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ORIGINAL PAPER

ESI–MS study of copper chloride/phase-transfer catalytic systems for oxidation of cumene with 1-methyl-1-phenylethyl hydroperoxide

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Abstract Oxidation of cumene with 1-methyl-1-phenylethyl hydroperoxide in the presence of copper chloride/phase transfer catalytic systems was investigated by ESI–MS. For catalytically active copper(II) chloride/crown ethers, copper(II) chloride/crown ethers/alkaline metal salts, and copper(II) chloride/tetrabutylammonium chloride systems, the presence of a few kinds of copper complexes in the organic phase was detected by use of ESI–MS. When copper(II) chloride/podand systems were used, the conversion of hydroperoxide and the yield of oxidation product were close to zero, although the concentration of copper complexes in the organic phase was high. Addition of bis(2-hydroxyethyl) ether to the catalytically active copper(II) chloride/18-crown-6 system resulted in an inhibition effect.

Keywords Copper(II) chloride · Crown ethers · Catalytic systems · ESI–MS · Oxidation · Peroxides

Introduction

Catalytic oxidation of hydrocarbons by various oxidizing agents in the presence of copper(I), copper(II), cobalt(II), or manganese(II) salts has been widely investigated for many years. Salts of copper(I) and copper(II) have been used as effective catalysts in the oxidation of hydrocarbons (RH) possessing an active hydrogen with tertiary hydroperoxides (Eq. 1) [1, 2].

$$2\mathrm{ROOH} + \mathrm{R'H} \rightarrow \mathrm{ROOR'} + \mathrm{ROH} + \mathrm{H_2O} \quad (1)$$

Symmetric and unsymmetric di-tertiary organic peroxides [3]—important components in the polymer industry—are the most desired products of such reactions.

According to Kharasch's proposal [2], the main steps of the reaction can be described by Eqs. 2–7:

$$\mathrm{ROOH} + \mathrm{Cu^+} \rightarrow \mathrm{RO\cdot} + \mathrm{Cu^{2+}} + {}^{-}\mathrm{OH} \quad (2)$$

$$\mathrm{RO\cdot} + \mathrm{R'H} \rightarrow \mathrm{ROH} + \mathrm{R'\cdot} \quad (3)$$

$$\mathrm{R'\cdot} + \mathrm{ROOH} \rightarrow \mathrm{R'\cdot HOOR} \quad (4)$$

$$\mathrm{ROOH} + \mathrm{Cu^{2+}} \rightarrow \mathrm{ROO\cdot} + \mathrm{Cu^+} + \mathrm{H^+} \quad (5)$$

$$\mathrm{ROO\cdot} + \mathrm{R'H} \rightarrow \mathrm{R'\cdot HOOR} \quad (6)$$

$$\mathrm{R'\cdot HOOR} + \mathrm{Ox} \rightarrow \mathrm{R'OOR} + (\mathrm{Ox} + \mathrm{e}) + \mathrm{H^+} \quad (7)$$

where $R = (CH_3)_3C–$, $R' = Ph(CH_3)_2C–$, and Ox is Cu^{2+} or hydroperoxide.

Kochi [1] suggested that copper catalyst was involved in the formation of intermediate complexes (Eqs. 8–11):

$$\mathrm{ROOH} + \mathrm{Cu^+} \rightarrow \mathrm{RO\cdot} + [\mathrm{CuOH}]^+ \quad (8)$$

$$[\mathrm{CuOH}]^+ + \mathrm{ROOH} \rightleftharpoons [\mathrm{CuOOR}]^+ + \mathrm{H_2O} \quad (9)$$

$$\mathrm{RO\cdot} + \mathrm{R'H} \rightarrow \mathrm{ROH} + \mathrm{R'\cdot} \quad (10)$$

$$\mathrm{R'\cdot} + [\mathrm{CuOOR}]^+ \rightarrow \mathrm{R'OOR} + \mathrm{Cu^+} \quad (11)$$

where $R = (CH_3)_3C–$ and $R' = Ph(CH_3)_2C–$.

It has been found that the oxidation process is much more efficient and can be performed under milder conditions when systems composed of transition metal salts and phase-transfer catalysts, for example onium salts or crown ethers, were used [4–9].

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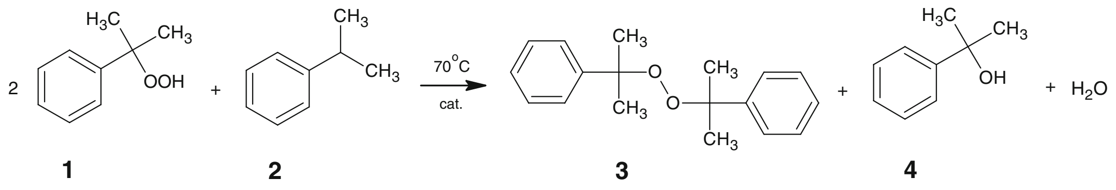

Scheme 1

In our previous papers [10, 11] we presented some results concerning the oxidation of isopropyl arenes with tertiary hydroperoxides in the presence of copper salt/crown ether/alkali metal salt catalytic systems ($CuCl_2 \cdot H_2O$/12-crown-4/LiCl, $CuCl_2 \cdot H_2O$/15-crown-5/NaCl, $CuCl_2 \cdot H_2O$/18-crown-6/KCl). Clear evidence was provided of the occurrence phase-transfer catalysis (PTC) in the reactions investigated. We proposed that copper was transferred to the organic phase in the form of complexes with crown ethers and, sometimes, alkali metal cations, with copper being transferred in the form $CuCl_4^{2-}$ or $CuCl_3^-$ counterions, or even as $Cu[CuCl_3]$ or $Cu[CuCl_4]$ complexes. Moreover, the essential role of water in the catalytic process was discussed.

Murahashi [12] and Komiya et al. [13] reported isolation of a few types of copper/crown ether systems and their application in oxidation of cyclohexane with molecular oxygen, in the presence of acetaldehyde in CH_2Cl_2 at room temperature. The use of $CuCl_2$ with 18-crown-6 gave the best results. The structure of the complex of $CuCl_2$ with 18-crown-6 was established by single-crystal X-ray structure determination. The complex consisted of tetrameric $(CuCl_2)_4$, two molecules of crown ethers, and two water molecules. The complex of $CuCl_2$ with 18-crown-6 and KCl, which consisted of a dinuclear $[Cu_2Cl_6]^{2-}$ anion and two $[K(18\text{-crown-}6)]^+$ cations, was much more efficient [14]. A similar complex with 15-crown-5/NaCl was also effective. Such observations are in good agreement with data obtained during our study on the oxidation of isopropyl arenes with tertiary hydroperoxides.

In this paper we present experimental evidences, obtained by ESI–MS, that crown ethers in the presence of alkali metal salts, and some other phase-transfer catalysts, are able to transfer copper containing complexed anions, and sometimes Cu^+ or Cu^{2+}/crown ether complexes also, to the organic phase. ESI–MS can be used for ionization of molecules and ionic chemical species, and to form charged ions from relatively non-volatile, thermally labile compounds up to a concentration of 10^{-7} mol dm^{-3}. ESI–MS is therefore a perfect tool for determination of the formulae and concentrations of the different ions and complexes of catalysts present in the investigated reaction mixture.

Results and discussion

The oxidation of cumene (**2**) with 1-methyl-1-phenylethyl hydroperoxide (**1**) was chosen as model reaction because it is used for the large-scale production of dicumyl peroxide, an initiator of many free radical processes. Another reason for this selection was the availability of reactants and simple analytical methods for monitoring the course of the reaction. Catalysts consisting of $CuCl_2 \cdot 2H_2O$ and alkylammonium salts, crown ethers, or podands were used (Scheme 1).

Table 1 presents the results of the reaction of hydroperoxide **1** with **2** in the presence of different catalytic systems.

The total concentration of Cu ions in cumene solution was about 10^{-5} mol dm^{-3} for all the catalytic systems studied except for $CuCl_2$/12-crown-4, for which it was below 10^{-6} mol dm^{-3} (determined by ICP). Distribution of copper salts formed in the cumene phase was determined by ESI–MS. In negative-ion ESI–MS spectra obtained from the cumene phase we observed the following peaks for ion complexes with copper: $m/z = 133$ for $CuCl_2^-$, $m/z = 168$ for $CuCl_3^-$, $m/z = 196$ for $Cu_2Cl_2^-$, $m/z = 231$ for $CuCuCl_3^-$, and $m/z = 266$ for $CuCuCl_4^-$, calculated for isotopes ^{63}Cu (69%) and ^{35}Cl (75%) (Table 1). Typical spectra are presented in Figs. 1 and 2, possible combinations of the oxidation states for the observed copper complexes are presented in Table 2 [15]. The mechanism of reduction of Cu(II) observed in ESI–MS was described by Gianelli et al. [16].

For the system $CuCl_2 \cdot 2H_2O$/12-crown-4, for which the conversion of hydroperoxide **1** and the yield of peroxide **3** were very low, only traces of copper complexes were observed in the cumene phase. On the other hand, a very intense signal of the $CuCl_2^-$ ion (Fig. 1) occurred when LiCl was added to the system. In that case high conversion of hydroperoxide **1** and relatively high yield of peroxide **3** were observed. In the positive-ion ESI–MS spectrum there were signals of a $(12\text{-crown-}4/Li)^+$ complex. Analogous results were also obtained for the systems with other crown ethers. For the systems with 15-crown-5 or 18-crown-6 additional signals of $(\text{crown ether}/Cu)^+$ complexes were observed. The stability constants (log *K*) of Cu(II) with 15-

Table 1 Anions observed by negative-ion ESI–MS

Catalytic system[a,b,c]	Conv. of **1** (%)	Yield of **3** (%)	Anions observed in negative-ion ESI–MS, and relative intensity (%)				
			$m/z = 133$ $CuCl_2^-$	$m/z = 168$ $CuCl_3^-$	$m/z = 196$ $Cu_2Cl_2^-$	$m/z = 231$ $CuCuCl_3^-$	$m/z = 266$ $CuCuCl_4^-$
A	9[d]	8[d]	–	–	Trace	–	–
B	84[d]	46[d]	100	–	–	–	–
C	82[d]	42[d]	–	–	100	–	–
D	82[d]	48[d]	100	20	20	40	–
E	72[d]	33[d]	100	20	50	20	–
F	88[d]	46[d]	100	–	30	10	–
G	83	41	100	20	40	–	–
H	92	50	100	–	–	–	–
I	79	32	100	20	–	–	–
J	84	40	100	40	–	–	–
K	86	63	60	–	100	–	–
L	0	0	100	40	25	10	6
M	0	0	100	40	20	15	8
N	23	5	100	40	20	12	8

[a] Catalytic systems used **A** $CuCl_2 \cdot 2H_2O$ + 12-crown-4, **B** $CuCl_2 \cdot 2H_2O$ + 12-crown-4 + LiCl, **C** $CuCl_2 \cdot 2H_2O$ + 15-crown-5, **D** $CuCl_2 \cdot 2H_2O$ + 15-crown-5 + NaCl, **E** $CuCl_2 \cdot 2H_2O$ + 18-crown-6, **F** $CuCl_2 \cdot 2H_2O$ + 18-crown-6 + KCl, **G** $CuCl_2 \cdot 2H_2O$ + dibenzo-18-crown-6, **H** $CuCl_2 \cdot 2H_2O$ + dibenzo-18-crown-6 + KCl, **I** $CuCl_2 \cdot 2H_2O$ + dibenzo-24-crown-8, **J** $CuCl_2 \cdot 2H_2O$ + dibenzo-24-crown-8 + KCl, **K** $CuCl_2 \cdot 2H_2O$ + Bu_4NCl, **L** $CuCl_2 \cdot 2H_2O$ + $HOCH_2CH_2OCH_2CH_2OH$, **M** $CuCl_2 \cdot 2H_2O$ + $CH_3OCH_2CH_2OCH_2CH_2OH$, **N** $CuCl_2 \cdot 2H_2O$ + poly(ethylene glycol)-350-monomethyl ether

[b] Ionic diameters, Cu^{2+} 1.38 Å; Li^+ 1.20 Å; Na^+ 1.90 Å; K^+ 2.66 Å

[c] Cavity diameters of crown ethers, 12-crown-4 1.1 ÷ 1.4 Å; 15-crown-5 1.7 ÷ 2.2 Å; 18-crown-6 2.6 ÷ 3.2 Å; dibenzo-18-crown-6 2.6 ÷ 3.2 Å

[d] Refs. [10, 11]

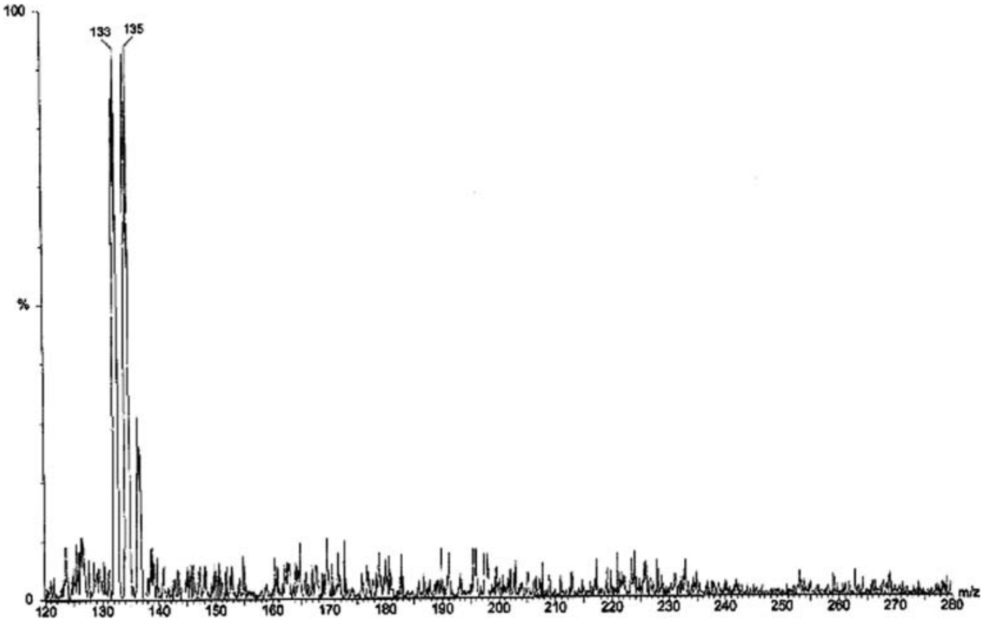

Fig. 1 ESI–MS spectrum obtained from the $CuCl_2 \cdot 2H_2O$ and 12-crown-4–LiCl system in cumene solution

crown-5 and 18-crown-6 are 2.26 and 2.01 in 90% DMSO–water solvent [17] or 2.04 and 1.85 in 40% ethanol–water solvent [18]. The stability constants of (crown ether/Cu)$^+$ complexes are smaller.

The highest concentration and variety of different ionic copper complexes were observed for podands, whereas for the $CuCl_2 \cdot 2H_2O/Bu_4NCl$ system (Fig. 2) the concentration of copper complexes was approximately a factor of two

Fig. 2 ESI–MS spectrum obtained from the $CuCl_2{\cdot}2H_2O$ and Bu_4NCl system in cumene solution

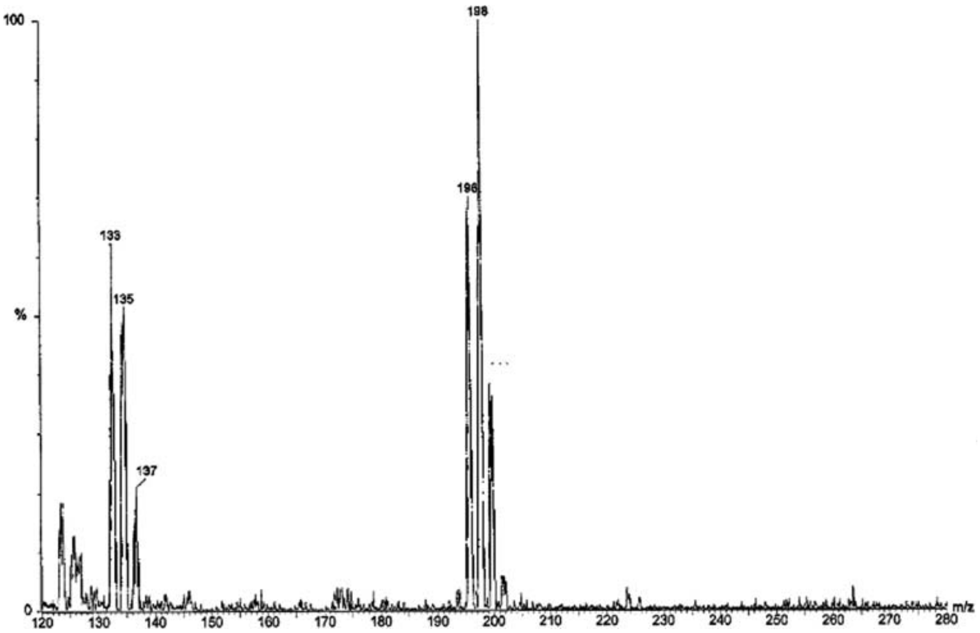

Table 2 Possible combinations of the oxidation states for the copper complexes observed [15]

Chemical formula	Description (oxidation states)
$CuCl_2^-$	$[Cu(I) + 2\ Cl]^-$
$CuCl_3^-$	$[Cu(II) + 3\ Cl]^-$
$Cu_2Cl_2^-$	$[Cu(0) + Cu(I) + 2\ Cl]^-$
$CuCuCl_3^-$	$[2\ Cu(I) + 3\ Cl]^-$
$CuCuCl_4^-$	$[Cu(I) + Cu(II) + 4\ Cl]^-$

lower. Unexpectedly, with podands the high concentration of copper complexes in the organic phase was accompanied by conversion of hydroperoxide **1** and a yield of peroxide **3** close to zero, whereas for the system with Bu_4NCl both conversion and yield were extremely high.

When bis(2-hydroxyethyl) ether was added to the catalytically active $CuCl_2{\cdot}2H_2O$/18-crown-6 system, the conversion and the yield of peroxide decreased significantly from 72 to 14%, and from 33 to 5%, respectively.

Conclusion

Our results confirm that the transfer of copper complexes with crown ethers or crown ethers and alkali metal salts or Bu_4NCl to the cumene phase is responsible for the catalytic effect in the process of the oxidation of cumene with 1-methyl-1-phenylethyl hydroperoxide.

It seems that with podands no reaction is observed because the complexation of copper ions by podands is too strong, or because specific inhibition caused by above mentioned compounds occurs. This assumption accounts for the inhibition effect observed for bis(2-hydroxyethyl) ether added to the catalytically active $CuCl_2{\cdot}2H_2O$/18-crown-6 system.

The ESI–MS method provides new opportunities for examination of the oxidation of cumene with 1-methyl-1-phenylethyl hydroperoxide in the presence of catalytic systems consisting of $CuCl_2{\cdot}2H_2O$ and crown ethers or other phase-transfer catalysts [19].

Experimental

Materials

1-Methyl-1-phenylethyl hydroperoxide was purchased as technical product from PKN “Orlen”, Płock, Poland. It was purified using the method described in the literature [20]. Cumene was purchased from Merck and washed with concentrated sulfuric acid, neutralized, dried with anhydrous magnesium sulfate, and distilled over sodium (152.0-152.5 °C). Other reagents and catalysts were purchased from Merck and used as received.

Oxidation of cumene with 1-methyl-1-phenylethyl hydroperoxide

In a typical procedure a 70% solution of 35 g 1-methyl-1-phenylethyl hydroperoxide (0.23 mol) in cumene was added at a rate of 0.27 cm^3/min to a mixture of 16.4 g cumene (0.14 mol), copper(II) chloride dihydrate (4.1 mmol), phase-transfer catalyst (8.4×10^{-2} mmol) and, in some experiments, lithium chloride, sodium chloride, or potassium chloride (4.1 mmol). Crown ethers, tetrabutylammonium salts, and podands were used as phase-transfer catalysts. The reaction was carried out at 70 °C for ~3 h. The reaction rate and the composition of the post-reaction mixture were analysed by use of iodometric [21] and HPLC [22] methods.

Mass spectrometry

The ESI–MS spectra were recorded on a Waters/Micromass (Manchester, UK) ZQ mass spectrometer equipped with a Harvard Apparatus syringe pump. A solution of cumene with alkylammonium salts, podands, or crown ethers was shaken with $CuCl_2 \cdot 2H_2O$ for 10 min. The sample solutions were prepared in methanol–water (1:1) at a concentration of approximately 10^{-5} mol dm^{-3}. The samples were infused into the ESI source using a Harvard pump at a flow rate of 20 mm^3 min^{-1}. The ESI source potentials were: capillary 3 kV, lens 0.5 kV, extractor 4 V. For standard ESI–MS spectra the cone potential was 30 V. Source temperature was 120 °C and desolvation temperature was 300 °C. Nitrogen was used as the nebulizing and desolvation gas at flow rates of 100 and 300 dm^3 h^{-1}, respectively.

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