Copper Catalysed Reactions of Di-t-butyl Peroxide: Evidence for Copper(II) Alkoxide Intermediates and a Non-radical Reaction Mechanism

George E. Morris,* Douglas Oakley, David A. Pippard, and David J. H. Smith
BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN, U.K.

Reaction of di-t-butyl peroxide, $(Bu^tO)_2$, with Cu^I chloride species gives Cu^{II} alkoxy chlorides which are intermediates in the oxidative carbonylation reaction of alcohols to dialkyl carbonate, oxalate, or succinate esters and evidence is presented that these reactions do not involve free radicals.

We have reported[1] that $(Bu^tO)_2$ can be used as the oxidant in oxidative carbonylation reactions of alcohols catalysed by CuCl or CuCl–Pd(acac)$_2$ [(Hacac) = MeCOCH$_2$COMe], optionally in the presence of pyridines as promoters, to give dialkyl carbonate, oxalate, or succinate esters. We now present evidence that Cu^{II} alkoxides, species which can be intermediates in such reactions, are formed under these conditions and that activation of the peroxide does not appear to involve free radicals.

Reaction of CuCl with $(Bu^tO)_2$ in MeOH under N_2 or CO

(10 bar; 1 bar = 10^5 Pa) at 90 °C gave the insoluble compound $CuCl(OMe)$ and Bu^tOH [reaction (1)]. $CuCl(OMe)$ has been made before by several routes, including oxidation of CuCl with O_2 in MeOH[2] and is believed to be polymeric.[3]

$$\tfrac{1}{2}(Bu^tO)_2 + CuCl + MeOH \rightarrow CuCl(OMe) + Bu^tOH \tag{1}$$

Similar reactions using either O_2[4] or $(Bu^tO)_2$ (this work) in the presence of pyridine or substituted pyridines (py) gave 1 : 1 $CuCl(OMe)$–py adducts which are known to be methoxide bridged dimers $[CuCl(OMe)py]_2$ in the solid state[5] [reaction (2)]. These are moderately soluble in MeOH–py at 90 °C. We have found that at this temperature the adducts undergo a thermal decomposition to give the corresponding CuCl–py complex, $[CuClpy]_4$,[6] and we believe, MeOH oxidation products such as H_2CO [reaction (3)]. $CH_2(OMe)_2$ and HCO_2Me were detected in this reaction and acetaldehyde oligomers in a similar reaction using EtOH. These two steps, reaction of the peroxide with CuCl, [reaction (2)], to give a Cu^{II} alkoxide and its subsequent breakdown [reaction (3)], form the basis of a cycle for Cu catalysed peroxide decomposition. Copper species are known to lead to a modest increase in peroxide decomposition rates.[7] We found this also to be the case in the presence of pyridines.

Cu^{II} alkoxide species such as $CuCl(OMe)$ are known to react with CO to give $(MeO)_2CO$ and CuCl,[2,8] and in the presence of $Pd(acac)_2$ they react with CO to give oxalates[9] and with CO and alkenes to give succinates.[10] These and the present results suggest that Cu^{II} alkoxides are intermediates in Cu catalysed oxidative carbonylations using $(Bu^tO)_2$ as the oxidant. However, the rate of $(Bu^tO)_2$ consumption in a reaction such as $(MeO)_2CO$ synthesis is considerably greater than that in CuCl catalysed $(Bu^tO)_2$ decomposition. In MeOH–2,6-Me_2py but in the presence of CO (50 bar) the half life for gas uptake, which approximates closely to that of $(Bu^tO)_2$ consumption, was only about 1 h at 92 °C. The rate of reaction, which is independent of CO pressure above 50 bar, is close to first order in [CuCl] and $[(Bu^tO)_2]$. These facts and the high but not quantitative yield of $(MeO)_2CO$ can be explained by a rate determining step [reaction (4)] of Cu^I with $(Bu^tO)_2$ to give the Cu^{II} intermediate followed by two competing reactions of the intermediate, a relatively rapid carbonylation [reaction (5)] giving $(MeO)_2CO$ and the much slower decomposition [reaction (6)] giving MeOH oxidation. Both reactions involve return to the Cu^I state. In oxalate or succinate synthesis, reactions which are both known to occur at a Pd centre,[11,12] but which additionaly require the presence of Cu if $(Bu^tO)_2$ is used as the oxidant, reaction of the Cu^{II} intermediate with Pd must be far more efficient that carbonylation of Cu^{II}.

$$\tfrac{1}{2}[CuClpy]_4 + (Bu^tO)_2 + 2MeOH \rightarrow [CuCl(OMe)py]_2 + 2Bu^tOH \tag{2}$$

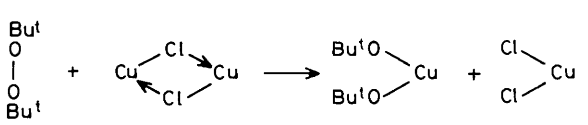
$$[CuCl(OMe)py]_2 \rightarrow \tfrac{1}{2}[CuClpy]_4 + H_2CO + MeOH \tag{3}$$

$$2Cu^I + (Bu^tO)_2 \xrightarrow{MeOH} 2Cu^{II}(OMe) + 2Bu^tOH \tag{4}$$

$$2Cu^{II}(OMe) + CO \rightarrow 2Cu^I + (MeO)_2CO \tag{5}$$

$$2Cu^{II}(OMe) \rightarrow 2Cu^I + MeOH + \text{'}H_2CO\text{'} \tag{6}$$

In the reactions we have described the rates are very different from those associated with O–O bond homolysis of $(Bu^tO)_2$.[7] These observations and the absence of acetone, the major product of fragmentation of $Bu^tO^\bullet$, lead us to propose that free radicals may not be significant in our reactions.



Scheme 1

Previously the reaction of peroxides with Cu^I species and rate enhancements over uncatalysed thermal reactions have been ascribed to an induced radical mechanism,[13] [reaction (7)].

$$(RO)_2 + Cu^I \rightarrow Cu^{II}OR + RO^\bullet \tag{7}$$

Our results do not distinguish between a concerted process for $(Bu^tO)_2$ activation and an induced radical reaction in which the radical is rapidly captured by a second Cu^I centre. However, halide bridged structures containing two or more Cu^I centres are well known in Cu^{II} halide chemistry[14] and could provide a route for a concerted process (Scheme 1). Exchange of the butoxide intermediate with an alcohol and rearrangement would lead to our observed alkoxide species. $Cu(OBu^t)_2$ can be made by reaction of $Cu(OBu^t)$ and $(Bu^tO)_2$ and exchanges readily with MeOH to give $Cu(OMe)_2$[15] which with $CuCl_2$ disproportionates to $CuCl(OMe)$.[3]

We conclude that the primary reaction of activation of $(Bu^tO)_2$ by Cu^I halide species is considerably faster than straightforward homolysis of the O–O bond. The modest rate increases observed for Cu catalysed decomposition reflect the stability of the intermediate Cu^{II} alkoxide, not the rate of the primary step. The Cu^{II} alkoxides formed can be intermediates in reactions such as oxidative carbonylation, which occur at much faster rates than peroxide decomposition and without the apparent intervention of free butoxy radicals.

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