

## Copper Salt - Crown Ether Systems as Catalysts for the Oxidation of Cumene with 1-Methyl-1-phenylethylhydroperoxide to bis(1-Methyl-1-phenylethyl)peroxide

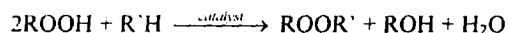
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Received 8 February 1999; accepted 29 March 1999

**Abstract:** Evidence for phase transfer catalysis in the oxidation of cumene with 1-methyl-1-phenylethylhydroperoxide to bis-(1-methyl-1-phenylethyl)peroxide in the presence of copper salt - crown ether catalysts is given. © 1999 Elsevier Science Ltd. All rights reserved.

Organic peroxides are important components in the polymer industry. They can be obtained from catalytic reactions of hydrocarbons with an active hydrogen and hydroperoxides. Salts of Cu(I), Cu(II), Co(II), Mn(II)<sup>1,2,3,4,5</sup> are usually used as catalysts. The reaction proceeds according to the following equation (Scheme 1):



Scheme 1

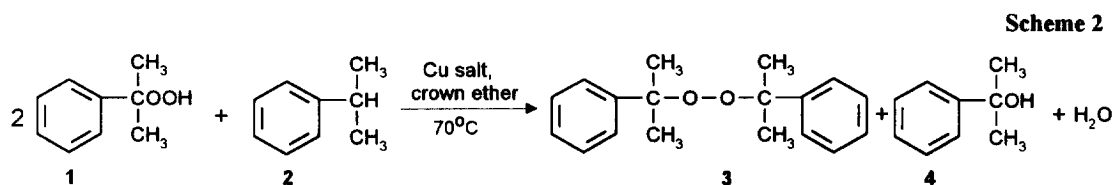
It is known from our previous studies, that the synthesis of ditertiary peroxides is much more efficient in the presence of a catalytic system composed of a variable valence metal salt and an alkylammonium or alkylphosphonium salt, and can be carried out in moderate conditions, without an additional solvent.<sup>6,7</sup>

Feldberg and Sasson<sup>8</sup> have also applied a catalytic system consisting of copper(II) chloride and tetrabutylammonium bromide in the oxidation of tetralin to 1-(*tert*-butylperoxy)tetralin by *tert*-butylhydroperoxide (as a 70% solution in water). The process was carried out in methylene chloride, using a two-phase aqueous/organic system.

Barak and Sasson<sup>9</sup> stated that quaternary ammonium salts may play a dual role in the metal-assisted oxidation of styrene to benzaldehyde or acetophenone by hydrogen peroxide. It extracts both metal and hydrogen peroxide into organic solvents of low polarity. It also modifies the nature of the metal by complexation, resulting in an improved catalytic activity and higher resistance of the metal towards reduction. An extraction mechanism involving the formation of a lipophilic ion pair, soluble in an organic solvent, is postulated for many types of reactions occurring in the presence of catalysts consisting of metal salts and onium salts.<sup>10</sup>

Our studies on the reaction of 1-methyl-1-phenylethyl hydroperoxide (1) with cumene (2) in the presence of catalysts composed of Cu(II), Cu(I), Co(II), Mn(II) salts and alkylammonium or alkylphosphonium salts<sup>11</sup> also indicate such a kind of catalysis (transfer of the catalyst in the form of a complex or ion pair with onium salt to the organic phase).

In this paper we present some experimental evidence for phase transfer catalysis in the oxidation of cumene (2) with 1-methyl-1-phenylethyl hydroperoxide (1) to bis(1-methyl-1-phenylethyl)peroxide (3) in the presence of copper salts and crown ethers (Scheme 2).



12-Crown-4, 15-crown-5, 18-crown-6 as well as Kryptofix 21 and Kryptofix 22 were applied with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{CuCl}$ . The inner diameters of 12-crown-4 (1,1÷1,4Å) and 15-crown-5 or Kryptofix 21 (1,7÷2,2Å) are adequate for the  $\text{Cu}^{2\oplus}$  (1,38Å) and  $\text{Cu}^\oplus$  (1,92Å) ionic diameters. The process was carried out without any additional solvent and the aqueous phase was formed during the reaction (water is one of the products of this reaction).

In a typical procedure 0.23 mol of (1) (as a 70% solution in cumene) was added with a dosage rate of 0.27 cm<sup>3</sup>/min to 0.14 mol of (2) with  $4.1 \cdot 10^{-3}$  mol of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (or  $\text{CuCl}$ ),  $8.4 \cdot 10^{-5}$  mol of crown ether (or tetrabutylammonium bromide) and in some experiments  $4.1 \cdot 10^{-3}$  mol of  $\text{LiCl}$  (or  $\text{NaCl}$ , or  $\text{KCl}$ ). The reaction was carried out at 70°C for 3h. The reaction rate as well as the composition of a post-reaction mixture were analysed using the iodometric method<sup>12</sup> and a HPLC method.<sup>13</sup> The results are presented in Table 1.

We have found that the best results in the reaction of (1) with (2) were obtained in the presence of catalysts composed of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and crown ethers with inner diameters larger than the ionic diameters of copper ions (15-crown-5 as well as Kryptofix 22). Moreover, we have also found that the presence of both components of the catalyst, i.e. copper salt and crown ether, is essential. No reaction was detected (under the applied conditions) in the absence of copper salt, on the other hand, only a 4% conversion of CHP was observed without crown ether.

The efficiency of the  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  - crown ether catalytic system was enhanced markedly by adding some complexing salts like  $\text{KCl}$ ,  $\text{NaCl}$ ,  $\text{LiCl}$ , with the cation diameter corresponding to the inner diameter of the crown ether. The most striking results were obtained adding  $\text{LiCl}$  to a hardly active catalyst composed of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and 12-crown-4. In the presence of  $\text{LiCl}$  both the reaction rate and the yield of peroxide increased considerably. The possibility of a catalytic activity of the 12-crown-4/ $\text{LiCl}$  and 18-crown-6/ $\text{KCl}$  systems was excluded by demonstrating that no oxidation takes place without  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ .

**Table 1. The influence of crown ethers on the oxidation of cumene with 1-methyl-1-phenylethylhydroperoxide to bis(1-methyl-1-phenylethyl)peroxide in the presence of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$**

Copper salt	Crown ether	Complexing salt	Conversion of 1 [%]	Yield of 3 [%]
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	-	-	4	1
-	18-crown-6	-	0	0
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	12-crown-4	-	9	8
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	12-crown-4	LiCl	84	46
-	12-crown-4	LiCl	0	0
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	15-crown-5	-	82	42
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	15-crown-5	NaCl	82	48
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	18-crown-6	-	72	33
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	18-crown-6	KCl	88	46
-	18-crown-6	KCl	0	0
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	Kryptofix22	-	80	45
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	Kryptofix21	-	82	36
CuCl	15-crown-5	-	6	4
<i><math>\text{CuCl}_2 \cdot 2\text{H}_2\text{O}</math></i>	<i>TBAB</i>	-	83	63

*Ionic diameters:*  $\text{Cu}^{\oplus}$  1,92Å;  $\text{Cu}^{2\oplus}$  1,38Å;  $\text{Li}^{\oplus}$  1,20Å;  $\text{Na}^{\oplus}$  1,90Å;  $\text{K}^{\oplus}$  2,66Å; *Inner diameter of crown ethers:* 12-crown-4 1,1÷1,4Å; 15-crown-5 1,7÷2,2Å; 18-crown-6 2,6÷3,2Å; Kryptofix 21 1,7÷2,2Å; Kryptofix 22 2,6÷3,2Å

The results obtained confirm strongly that phase transfer catalysis operates in the reaction of (1) with (2). In general, phase transfer catalysis consists in the transfer of copper ions to the organic layer. The copper ions can be transferred in the form of complexes of a copper cation with a crown ether. Our results prove that copper cations may be transferred to the organic layer also as complexes of  $\text{Li}^{\oplus}$ ,  $\text{Na}^{\oplus}$  or  $\text{K}^{\oplus}$  cations with the crown ether and copper bonded in  $\text{CuCl}_4^{2\ominus}$ ,  $\text{CuCl}_3^{\ominus}$  or  $\text{CuCl}_2^{\ominus}$  counterions. Copper ions can also be transferred in the form of complexes  $\text{Cu}[\text{CuCl}_3]$ ,  $\text{Cu}[\text{CuCl}_4]$ . The complexes discussed are known from literature.<sup>14, 15</sup>

The compositions of the post-reaction mixtures in the cases of applying 15-crown-5, 15-crown-5+NaCl and TBAB in the reactions of (1) with (2) in the presence of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  were compared (Table 2). If the 15-crown-5 +  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  system is applied, nearly twice the amount of alcohol is formed (compared with that formed in the presence of TBAB +  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ). It results from intensive activity of the catalyst in the decomposition of (1) to by-products (particularly to (4)). The addition of NaCl to 15-crown-5 +  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

does not affect any change in the composition of the product. Investigations have proved that in the presence of crown ether 15-crown-5, at 70°C, after 5 hours peroxide is not decomposed.

**Table 2. Composition of the reaction mixture after the oxidation of cumene with 1-methyl-1-phenylethylhydroperoxide in the presence of catalytic systems  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} + 15\text{-crown-5}$  or  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} + 15\text{-crown-5} + \text{NaCl}$  or  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} + \text{TBAB}$**

Catalyst	1 [mol]	3 [mol]	4 [mol]	PhAc* [mol]
15-crown-5+ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	0,04	0,05	0,20	0,04
15-crown-5 + $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ +NaCl	0,04	0,06	0,21	0,04
TBAB+ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	0,02	0,07	0,13	0,05

\*PhAc=Acetophenone

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