# Oxidation of 2,3,6-trimethylphenol to trimethyl-1,4-benzoquinone with catalytic amount of CuCl$_2$

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## Abstract

The selective, one step oxidation of 2,3,6-trimethylphenol (TMP) to 2,3,6-trimethyl-1,4-benzoquinone (TMQ) by a catalytic amount of CuCl$_2$ (up to 100 turnovers) and NH$_2$OH · HCl has been investigated. TMQ was obtained in up to 80% yield using only 1.5 wt% CuCl$_2$ catalyst (related to the amount of TMP) and 2.8 wt% NH$_2$OH · HCl co-catalyst under ambient conditions. The initial oxidation state of copper had no influence on the rate or selectivity of the reaction. The synergy between catalyst and co-catalyst was most prominent in the low concentration range. Highest TMQ yield was obtained with tert-butyl hydroperoxide (TBHP), whereas the use of molecular oxygen (under pressure) resulted in relatively poor yield. At low TBHP/TMP ratio, the dimer content of the product is significant, but can be efficiently suppressed by applying the oxidant in 10–25 mol% excess to the stoichiometric ratio. The TMQ yield could be improved by adding TMP in portions during oxidation, and by using TBHP in air instead of nitrogen atmosphere. The presence of Cl$^-$ ion proved to be important for obtaining good selectivity, but the formation of 4-chloro-2,3,6-trimethylphenol as an intermediate can be excluded, when the amount of catalyst is less than 3 wt%. Electrochemical and catalytic investigations revealed that the reduction of Cu$^{2+}$ by TMP and its reoxidation by TBHP are fast, but the further oxidation of the dimer intermediate to TMQ is slow.

*Keywords:* Oxidation; Trimethyl benzoquinone; Phenol; Copper

## 1. Introduction

Vitamin E is produced on a large scale due to its biological and anti-oxidant activity. An important synthesis route to vitamin E starts with the oxidation of 2,3,6-trimethylphenol (TMP) to 2,3,6-trimethyl-1,4-benzoquinone (TMQ), according to Scheme 1. In a patent from the early seventies [1], CuCl$_2$ catalyst and molecular oxygen under moderate pressure (30 bar) are proposed for the oxidation. In acetone/water mixture the yield is 80–87% at full conversion. Several modifications of this reaction have been developed using copper halides together with alkali, alkali earth and ammonium halides [2–9]. A serious drawback of the method is that an almost stoichiometric amount of CuCl$_2$ is required for complete and selective oxidation of TMP.
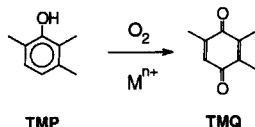
Scheme 1.

A milestone in the development of the oxidation of TMP to TMQ, was the work of Japanese researchers who were the first to reduce the amount of $CuCl_2$ by applying nitrogen containing compounds as co-catalysts [10–14]. The best co-catalyst is hydroxylamine hydrochloride, but some oximes and amines (as hydrochlorides) are also effective. However, during scale-up of the process the amount of $CuCl_2$ has to be increased to obtain good yield. For example, the oxidation of 270 mg TMP with 80% yield requires 12,5 wt% $CuCl_2 \cdot 2H_2O$ related to the reactant, but the oxidation of 680 mg TMP necessitates 25 wt% $CuCl_2 \cdot 2H_2O$ for obtaining the same yield [14]. The selectivity to TMQ obtained with equimolar amount of $CuCl_2$ 'catalyst' can also be improved by the addition of $NH_4VO_3$, $MnCl_2$ or $CoCl_2$ [15–17], but the amount of $CuCl_2$ cannot be reduced by this way.

Some heteropolyacids, such as $H_{3+n}PMo_{12-n}V_nO_{40}$, also catalyse the oxidation of TMP with molecular oxygen [18–20]. TMQ yields up to 86% have been obtained in polar solvents, but the amount of catalyst is rather high, over 25 wt% related to TMP.

Hydrogen peroxide is also frequently used as oxidising agent in the synthesis of TMQ. Various metal salt catalysts have been tested and the best result, 90% yield at full conversion, was achieved using only 1.5 wt% $RuCl_3$ in AcOH [21,22]. However, $RuCl_3$ is rather expensive and other catalysts, such as Cu, Fe or Mo salts, were hardly selective. For example, using $CuCl_2$ or CuCl the yields were only 32% and 37%, respectively.

Several heteropolyacids, containing Si, Mo, W or P, catalyse the oxidation of TMP with $H_2O_2$ in acetic acid [23–25]. Interestingly, the selectivity of heteropolyacids is lower with $H_2O_2$ than with molecular oxygen and TMQ yields of only 57–72% have been obtained even at relatively high catalyst/reactant ratio ($> 33$ wt%).

Here we show that the amount of $CuCl_2$ catalyst can be substantially reduced compared to literature data, if the oxidation of TMP is carried out with alkylhydroperoxides as oxidant in acetic acid. The TMQ yield can be increased by applying co-catalysts such as $NH_2OH \cdot HCl$. The influence of some important reaction parameters has been studied and a kinetic analysis of the rather complex reaction, supported with UV–Vis and electrochemical potential measurements is presented.

## 2. Experimental

### 2.1. Materials

Analytical grade reagents were used, except TMP and TMQ, which were of technical grade (supplied by Hoffman–La Roche AG). TMP was recrystallised from hexane before use. For the experiments the following solutions were used: tert-butyl hydroperoxide (TBHP, 70 wt% in water), cumene hydroperoxide (CHP, 80 wt% in cumene), peracetic acid (32 wt% in AcOH) and $H_2O_2$ (35 wt% in water).

### 2.2. General oxidation procedure

The oxidation of TMP was performed in a 200 ml flat-bottomed, thermostated glass batch reactor, equipped with gas inlet and outlet, reflux condenser, magnetic stirrer and thermometer. In a typical oxidation procedure TMP (2.5 g, 18.4 mmol), $CuCl_2$ catalyst (25 mg, 0.19 mmol), $NH_2OH \cdot HCl$ co-catalyst (140 mg, 2.0 mmol) and AcOH (30 ml) were put into the reactor and flushed with nitrogen (99.999%). TBHP (6 ml, 44 mmol) was added to the stirred mixture after 5 min. Other reaction parameters are indicated in the tables and in the figure

captions. The relative amount of catalyst (in wt%) is defined as catalyst:TMP weight ratio.

Yield and conversion were determined using gas chromatography. An HP 5890 chromatograph equipped with cool on-column injection and an HP-1 fused silica capillary column with a retention gap were used. Several by-products, including 4-chloro-2,3,6-trimethylphenol (ClTMP), 2,3,6-trimethyl-1,4-hydroquinone (TMHQ) and the dimers: 2,2′,3,3′,6,6′-hexamethyl-4,4′-biphenyldiol (D) and 2,2′,3,3′,6,6′-hexamethyl-4,4′-biphenylquinone (DQ) could be detected. Unfortunately, D and DQ could not be separated properly and the presence of polymers was undetectable. GC–MS was used for identification of the peaks and pentadecane was applied as an inner standard for quantitative analysis.

## 2.3. Physico-chemical measurements

The measurement of electrochemical potential was performed in a magnetically stirred 200 ml electrochemical cell (Metrohm No.: 6.1415.250). The reference electrode was Ag|AgCl|KCl (0.1 M) (Metrohm No.: 6.0724.140) with a double bridge filled with 0.1 M KCl to protect the reference electrode from the reaction medium. The working electrode was a bright Au rod (Metrohm No.: 6.0331.060).

The solvent was 30 ml AcOH deoxygenated with nitrogen before the measurement. The potentials in the figures and text are referred to the applied reference electrode.

UV–Vis spectra were measured at wavelengths between 200 and 900 nm of samples in quartz cells (10 mm path lengths) employing a Perkin Elmer Lambda 16 spectrophotometer. For the measurements the samples and reference materials were diluted with AcOH.

## 3. Results

### 3.1. Synergy between catalyst and co-catalyst

A strong interaction was found between the influence of the amount of catalyst and co-catalyst. Selectivities obtained in the oxidation of TMP with $CuCl_2$ catalyst and $NH_2OH \cdot HCl$ co-catalyst are presented in Fig. 1. With increasing amount of $CuCl_2$ the reaction is faster, and in the presence of at least 1 wt% $CuCl_2$ the conversion is always complete in 2 h. Without catalyst and co-catalyst only 10% conversion and no selectivity to TMQ was achieved. The higher the amount of $CuCl_2$ (without co-catalyst), the more selective is the oxidation to TMQ.
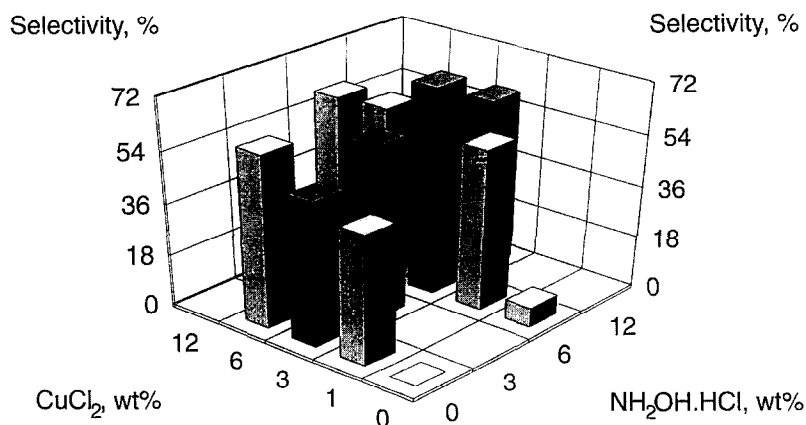
In the presence of $NH_2OH \cdot HCl$ co-catalyst



Fig. 1. Influence of the amount of $CuCl_2$ catalyst and $NH_2OH \cdot HCl$ co-catalyst on the selectivity of TMP → TMQ transformation. Conditions: 2.5 g TMP, 30 ml AcOH, 6 ml TBHP, 25°C, 2 h.

there is an optimum in the amount of $CuCl_2$. As an example to these local maxima, 100% conversion and 72% selectivity was achieved with 3 wt% catalyst and 6 wt% co-catalyst. Interestingly, the lower the amount of $CuCl_2$, the higher is the synergic effect between catalyst and co-catalyst.

## 3.2. Chemical nature of catalyst and co-catalyst

Substitution of $CuCl_2$ by $CuCl$ as catalyst, under otherwise identical conditions, had no detectable influence on conversion and selectivity. The role of the *initial* oxidation state of copper will be discussed later. Concerning the nature of the anion, $Cl^-$ ions provided far better results than acetate, sulphate or nitrate ions. Substitution of $CuCl_2$ by $FeCl_3$ was detrimental to the selectivity. Note, that $FeCl_3$ is a good catalyst in the hydroxylation of phenols with



Fig. 3. TMP oxidation with (—) and without (- - -) $NH_2OH \cdot HCl$. Conditions: 2.5 g TMP, 25 mg $CuCl_2$, 140 mg $NH_2OH \cdot HCl$, 30 ml AcOH, 6 ml TBHP, 30°C, 2 h.

$H_2O_2$ when applying it in stoichiometric amounts [26–28].

Fig. 2 shows the influence of some co-catalysts on the conversion of TMP and selectivity to TMQ and dimers $(D + DQ)$ in the presence of 1 wt% $CuCl_2$. The selection of these compounds was based on the analogy to well-known oxidising systems such as Fenton's, Hamilton's and Udenfriend's reagents [26–28]. All compounds (and several others not shown in Fig. 2) provided lower selectivity to TMQ and sometimes also a lower rate of conversion than $NH_2OH \cdot HCl$. Similarly, hydroxylamine hydrochloride was more efficient in improving the rate and selectivity of the $CuCl_2$-catalysed oxidation than other salts of hydroxylamine, in agreement with earlier observations [14]. When applying HCl (in equivalent amount) instead of $NH_2OH \cdot HCl$, conversion and selectivity dropped to 88% and 42%, respectively. This is an indication that HCl alone is not a good co-catalyst, but the $Cl^-$ ion is important in the
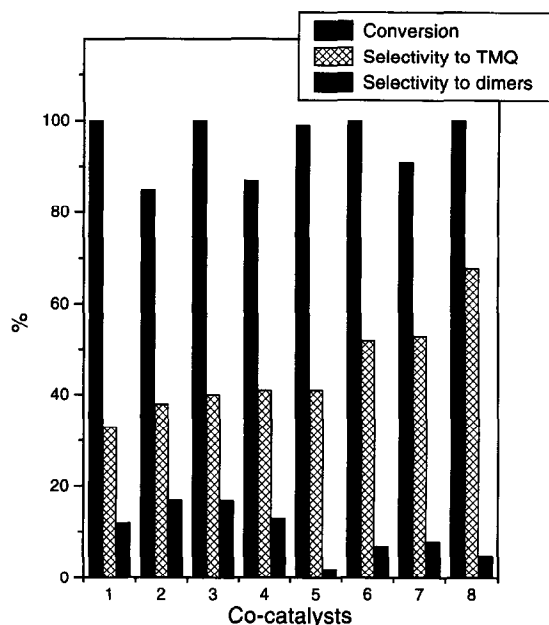


Fig. 2. Influence of the chemical nature of co-catalyst on conversion and selectivity of TMP oxidation; 1: acetone oxime, 2: ethylenediaminetetraacetic acid disodium salt dihydrate, 3: hexamethylenetetramine, 4: ascorbic acid, 5: pyrocatechol, 6: without co-catalyst, 7: $NH_2OH \cdot H_2SO_4$, 8: $NH_2OH \cdot HCl$. Conditions: 2 mmol co-catalyst, 2.5 g TMP, 25 mg $CuCl_2$, 30 ml AcOH, 6 ml TBHP, 30°C, 2 h.

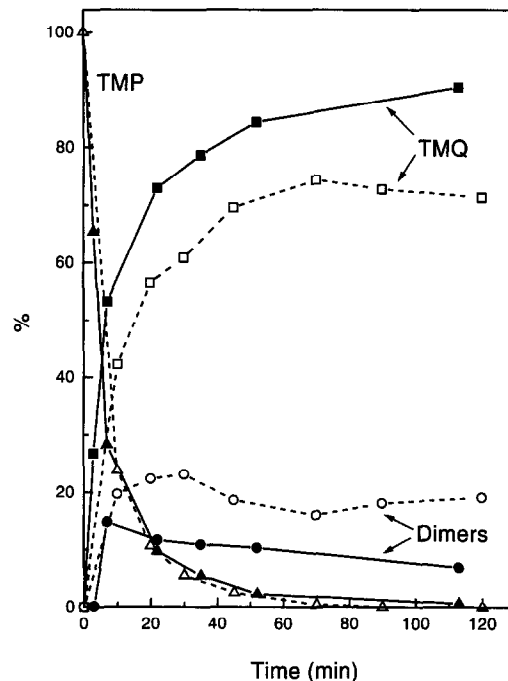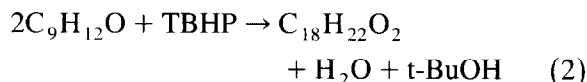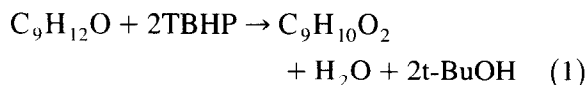interaction between $CuCl_2$ and $NH_2OH \cdot HCl$ (reduction of $Cu^{2+}$ and complexation, see later).

The influence of $NH_2OH \cdot HCl$ on TMP conversion and the formation of TMQ and dimers during reaction is presented in Fig. 3. Note that in this case the inner standard could not be used and the % values represent only the integrated area of the peaks of the gas chromatogram. The conversion of TMP was scarcely influenced by the addition of $NH_2OH \cdot HCl$, but the yield of TMQ increased and the actual concentration of dimers was suppressed by the co-catalyst. It seems that the role of $NH_2OH \cdot HCl$ as a co-catalyst is most probably to promote the further oxidation of dimers to TMQ, as has been proposed earlier [18].

### 3.3. Oxidising agent

The oxidation of TMP to TMQ or D are shown by the formal Eqs. (1) and (2), respectively:

$$C_9H_{12}O + 2TBHP \rightarrow C_9H_{10}O_2$$
$$+ H_2O + 2t\text{-BuOH} \quad (1)$$
$$2C_9H_{12}O + TBHP \rightarrow C_{18}H_{22}O_2$$
$$+ H_2O + t\text{-BuOH} \quad (2)$$

In agreement with this stoichiometry, 2–2.5 mole TBHP/mole TMP were necessary to achieve full conversion and good yield, as illustrated in Fig. 4. At low TBHP/TMP ratio the dimer content in the product was significant, but could be efficiently suppressed by applying at least 2 mole oxidant per mole reactant. (Note that there was always some unused TBHP present at the end of the reaction, but its amount was not determined quantitatively.)

Table 1 shows that concerning the TMQ yield (conversion × selectivity), molecular oxygen (under pressure) was the poorest and TBHP was the best oxidising agent. Note that TBHP is a stable organic peroxide and safer to handle than peracetic acid or hydrogen peroxide. Usually, the reactions were carried out under nitrogen at 1 bar. Interestingly, when the nitrogen atmosphere was substituted by air, the TMQ
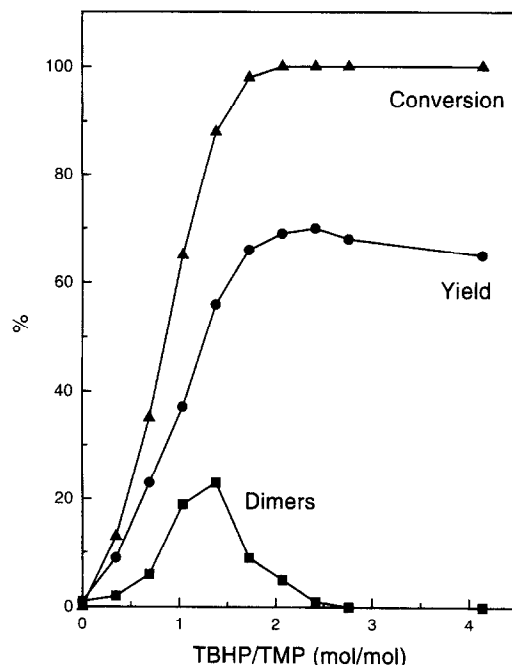


Fig. 4. Influence of oxidant/reactant molar ratio on TMP conversion and products formation. Conditions: 2.5 g TMP, 25 mg $CuCl_2$, 140 mg $NH_2OH \cdot HCl$, 30 ml AcOH, 30°C, 2 h.

yield slightly increased (by 2–5%) and the amount of dimers decreased.

### 3.4. Intermediates and by-products

The time dependence of TMP conversion to TMQ using 1 or 3 wt% $CuCl_2$ is depicted in Figs. 3 and 5, respectively. Interestingly, the amount of TMQ increased even when TMP was fully converted. For example, in the presence of 3 wt% $CuCl_2$ (Fig. 5) TMP was consumed in 60 min but the amount of TMQ increased slowly

Table 1
Efficiency of various oxidising agents

| Oxidising agent | Conversion % | Selectivity % |
|---|---|---|
| $O_2$ (50 bar) | 57 | 48 |
| $H_2O_2$ [a] | 100 | 48 |
| Peracetic acid | 100 | 48 |
| CHP | 90 | 63 |
| TBHP | 100 | 68 |
| TBHP/air | 100 | 72 |

Conditions: 2.5 g TMP, 30 ml AcOH, 25 mg $CuCl_2$, 140 mg $NH_2OH \cdot HCl$, 2.2 equiv. oxidising agent, 25°C, 2 h.
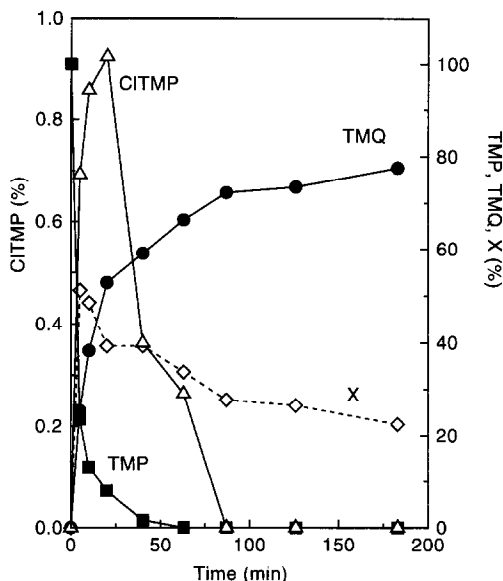[a] 75 mg $CuCl_2$.

Fig. 5. Time-resolved consumption of TMP and formation of TMQ, ClTMP and other products ( X: all products except TMQ), (2.5 g TMP, 75 mg CuCl₂, 140 mg NH₂OH·HCl, 30 ml AcOH, 6 ml TBHP, 25°C, 2 h).

up to 180 min and then remained constant. (Decomposition of TMQ was found to be negligible under the mild reaction conditions.) The shift on the time scale between the consumption of TMP and formation of TMQ can easily be explained by assuming that TMQ is formed – at least partly – via an intermediate. It has been proposed previously [18] that TMP is transformed to TMQ via dimer formation, as shown
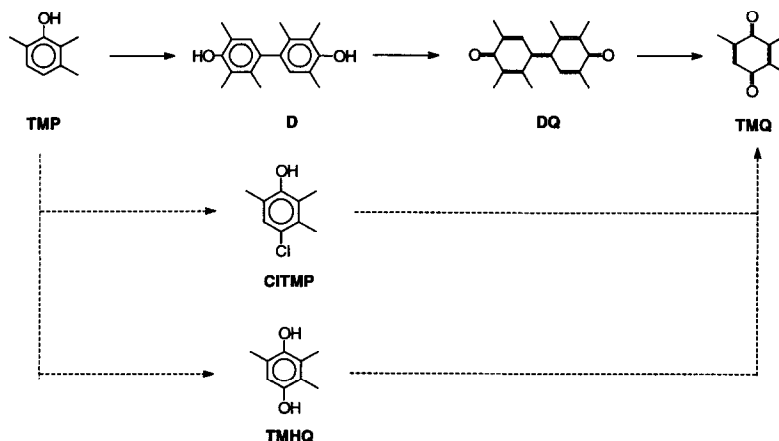
in Scheme 2. Our results support this assumption. The total amount of intermediates and by-products, defined as $X$ in Fig. 5 and determined by gas chromatographic analysis, represents the material formed in the reaction excluding TMQ. The time-resolved amount of $X$ reached almost 50% at the beginning of the reaction and decreased slowly, parallel to the formation of TMQ.

Besides the dimers, there are two other compounds proposed as intermediates [14,18]:

(i) When oxygen and a large amount of CuCl₂ as catalyst are used, a considerable amount of 4-chloro-2,3,6-trimethylphenol (ClTMP) is produced [14], which is mostly consumed by the end of the reaction (Scheme 2). In our case the maximum amount of ClTMP was less than 1% in the presence of 3 wt% CuCl₂, as shown in Fig. 5, and it was below the detection limit (ca. 0.01%) throughout the reaction when only 1 wt% CuCl₂ was used.

(ii) Direct hydroxylation of TMP results in 2,3,6-trimethyl-1,4-hydroquinone (TMHQ, Scheme 2). This intermediate was hardly detectable ( < 0.1%) even at the beginning of the reaction, independent of the reaction conditions. This observation suggests that in the (CuCl₂– NH₂OH · HCl–TBHP–AcOH) oxidising system, TMQ formation via direct hydroxylation of TMP to TMHQ is less important than the reaction via dimers.



Scheme 2.

## 3.5. Addition of TMP in portions

An interesting and hitherto not reported observation is that the yield of TMQ can be increased by adding TMP in portions to the reaction mixture. The best result was obtained when two portions of TMP were added, with the second portion being added 10–20 min after starting the oxidation reaction. Applying shorter or longer time intervals or continuous dosing of TMP diminished the effect. About 10% increase in TMQ yield was obtained by this method, compared to the reaction performed under identical conditions but adding the total amount of TMP at the beginning of the reaction. For example, 80% TMQ could be prepared by adding TMP in two portions and using only 1.5 wt% overall catalyst/reactant ratio (reaction conditions: 5 g TMP, 75 mg $CuCl_2$, 140 mg $NH_2OH$ · HCl, 30 ml AcOH, 12 ml TBHP, 25°C, 2 h, nitrogen atmosphere). Note, that this reaction was repeated on a tenfold greater scale without losing TMQ yield.

## 3.6. Physico-chemical measurement

In order to gain some information on the nature of interaction between catalyst, co-catalyst and reactant, UV–Vis and electrochemical potential measurement were undertaken. A shift in the UV–Vis spectrum at around 400–500 nm was observed when $CuCl_2$ and $NH_2OH$ · HCl were mixed in AcOH, and there was no detectable change when mixing $CuCl_2$ and TMP or TMQ. However, the concentrations were several orders of magnitude lower (due to the requirements of the method) than the usual concentrations during TMP oxidation.

Fig. 6 and Table 1 show the electrochemical potentials measured during mixing of the reaction components in a nitrogen atmosphere and during oxidation with TBHP. The potential of $CuCl_2$ in AcOH in the reactor is about the same as the redox potential of a $CuCl_2/CuCl = 40$ mol/mol system (mixture A in Table 2). Note that this potential was rather stable and not
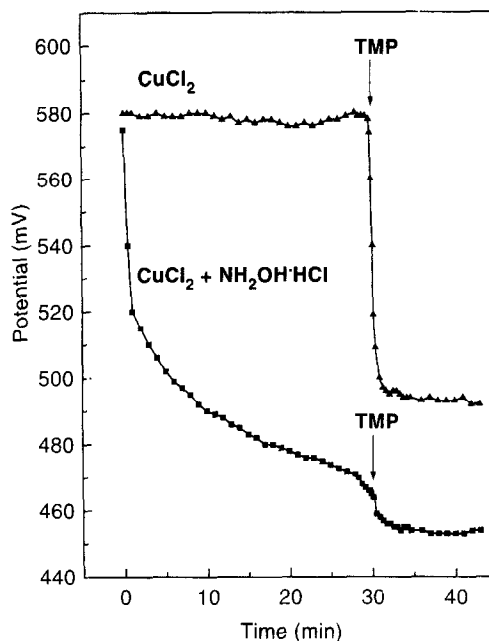


Fig. 6. Change of the electrochemical potential of the reaction mixture during the addition of TMP to $NH_2OH$ · HCl and $CuCl_2$ dissolved in AcOH (1.4 g TMP, 75 mg $CuCl_2$, 140 mg $NH_2OH$ · HCl, 30 ml AcOH, 25°C).

influenced by substituting the nitrogen atmosphere to air. When TMP was added to the $CuCl_2$ catalyst, the electrochemical potential rapidly decreased to a value which corresponded to the reduced state of the catalyst (mixture B). This observation explains why both $CuCl_2$ and CuCl are equally good catalysts for TMP oxidation.

Table 2
Electrochemical potentials measured before and during reaction

| Composition | Potential, mV |
|---|---|
| *Reaction mixtures:* | |
| $CuCl_2$ | 575–585 |
| $CuCl_2$ + TMP | 490–495 |
| $CuCl_2$ + $NH_2OH$ · HCl + TMP | 450–460 |
| $CuCl_2$ + $NH_2OH$ · HCl + TMP + TBHP | 560–600 |
| *Model mixtures:* | |
| A: ($CuCl_2$ /CuCl = 40 mol/mol) | 580 |
| B: ($CuCl_2$ /CuCl = 0.05 mol/mol) | 495 |
| C: ($CuCl_2$ /CuCl = 0.015 mol/mol) + $NH_2OH$ · HCl | 455 |

75 mg $CuCl_2$, 1.4 g TMP, 30 ml AcOH solvent, 140 mg $NH_2OH$ · HCl, 6 ml TBHP, 25°C, potentials referred to Ag/AgCl/KCl (0.1 M) reference electrode.

When $NH_2OH \cdot HCl$ was added first to $CuCl_2$ in AcOH, the electrochemical potential decreased slowly (steady state value after 1 h). Addition of TMP increased the rate of catalyst reduction without changing the final value, which was about 40 mV lower than that measured in the absence of co-catalyst. Similarly, a 40 mV negative shift was observed between the electrochemical potentials of model mixtures B and C (Table 2), which is due to the effect of co-catalyst. The negative potential shift is likely due to complex formation between catalyst and co-catalyst. Comparison of the data in Table 2 indicates that the co-catalyst had a dual effect: it reduced the potential (i) by reducing the oxidation state of the catalyst and (ii) by complexation.

As soon as the oxidant was dropped into the reaction mixture, the electrochemical (mixed) potential rose up to 560–600 mV and did not decrease during reaction (2 h), in agreement with the continuous presence of some TBHP detected by gas chromatography. No unambiguous difference in the electrochemical potential could be recognised in the presence or absence of co-catalyst, likely because the mixed potential is determined mainly by the oxidant.

## 4. Discussion

Our study demonstrates that the oxidation of 2,3,6-trimethylphenol (TMP) to 2,3,6-trimethyl-1,4-benzoquinone (TMQ) can be performed with a catalytic amount of $CuCl_2$. A yield of 80% at full conversion was obtained at a catalyst turnover of about 100 without optimising the reaction parameters. Considering the yield of TMQ and the amount of catalyst (without recycling), the method is superior to other known processes.

The good performance of $CuCl_2$ necessitates the presence of $NH_2OH \cdot HCl$ co-catalyst and the use of tert-butylhydroperoxide (TBHP) as

oxidant. The role of co-catalyst is not fully understood yet. Electrochemical measurements indicated that the co-catalyst plays a dual role: it reduces the $Cu^{2+}$ catalyst to $Cu^+$ and forms a complex with the latter. The reduction seems to be of minor importance as TMP reduces $Cu^{2+}$ more rapidly. The role of $NH_2OH \cdot HCl$ as co-catalyst is most probably to promote the further oxidation of the intermediate (dimers) to TMQ.

A comparison of several catalysts and co-catalysts uncovered the crucial role of $Cl^-$ ions. The presence of $Cl^-$ ions can be important in the $Cu^{2+}/Cu^+$ transformation and also in the complexation of the catalyst, but the considerable formation of 4-chloro-2,3,6-trimethylphenol (ClTMP, Scheme 2) as an intermediate could be excluded, when only small a amount of $CuCl_2$ catalyst is used.

Our catalytic study indicates that the likely intermediates of the TMP → TMQ transformation are dimers: 2,2',3,3',6,6'-hexamethyl-4,4'-biphenyldiol (D) and 2,2',3,3',6,6'-hexamethyl-4,4'-biphenylquinone (DQ), as shown in Scheme 2. Dimers are possibly formed by abstraction of a phenolic proton from TMP and by subsequent tautomerisation, dimerisation and oxidation [14]. Electrochemical and catalytic investigations disclosed that the reaction of TMP with $CuCl_2$ in AcOH is fast and the decomposition of dimers to produce TMQ is slow, especially when only stoichiometric or even lower amounts of TBHP are used. Direct hydroxylation of TMP to 2,3,6-trimethyl-1,4-hydroquinone (TMHQ, Scheme 2) is also found to be unlikely under the reaction conditions.

$Cu^+$ ions, which formed by interaction with TMP and $NH_2OH \cdot HCl$, are reoxidised by TBHP, while generating $HO^\cdot$ radicals which are important in the oxidation process. It seems to be crucial, that none of the redox cycles (the interaction of catalyst with TMP and its oxidised intermediates, and with the oxidant) is hindered under the very mild reaction conditions which enables the use of catalytic amount of $CuCl_2$.

## 5. Conclusions

The oxidation of 2,3,6-trimethylphenol to 2,3,6-trimethyl-1,4-benzoquinone with the $-(CuCl_2-NH_2OH \cdot HCl-TBHP-AcOH)-$ system affording 80% yield provides an alternative to the $CuCl_2$-catalysed aerobic oxidation. The advantage of the former is that only a catalytic (instead of stoichiometric) amount of $CuCl_2$ is necessary, whereas the drawback is the use of a more expensive oxidant (TBHP). The TMQ yield achieved so far could be further improved by optimising the reaction conditions, particularly by fine tuning the dosing of TMP which was found to have significant effect.

## Acknowledgements

## References

[1] Ger. Offen. 2 221 624 (1972); to F. Hoffman–La Roche AG.
[2] Eur. Pat. 127,888 (1984); to Mitsubishi Gas Chemical Co.
[3] Jpn. Pat. 60,255,745 (1985); to Mitsubishi Gas Chemical Co.
[4] Eur. Pat. 167 153 (1986); to Mitsubishi Gas Chemical Co.
[5] US Pat. 4,828,762 (1989); to Mitsubishi Gas Chemical Co.
[6] Eur. Pat. 475 272 (1992); to BASF AG.
[7] Jpn. Pat. JP 63 17,842 (1986); to Mitsui Toatsu Chemicals. Inc.
[8] Jpn. Pat. JP 63 41,438 (1988); to Mitsui Toatsu Chemicals. Inc.
[9] Jpn. Pat. JP 63,280,040 (1987); to Eisai Co.
[10] K. Takehira, M. Shimizu, Y. Watanabe, H. Orita and T. Hayakawa, Tetrahedron Lett., 30 (1989) 6691.
[11] K. Takehira, M. Shimizu, Y. Watanabe, H. Orita and T. Hayakawa, J. Chem. Soc., Chem. Commun., (1989) 1705.
[12] Jpn. Pat. JP 02.270.839 (1989); to C.K. Fine Chemicals K.K.
[13] Eur. Pat. 369 823 (1990); to Agency of Industrial Science and Technology.
[14] M. Shimizu, Y. Watanabe, H. Orita, T. Hayakawa and K. Takehira, Bull. Chem. Soc. Jpn., 65 (1992) 1522.
[15] Jpn. Pat. JP 02,209,841 (1989); to C.K. Fine Chemicals K.K.
[16] Jpn. Pat. JP 02,300,146 (1990); to C.K. Fine Chemicals K.K.
[17] Jpn. Pat. JP 02,268,132 (1989); to C.K. Fine Chemicals K.K.
[18] O.A. Kholdeeva, A.V. Golovin, R.I. Maksimovskaya and I.V. Kozhevnikov, J. Mol. Catal., 75 (1992) 235.
[19] USSR Pat. SU 1,719,392 (1992); to Institute of Catalysis. Novosibirsk.
[20] M. Lissel, H. Jansen in de Wal and R. Neumann. Tetrahedron Lett., 33 (1992) 1795.
[21] S. Ito, K. Aihara and M. Matsumoto, Tetrahedron Lett., 24 (1983) 5249.
[22] Eur. Pat. 107 176 (1984); to Segami Chemical Center.
[23] Eur. Pat. 338 666 (1989); to Agency of Industrial Science and Technology.
[24] M. Shimizu, H. Orita, T. Hayakawa and K. Takehira, Tetrahedron Lett., 30 (1989) 471.
[25] Jpn. Pat. JP 01,238,552 (1988); to Agency of Industrial Science and Technology.
[26] E.A. Karakhanov, S. Yu. Narin and A.G. Dedov. Appl. Organomet., Chem., 5 (1991) 445.
[27] S. Patai (Ed.), The Chemistry of Hydroxyl, Ether and Peroxide Groups. Supplement 2, Wiley, Chichester. 1993, p. 622.
[28] S. Patai (Ed.), The Chemistry of Hydroxyl Group, Wiley, Chichester, 1971.