{Cu}(\text{III})$  compounds have been investigated by Margerum<sup>3</sup> and  $-\text{Cu}(\text{II})-\text{O}-\text{O}-\text{Cu}(\text{II})-$  species by Karlin<sup>4</sup>. At the present time, we have no conclusive spectroscopic data, nevertheless the whole of redox properties of this new compound 1 seems to be in better agreement with a trivalent copper structure than with the copper(II) peroxide one :

For example, compound 1 rapidly reacts with water in dilute sulfuric acid, like  $\text{Cu}(\text{III})$  species<sup>5,6</sup>, with formation of hydrogen peroxide ( $\text{TiCl}_4$  test) and dioxygen release ; dioxygen should not be produced by acid hydrolysis of some copper(II) peroxy structure which would only give rise to  $\text{Cu}(\text{II})$  sulfate and hydrogen peroxide<sup>7</sup>, nearly unreactive in this pH range<sup>8</sup>.

Once the  $\text{H}_2\text{O}_2$  produced is destroyed by a temporary pH rise with sodium hydroxide, the copper content of 1, as  $\text{Cu}(\text{II})$ , is titrated by the iodide-thiosulfate method<sup>9</sup> ; average results :  $\text{Cu}\%$  :  $66 \pm 0.5\%$  (calculated : 65.81% for  $\text{CuO}_2\text{H}$ ) . If compound 1 is directly added to a iodide solution, no more dioxygen evolves and compound 1 itself is quantitatively titrated : the average result is double :  $132 \pm 1\%$  in agreement either with  $\text{Cu}(\text{III})$  or  $\text{Cu}(\text{II})-\text{OO}-$  structures.

The dark brown compound 1 is stable for weeks at room temperature in a dry atmosphere. At  $150^\circ\text{C}$  it very rapidly decomposes into cupric oxide  $\text{CuO}$  (100%), dioxygen and water.

As shown in the Table, copper compound 1 also gives rise to several reactions we have previously obtained on organic substrates (alcohols<sup>10</sup>, carboxylic acids<sup>11</sup>, primary amines<sup>12</sup>) from the interaction of monovalent copper and molecular oxygen. These oxidations precisely supposed the intervention, via transient copper(II) peroxo intermediates, of trivalent oxo-copper  $\text{-Cu(III)=O}$  ("cupryl species")<sup>13</sup>. Moreover this new oxidizing reagent not only readily reacts with triphenylphosphine, what is not surprising, but oxidizes toluene, and in higher yield than bis(biuretato) Cu(III) in acid medium<sup>14</sup> do. Structural features as well as synthetic usefulness of this versatile oxidizing reagent, which acts as a source of reactive trivalent copper, are currently under investigation.

Substrate	Solvent / temp.(°C) / time (h)	Isolated product (yield %)
$\text{CH}_3\text{CH}_2\text{OH}$	excess substrate / 45 / 4 (*)	$\text{CH}_3\text{CHO}$ (100) as 2,4 DNP
$\text{Ph}_3\text{CHCO}_2\text{H}$	$\text{CH}_3\text{CN}$ / 75 / 20 (*)	Benzophenone (55)
$\text{Ph}_2\text{CHNH}_2$	$\text{CH}_3\text{CN} + \text{H}_2\text{O}$ (50-50) / 20 / 24	Benzaldehyde (60)
$\text{P(Ph)}_3$	$\text{CH}_3\text{CN}$ / 70 / 6	$\text{O=P(Ph)}_3$ (100)
$\text{Ph-CH}_3$	excess substrate / 70 / 3 (*)	benzyl alcohol (60) + benzaldehyde (10)

(\*) sonicated with a 30 W probe.

Table : Organic substrates oxidation by  $\text{CuO}_2\text{H}$  (1)

#### References and notes :

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- To a cooled (10°C) solution of copper nitrate trihydrate (12 g) in water (200 ml) are added under stirring 30% hydrogen peroxide (20 ml) then, in 10 minutes, a solution of  $\text{KHCO}_3$  (7.5 g) in water (50 ml). The precipitate, initially colloidal, turns progressively granular; it is collected by filtration on a sintered glass, and thoroughly washed with ice-cooled water (3x 50 ml). Vacuum-drying over KOH then phosphorus pentoxide (such a powerful desiccant must be used) yields 3.8 g of 1.
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