Copper Catalysed Reactions of Di-t-butyl Peroxide: Oxidative Carbonylation of Alcohols to give Dialkyl Carbonates, Oxalates, or Succinates

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Di-t-butyl peroxide, $(Bu^tO)_2$ is an efficient and convenient oxidant in the copper(I) chloride or copper(I) chloride–palladium(II) acetylacetonate catalysed oxidative carbonylation of alcohols to dialkyl carbonate, oxalate, or succinate esters.

Previously the oxidative carbonylation of alcohols has been carried out using a variety of oxidising agents including O_2 to give dialkyl carbonate,[1] oxalate,[2] or succinate[3] esters, [reactions (1)—(3)]. Copper or palladium species or both together have generally been used as the catalysts for these reactions.

$$2ROH + CO + \tfrac{1}{2}O_2 \rightarrow (RO)_2CO + H_2O \qquad (1)$$

$$2ROH + 2CO + \tfrac{1}{2}O_2 \rightarrow (ROCO)_2 + H_2O \qquad (2)$$

$$C_2H_4 + 2ROH + 2CO + \tfrac{1}{2}O_2 \rightarrow C_2H_4(ROCO)_2 + H_2O \qquad (3)$$

Dialkyl carbonates are potential alternatives to phosgene in a number of important industrial processes.[1] Dialkyl oxalates can be reduced to ethylene glycol and would therefore be intermediates in a syngas (CO–H_2) route to this compound.[2] We have now shown that $(Bu^tO)_2$ can act as the oxidant in oxidative carbonylation reactions so coproducing Bu^tOH, a useful gasoline supplement.[4]

On repeating the CuCl catalysed reaction of $(Bu^tO)_2$ with CO at 150 °C and 50 bar (1 bar = 10^5 Pa) in 2,2,4-trimethylpentane to give $MeCO_2Bu^t$ and Me_2CO[5] we observed that $(Bu^tO)_2CO$ is also formed in low yield. In the presence of excess of MeOH we found that the exothermic reaction gave

$(MeO)_2CO$ and Bu^tOH [reaction (4)] as well as some $MeCO_2Me$ and Me_2CO. However, if the reaction temperature is controlled (90—100 °C) 70—80% yields of $(MeO)_2CO$ can be achieved in the presence of excess of MeOH. The CuCl may be recovered and re-used. Similar reactions using O_2 [reaction (1)] lead to the formation of water which brings about catalyst deactivation and oxidation of CO to CO_2.[1] The use of $(Bu^tO)_2$ avoids these problems and the risks associated with $CO–O_2$ mixtures.

The carbonate ester synthesis can be carried out efficiently with a stoicheiometric amount of the alcohol by using pyridine or a substituted pyridine as a catalyst promoter, again under conditions of controlled temperature. With 2,6-dimethylpyridine (2,6-Me_2py) (92 °C, 50 bar), yields of $(MeO)_2CO$ and Bu^tOH were greater than 90% and 98% respectively. A relatively small amount (*ca.* 2%) of the mixed carbonate $(MeO)CO(OBu^t)$ was found, far less than if the carbonate esters and alcohols were at equilibrium (>30%). The 1:1 2,6-Me_2py–CuCl adduct, presumably a tetramer $[CuCl(2,6\text{-}Me_2py)]_4$,[6] could be isolated from the reaction mixture and reused as the catalyst. Substantial partial pressures of CO_2 or H_2 (10 bar) did not influence the reaction. When EtOH or Pr^iOH were used in place of MeOH the corresponding carbonate esters were made in good yield.

The rate of gas uptake in the MeOH reaction at 92 °C, 50 bar, shows a first order dependence on [CuCl] and $[(Bu^tO)_2]$. Rate and selectivity increase with CO pressure up to 50 bar. Under these conditions the half life of the carbonylation reaction is of the order of 1 h. This is a very much faster rate than that associated with normal thermal reactions of $(Bu^tO)_2$ involving O–O bond homolysis where a temperature of about 150 °C is required to give a comparable half life.[7]

When the same reactions are carried out in the presence of a palladium compound such as $Pd(acac)_2$ [(Hacac) = $MeCOCH_2COMe$] as well as CuCl, dialkyl oxalates [reaction (5)] and dialkyl carbonates are produced. Rate and selectivity to total carbonylation products are again enhanced by the presence of pyridines under conditions similar to those used for the carbonate synthesis. With MeOH, EtOH, or Pr^iOH the oxalate–carbonate ratio increased at lower reaction temperatures, higher CO pressures, and lower pyridine concentrations (less basic medium). Similar influences on oxalate–carbonate ratios are known in Pd catalysed oxidative carbonylations using other oxidants.[2,8] Thus at 92 °C, 50 bar with 1:1 CuCl–pyridine and $Pd(acac)_2$ methanol gave $(MeOCO)_2$ (80%) and $(MeO)_2CO$ (11%). Using Bu^tOH a very selective reaction gave $(Bu^tOCO)_2$ even at 25 bar (90% yield, oxalate–carbonate 30:1). Effectively this is a direct carbonylation of $(Bu^tO)_2$ [reaction (6)].

$$(Bu^tO)_2 + CO + 2MeOH \rightarrow (MeO)_2CO + 2Bu^tOH \quad (4)$$

$$2ROH + 2CO + (Bu^tO)_2 \rightarrow (ROCO)_2 + 2Bu^tOH \quad (5)$$

$$(Bu^tO)_2 + 2CO \rightarrow (Bu^tOCO)_2 \quad (6)$$

Preliminary experiments have demonstrated that $(Bu^tO)_2$ can be used as the oxidant in the synthesis of dimethyl succinate, at 50 °C, CO *ca.* 5 bar, C_2H_4 *ca.* 5 bar [reaction (7)]. The catalyst is similar to that for oxalate synthesis and some carbonate and oxalate ester can be formed in the reaction.

$$C_2H_4 + 2MeOH + 2CO + (Bu^tO_2) \rightarrow C_2H_4(MeOCO)_2 + 2Bu^tOH \quad (7)$$

$(Bu^tO)_2$ is thus a convenient alternative to O_2 for oxidative carbonylation reactions of alcohols with several advantages, in particular avoiding problems associated with the presence of water.

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