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A NEW OXIDIZING COPPER REAGENT : CuO_2H
PREPARATION AND PRELIMINARY STUDY OF REACTIVITY

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***Abstract** : Copper(II) ion and H_2O_2 in slightly acidic water give rise to an insoluble copper derivative 1 (raw formula CuO_2H), 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[1] to afford $\left\{\left[Cu^{II}(OH)\right]_2(OOH)(OAc)\right\}_n$ (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 : CuO_2H (**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[2], in 80% yield:

$$2\ Cu(NO_3)_2 + H_2O_2 + 2\ H_2O \longrightarrow 2\ CuO_2H\ (\mathbf{1}) + 4\ HNO_3$$

Nitric acid must be neutralized by added $KHCO_3$ to maintain $pH \simeq 5$.

This new copper compound **1** may be formulated either as a trivalent copper oxo-hydroxide with a monomeric : Cu(III)(O)OH or with a polymeric structure : $\left[\text{-O-Cu(III)(OH)-}\right]_n$ or as a peroxyhydroxide binuclear copper(II) compound : HO-Cu(II)-O-O-Cu(II)-OH. Recently, Cu(III) compounds have been investigated by Margerum[3] and -Cu(II)-O-O-Cu(II)- species by Karlin[4]. 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 Cu(III) species[5,6], with formation of hydrogen peroxide ($TiCl_4$ test) and dioxygen release ; dioxygen should not be produced by acid hydrolysis of some copper(II) peroxy structure which would only give rise to Cu(II) sulfate and hydrogen peroxide[7], nearly unreactive in this pH range[8].

Once the H_2O_2 produced is destroyed by a temporary pH rise with sodium hydroxide, the copper content of **1**, as Cu(II), is titrated by the iodide-thiosulfate method[9] ; average results : Cu% : 66 ± 0.5% (calculated : 65.81% for CuO_2H) . 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 ± 1% in agreement either with Cu(III) or Cu(II)-OO- structures.

The dark brown compound **1** is stable for weeks at room temperature in a dry atmosphere. At 150°C it very rapidly decomposes into cupric oxide 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[10], carboxylic acids[11], primary amines[12]) *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 -Cu(III)= O ("cupryl species")[13]. 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[14] 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 %)**
CH_3CH_2OH	excess substrate / 45 / 4 (*)	CH_3CHO (100) as 2,4 DNP
Ph_2CHCO_2H	CH_3CN / 75 / 20 (*)	Benzophenone (55)
$PhCH_2NH_2$	$CH_3CN + H_2O$ (50-50)/ 20 / 24	Benzaldehyde (60)
$P(Ph)_3$	CH_3CN / 70 / 6	$O{=}P(Ph)_3$ (100)
$Ph\text{-}CH_3$	excess substrate / 70 / 3 (*)	benzyl alcohol (60) + benzaldehyde (10)

(*) sonicated with a 30 W probe.

Table : Organic substrates oxidation by CuO_2H (**1**)

References and notes :

1 Ochiai, E.-I.; *Inorg.Nucl.Chem.Letters*, **1973**, *9*,987.

2 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 $KHCO_3$ (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** .

3 Margerum, D.W.; Owens, G.D.;*"Metal ions in biological systems"*, H.Sigel Editor, M. Dekker Inc., **1981**, *12*, 75, and references cited therein.

4 Tyeklar, Z.; Karlin, K.D.; *Acc.Chem.Res.*, **1989**, *22*, 241, and references cited therein

5 Anbar, M.; *Adv.Chem.Ser.*,**1965**, *49*, 143.

6 Meyerstein, D.; *Inorg.Chem.*, **1971** , *10*,638.

7 Tyeklar, Z.; Paul, P.P.; Jacobson, R.R.; Farooq, A.; Karlin, K.D.; Zubieta, J.; *J.Am.Chem.Soc.*, **1989** , *111*, 388.

8 Shpitalskii, E.I.; Konovalova, B.A.; *Žurnal Russkogo Fiziko- chimičeskogo Obščestva. Cast' Chimičeskaja* , **1930** , *62*, 1033 . *Chem.Abstr.*, **1931** , *25*, 3230.

9 Charlot, G.; *" Analyse quantitative minérale"*, Masson (Paris), **1961**, 4th ed. 717.

10 Capdevielle, P.; Audebert, P.; Maumy, M.; *Tetrahedron Lett.*,**1984** , *25*, 4397.

11 Toussaint, O.; Capdevielle, P.; Maumy, M.; *Tetrahedron Lett.*, **1984** , *25*, 3819.

12 Capdevielle, P.; Lavigne, A.; Maumy, M.; *Tetrahedron*, **1990**, *46*, 2835.

13 Capdevielle, P.; Maumy, M.; *l'Actualité Chimique*,**1986**, april, 5.

14 Jönsson, L.; *Acta Chem. Scand. B*, **1981** , *35*, 683.

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