Copper-catalysed Oxidation of Hydroxy Compounds by *tert*-Butyl Hydroperoxide Under Phase-transfer Conditions

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In the presence of quaternary ammonium phase-transfer agents copper salts catalyse the selective oxidative dehydrogenation of alcohols and hydroxy acids by *tert*-butyl hydroperoxide in aqueous–organic two-phase systems.

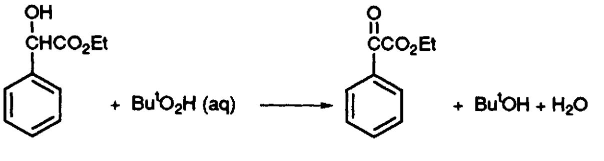
Several Ru^{II}[1–3] and Rh[4] phosphine complexes have recently been proposed as catalysts for the non-radical oxidative dehydrogenation of alcohols and hydroxy compounds to the corresponding ketones or aldehydes utilizing *tert*-butyl hydroperoxide (TBHP) as the primary oxidant. The active species in these systems is, reportedly, an oxometal intermediate which abstracts a hydride from the substrate at the rate-limiting step.[5]

In addition to the shortcomings associated with the application of precious metal catalysts, the above systems suffer from a parallel non-productive catalytic decomposition of TBHP which necessitate slow addition of the reagent to the reaction mixture, and also from instability of phosphine ligands which are simultaneously oxidized to phosphine oxides (though without loss in activity).[5] It has also been found that solvents in which TBHP is less stable are preferred for catalytic oxidation of alcohols and other substrates.[4]

We have now observed that by using an aqueous–organic two-phase system and in the presence of quaternary ammonium phase-transfer catalysts, cuprous or cupric salts, and even copper metal, are active catalyst precursors, which generate active catalytic systems for the TBHP oxidation of alcohols. In this novel catalytic system no decomposition of TBHP is observed and consequently no excess of reagent nor its gradual addition is required. A related copper assisted system has recently been reported by Barton *et al.*[6] but in this Gif-type reaction a stoichiometric amnount of copper salt is required.

In a typical example we have mixed ethyl mandelate (4.72 g, 26.20 mmol) in methylene chloride (10 ml) with TBHP (3.40g; 70% in water, 26.20 mmol) in the presence of 0.15 g tetra-*n*-butylammonium bromide (TBAB) (0.79 mmol, 3 mol%) and $CuCl_2$ (35.2 mg; 0.26 mmol, 1 mol%) at 25 °C for 24 h. Gas chromatographic analysis of the reaction mixture showed that 96% of the ethyl mandelate has been converted to ethyl benzyl formate with 100% selectivity, Scheme 1.

Oxidation of ethyl lactate to ethyl pyruvate, 1-phenylethanol to acetophenone and cyclooctanol to cyclooctanone proceed with a similar high selectivity, though with lower rate (60, 75 and 53% conversions respectively after 24 h). The addition of solvent is not critical, on the contrary, faster reaction rates are observed in the absence of added solvent. The presence of water is, on the other hand, important. Attempts to separate TBHP from water by extraction prior to the reaction (according to older procedures[7]) resulted in faster decomposition of the reagent and, consequently, in lower yields.



Scheme 1 *Reagents and conditions*: $CuCl_2$ (1 mol%), TBAB (3 mol%) CH_2Cl_2, 25 °C, 24 h, conversion 96%

The presence of both catalysts is essential. No reaction is detected in the absence of copper and less than 4% conversion is observed without the TBAB. Ammonium salts that do not contain a halide counter anion, *e.g.* tetra-*n*-butylammonium hydrogensulfate, are not active in the process. Nevertheless, it is not the bromide anion alone which is responsible for the catalysis, other sources of bromide anion such as potassium bromide or tetramethylammonium bromide were inactive. CuCl, $CuCl_2$ and even copper powder (which is *in situ* transformed into a soluble copper compound) have all shown identical catalytic activity.

In the absence of a substrate the reaction takes a different course, namely catalytic decomposition of TBHP to oxygen and *tert*-butyl alcohol. This decomposition has been suggested to proceed *via* a free-radical chain mechanism (Haber–Weiss mechanism). The decomposition mechanism is fundamentally different from the normal oxidation process. For example we have observed that the $CuCl_2$/TBAB catalysed TBHP decomposition reaction stops altogether after 30% conversion and resumes activity only upon addition of a fresh batch of $CuCl_2$. The deactivated catalyst is also inactive in the normal oxidation reaction.

Attempts to substitute TBHP with 30% aqueous hydrogen peroxide in Scheme 1 have failed. Rapid decomposition of H_2O_2 has been the major process observed. UV–VIS spectra of the aqueous phase in Scheme 1 showed absorbance maxima at 233, 465 and 708 nm. The absence of the absorption band at λ_{max} = 813 nm, typical of Cu^{II}, indicates that this species is not an active intermediate in the catalytic cycle.

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