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Epoxidation of cyclohexene with molecular oxygen by electrolysis combined with chemical catalysis

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Abstract This paper describes an electrochemical coupling epoxidation of cyclohexene by molecular oxygen (O₂) under mild reaction conditions. Herein, the electroreduction of O_2 to hydrogen peroxide (H₂O₂) efficiently proceeds in a relatively environmentally friendly acetone/ water medium containing electrolytes at 25-30 °C on a self-assembled H type of electrolysis cell with tree electrodes system, providing ca. 44.3 mM concentration of H₂O₂ under the optimal electrolysis conditions. The epoxidation of cyclohexene with in situ generated H₂O₂ simultaneously occurs upon catalysis by metal complexes, giving ca. 19.8 % of cyclohexene conversion with 78 % of epoxidative selectivity over the best catalyst 5-Cl-7-I-8quinolinolato manganese(III) complex (Q₃Mn^{III} (e)). The present electrochemical coupling epoxidation result is nearly equivalent to the epoxidation of cyclohexene with adscititious H_2O_2 catalyzed by the O_3Mn^{III} (e).

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Z. Fu e-mail: fzhhnnu@126.com **Keywords** Electrolysis · Chemical catalysis · Molecular oxygen · Coupling reaction · Cyclohexene epoxidation

Introduction

Epoxidation of olefins has outstanding importance in organic synthesis [1], since the epoxy compounds can be easily converted to a large variety of compounds [2, 3]. Therefore, there has been considerable interest in the development of highly efficient epoxidation catalysts [3-9]. For the epoxidation of olefins, iodosylarenes [10], tbutyl hydroperoxide [11, 12], hypochlorite [13, 14] and H_2O_2 [6, 15–18] are usually used as the oxidants because they provide a good yield of epoxides under relatively mild conditions. From an economic and environmental viewpoint, molecular oxygen (O_2) is more attractive than the above oxidants and thus it is considered to be the ultimate oxidant. Some effective processes upon catalysis by various transition metal βdiketonate complexes [19-23], Co(II)-Salen [24, 25] or Ru(II) complexes [26-28] have been developed for the epoxidation of alkenes with O₂. However, they generally need to employ isobutyraldehyde as the reductant, because the triplet nature of O₂ hampers the reaction with alkenes in its singlet state under mild reaction conditions. The use of electrochemical control technique can efficiently reduce O₂ to generate hydrogen peroxide (H_2O_2) [29, 30], so it has been successfully applied to the epoxidation of alkenes with O2 combined with transition metal Ru(II) [30], Fe(III) [31, 32] or Mn(III) [33-35] complexes. Recently, we have reported that 8-quinolinolato manganese(III) complexes (Q₃Mn^{III}) possessed a very excellent catalytic activity for the epoxidation of alkenes with H₂O₂ in environmentally friendly acetone–water media [9, 36]. Here, we introduce these relatively cheap Q_3Mn^{III} complexes into the electrochemical epoxidation of cyclohexene with O_2 .

Experimental

Materials and reagents

8-Hydroxyquinoline (8-HQ (**a**)), 5-chloro-8-HQ (**b**), 5,7dichloro-8-HQ (**c**), 5,7-dibromo-8-HQ (**d**) and 5-chloro-7iodo-8-HQ (**e**) were purchased from Alfa Aesar. The other commercially available chemicals, such as cyclohexene, acetone, tetraethylammonium perchlorate ($(Et)_4NClO_4$, TEAP), manganese acetate ($Mn(OAc)_2$), ammonium acetate (NH_4OAc), acetic acid (HOAc), 30 wt% aqueous H_2O_2 and other solvents were of analytical grade. Distilled water was used throughout this experiment.

Synthesis of metal complexes

A series of hexadentate binding 8-quinolinolato manganese complexes (Q_3Mn^{III} (**a–e**), see Fig. 1) were prepared as following the reported processes [9, 36]. For the sake of comparison, we also prepared hexadentate binding 5-chloro-7-iodo-8-quinolinolato Fe^{III} (Q_3Fe^{III} (**e**)) and oxobis (8-quinolinolato) V^{IV} (Q_2OV^{IV} (**a**)), as well as the tetradentate binding 8-quinolinolato Cu^{II} (Q_2Cu^{II} (**a**)) and salen–Mn^{III}Cl complexes based on our previously published literature [9, 37, 38].

Cyclic voltammetric measurements and controlledpotential electrolyses

Cyclic voltammetric (CV) measurement was conducted on a three-electrode configuration and an Autolab electrochemical workstation (Eco Chemie, Holland). The working electrode (WE), the counter electrode and the reference electrode were a glassy carbon electrode (GCE, 3-mmdiameter disk), a sheet of platinum foil, and a KCl-saturated calomel electrode (SCE), respectively. All the CV experiments were carried out at room temperature (20 °C).



Fig. 1 Structure of hexadentate binding 8-quinolinolato manganese complexes $(Q_3Mn^{\rm III}~(a{-}e)$

Controlled-potential electrolyses (CPE) experiments were conducted by using a CorrTest CS Electrochemical Workstation Model potentiostat and a self-assembled electrochemical H-type reaction device (see Fig. 2). Glassy carbon (20 mm \times 20 mm \times 3 mm), graphite (25 mm \times 25 mm \times 3 mm) and SCE electrodes were used as a working electrode, a counter electrode, and a reference electrode, respectively. All potentials here were reported versus the SCE. Anode and cathode electrolysis solutions were the same, consisting of acetone/water (30 mL, 3/1 V/ V), TEAP (3 mmol), NH₄OAc (6 mmol) and HOAc (3 mmol). The anode and cathode chambers was separated by a salt bridge. Cyclohexene (1 mmol) and catalyst Q₃Mn (0.4 mol% relative to cyclohexene) were added to the cathode chamber and the solution of the two chambers was stirred at 30 °C for 8 h under controlled potential (-0.75 V). An atmosphere of purified O₂ saturated with acetone and water was maintained over the reaction mixture. After electrolysis reaction, the catalyst was separated from the reaction mixture by filtration. The filtrate was analyzed chromatographically with an Agilent 6890N gas chromatograph (GC) with an SE-54 quartz capillary column $(30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ }\mu\text{m})$ and a flame ionization detector (FID) using cyclohexanone as an internal standard. The column temperature was 100 °C. Both injector and detector temperatures were set at 250 °C. In addition, the electrolysis experiments for reducing O_2 to generate H_2O_2 were carried out using the above-described conditions in the absence of the substrate and catalyst, and the concentration of H₂O₂ generated in the cathode chamber was also monitored by KMnO₄ chemical titration.



Fig. 2 Self-assembled electro-chemistry reaction device



Fig. 3 Cyclic voltammogram curves of molecular oxygen in acetone/ water (3/1) medium containing 0.1 mol/L TEPA

Results and discussion

Cyclic voltammetric measurement

Figure 3 shows the cyclic voltammetric (CV) curves of an acetone–water (V/V, 3/1) medium containing TEAP in different atmospheres. In the range of scanning potential, there were no redox current peaks observed under a N₂ atmosphere (curve 1). When this CV measurement was carried out under an air atmosphere, an obvious reducing peak at $p_c = -0.65$ V was observed in its CV curve 2. Notably, this reducing peak in pure O₂ atmosphere became very strong and shifted to $p_c = -0.75$ V, with the concomitant appearance of an oxidative peak at $p_a = 0.42$ V (curve 3). Undoubtedly, the reducing peak should be due to the reduction process of molecular oxygen, as reported by some literature [39–41]. Curve 4 illustrates that when 15 μ M of Q₃Mn^{III} (e) was added to acetone/water medium

(V/V, 3/1) under O₂, a pair quasi-reversible redox wave near (0.302 + 0.594)/2 = 0.448 V was observed, assigned to a redox process of the ligand's hydroxyls in the distorted Q₃Mn^{III} (e) [9]. Notably, the reducing potential of O₂ (-0.63 V) showed an obviously positive shift in the presence of Q₃Mn^{III} (e), indicating that the Q₃Mn^{III} (e) can promote the electrochemical reduction of O₂. On the other hand, the existence of Q₃Mn^{III} (e) could lead to a significant decrease in the reducing current of O₂, which was likely due to a gradual deposition of Q₃Mn^{III} (e) on the electrode surface.

Electroreduction of molecular oxygen

Figure 4a, b illustrates the effect of temperature and time on the concentration of H_2O_2 generated by the electrochemical reduction of O_2 in the absence of cyclohexene and catalyst, in which the curve of H_2O_2 concentration climbed continuously with the temperature or the time until it achieved a maximum at 25 °C and 12 h, respectively. After that, it fell rapidly due to an accelerating decomposition of H_2O_2 at a relatively high temperature and after a long time. The highest concentration of H_2O_2 (44.3 mM) was obtained when the electrolysis temperature and time were controlled at 25 °C and 12 h, respectively.

Epoxidation of cyclohexene with molecular oxygen

The electrochemical epoxidation of cyclohexene with O_2 upon catalysis by various metal complexes was investigated and the obtained data are summarized in Table 1. This epoxidation did not occur under N_2 atmosphere or in the absence of the catalyst or without the cathode potential (see entries 1, 2 and 3), but could proceed efficiently in the case of electrochemical control technique combined with the catalyst Q_3Mn^{III} (e) (entry 4), providing ca. 15.9 % of



Fig. 4 The temperature and time dependence of H_2O_2 concentration generated via electrochemical reduction of O_2 in acetone/water media (V/V, 3/1) containing TEAP (0.1 mol/L), NH₄OAc (0.2 mol/L) and HOAc (0.1 mol/L)

Table 1 Electrochemical epoxidation of cyclohexene with dioxygen over various metal complexes



Entry	Catalyst	Cathode potential (V)	Cyclohexene conversion (mol%)	Selectivity for products (%)		
				A	В	С
1 ^a	Q ₃ Mn (e)	-0.75	Trace	-	-	_
2	No	-0.75	Trace	-	_	-
3	Q ₃ Mn (e)	No	Trace	_	_	-
4	Q ₃ Mn (e)	-0.75	15.9	75	10	15
5 ^b	Q ₃ Mn (e)	No	16.2	80	4	16
6	$Q_3Mn(\mathbf{a})$	-0.75	7.3	75	5	20
7	Q_3Mn (b)	-0.75	13.1	72	5	23
8	$Q_3Mn(\mathbf{c})$	-0.75	14.6	77	5	18
9	$Q_3Mn(\mathbf{d})$	-0.75	15.0	80	5	15
10	$Q_3 F e^{III} (e)$	-0.75	Trace	_	_	-
11	$Q_2 C u^{II}(\mathbf{a})$	-0.75	2.4	70	15	15
12	Q ₂ OV ^{IV} (a)	-0.75	2.9	67	0	33
13	Salen-Mn-Cl	-0.75	1.6	64	14	22

Reaction conditions: cathode, 30 mL of acetone/water containing 0.1 mol/L TEAP + 0.2 mol/L NH₄OAc + 0.1 mol/L HOAc; cyclohexene, 1 mmol, catalyst: 0.4 % relative to mmol amount of substrate, oxygen atmosphere, 1 atm, reaction temperature and time, 30 °C and 5 h

A epoxycyclohexane, B cyclohexenol, C cyclohexanone

 $^{\rm a}~N_2$ atmosphere; other reaction conditions same as given above

^b Adding 0.3 mmol 30 wt% H₂O₂; temperature, 30 °C; time, 5 h

cyclohexene conversion with 75 % selectivity for epoxycyclohexane. Moreover, the epoxidation result in the entry 4 is nearly equivalent to that of the Q_3Mn^{III} (e)-catalyzed cyclohexene with adscititious H_2O_2 (Entry 5).

Entries 4 and 6–13 illustrate that the coupling epoxidation was influenced by the type of catalysts. Among the catalysts examined, a series of Q₃Mn^{III} (a-e) complexes with a hexadentate binding structure exhibited a good activity for this reaction (Entries 4, and 6–9, the conversion, 7.3-15.9 %; and the epoxidative selectivity, 72-80 %). However, other metal complexes, including both the hexadentate $Q_3 Fe^{III}$ (e) and $Q_2 OV^{IV}$ (a), as well as both the tetradentate Q₂Cu^{II} (**a**) and salen–Mn^{III}Cl, all provided very poor epoxidative efficiency under the same reaction conditions (entries 10-13). These facts suggest that the efficiency of these catalysts is influenced drastically by their metal ions, ligands and chelate modes, as previously reported by us for the Q₃Mn^{III} complexes that catalyzed the epoxidation of alkenes with H₂O₂ [9]. Entries 4 and 6–9 further show that the catalytic performances of Q₃Mn^{III} complexes were largely influenced by their ligand's substituent. Compared to the unsubstituted Q_3Mn^{III} (**a**), the 5-chlorinated Q_3Mn^{III} (**b**) and especially 5,7-dihalogenated Q_3Mn^{III} complexes (**c**-**e**) showed a higher epoxidative efficiency and their activity followed an increasing sequence of Q_3Mn^{III} (**e**) > Q_3Mn^{III} (**d**) > Q_3Mn^{III} (**c**) > Q_3Mn^{III} (**b**), most likely due to the increase of electron-donating effect of halogen substituents from Cl, Br to I on the ligand's aryl ring and the high resistance of halogenated 8-HQ ligands against oxidative degradation of the Q_3Mn^{III} , as reported for chlorinated porphyrin–Mn^{III} [42].

In the following experiments, the effects of various reaction parameters such as the amount of substrate and catalyst, cathode potential, reaction temperature and time, as well as acetone/water volume ratio on the coupling epoxidation were further checked using the best catalyst Q_3Mn^{III} (e) as an example and the results are shown in Table 2 and Figs. 5, 6 and 7. In the case of fixing substrate amount as 5 mmol, the conversion of cyclohexene and the utilization efficiency of the H_2O_2 generated via electroreduction of O_2 rapidly increased with increasing catalyst amount from 0.2 to 0.4 %; when the amount was higher

Entry	Catalyst amount ^a (mol%)	Subtrate amount (mmol)	Cyclohexene conversion (%)	Used efficiency of $H_2O_2^b$ (%)	Selectivity for products (%)		
					A	В	С
1	0.2	5.0	4.6	43.3	74	4	22
2	0.4	5.0	10.6	99.8	70	8	22
3	0.6	5.0	6.8	63.5	72	7	21
4	0.8	5.0	4	37.3	68	11	21
5	0.4	1	15.9	28.2	75	10	15
6	0.4	2.5	12.5	58.4	75	8	17
7	0.4	7.5	7.2	100.0	70	10	20
8	0.4	10	5.3	100.8	69	10	21
9 ^c	0.4	5	21.3	81.6	81	4	15
10 ^d	0.4	5	32.1	76.4	80	3	17

Table 2 Effect of the amount of catalyst and substrate on the electrochemical epoxidation of cyclohexene with dioxygen over Q₃Mn (e)

Reaction conditions: cathode potential, -0.75 V, 30 mL of acetone/water (3/1) containing 0.1 mol/L TEAP + 0.2 mol/L NH₄OAc + 0.1 mol/L HOAc; oxygen atmosphere, 1 atm; reaction temperature and time, 30 °C and 5 h

A epoxycyclohexane, B cyclohexenol, C cyclohexanone

^a Relative to mmol amount of substrate

^b The estimated efficiency of H_2O_2 (%) = [(the amount (mmol) of epoxycyclohexane + cyclohexenol + 2 cyclohexanone/the amount (mmol) of H_2O_2 generated by an electro-reduction of O_2 in the absence of Q_3Mn (e) (0.648 mmol)] × 100 %

^c Adding 1.5 mmol 30 wt% H_2O_2 , 30 mL of acetone/water (3/1) containing 0.2 mol/L NH₄OAc + 0.1 mol/L; temperature, 10 °C; time, 5 h

^d Adding 2.5 mmol 30 wt% H_2O_2 , 30 mL of acetone/water (3/1) containing 0.2 mol/L NH₄OAc + 0.1 mol/L; temperature, 10 °C; time, 5 h



Fig. 5 The effect of the volume ratio of acetone to water and cathode potential on the electrochemical epoxidation of cyclohexene with O_2 (Q_3Mn^{III} (e), 0.4 %; temperature, 30 °C)

than 0.4 %, both the values greatly dropped (see entries 1–4 in Table 2). A large decrease in epoxidative efficiency at high catalyst amount is likely due to the serious deposition of catalyst on the electrode surface. In the case of fixing catalyst amount at 0.4 %, when the amount of cyclohexene was increased from 1 to 10 mmol, the conversion obviously decreased from 15.9 to 5.3 %, while the utilization efficiency greatly increased from 28.2 to 100.8 %, with a concomitant slight decrease in epoxycyclohexane selectivity (see entries 5–8 in Table 2). This is likely due to a

decrease in substrate solubility. On the whole, the selectivity for epoxycyclohexane slightly decreased with increasing amount of substrate or catalyst, along with an increase in cyclohexanone or cyclohexenol selectivity. Entries 9 and 10 illustrate that the epoxidation of cyclohexene with adscititious H_2O_2 under its optimal reaction conditions could achieve ca. 76.4–81.6 % of the utilization efficiency of H_2O_2 , and this efficiency was lower than that obtained from the electrocatalytic epoxidation of cyclohexene with O_2 under the optimized substrate and catalyst



Fig. 6 The effect of reaction temperature and time on the electrochemical epoxidation of cyclohexene (5 mmol, Q_3Mn^{III} (e), 0.4 %, acetone/water, 3/1, 30 mL; cathode potential, -0.75 V)





amounts. Figure 5a illustrates that the coupling epoxidation was also influenced by the volume ratio of acetone to water; when the ratio was between 2:1 and 3.5:1, the conversion of cyclohexene gradually increased with increasing acetone amount, likely due to the improvement of substrate solubility. After that, the conversion slightly decreased. The selectivity of products was not nearly influenced by the volume ratio of acetone to water. Figure 5b illustrates that the coupling epoxidation was influenced significantly by the cathode potential; when the potential was controlled at lower or higher than -0.75 V, epoxycyclohexane yield drastically dropped. This is likely because the electrochemical reduction of O₂ is not easy to proceed in the case of cathode potential deviation from -0.75 V. Figure 6a and b illustrates that the conversion of cyclohexene increased continuously with temperature and time until it achieved a maximum at 30 °C and 12 h; afterward, it decreased to a great extent due to an accelerated decomposition of the in situ generated H₂O₂ at a relatively high temperature and after a long time. The effect of temperature and time on the selectivity for products had a very similar, i.e., the selectivity for epoxycyclohexane slowly increased and then decreased with both the parameters. Under the optimal conditions (cyclohexane, 5 mmol, catalyst, 0.4 %, acetone/ water volume ratio, 3.5/1, temperature, 30 °C, time, 12 h, cathode potential, -0.75 V), the conversion of cyclohexene, the selectivity for the epoxide and the utilization efficiency for the in situ generated H₂O₂ were ca. 19.0, 71.0 and 85.1 %, respectively.

Reaction mechanism

Based on the results presented here, as well as those in previous studies [29–35, 39–41], it is apparent that the above data are better explained according to the following reaction pathway (see Fig. 7). In this mechanism, molecular oxygen is reduced to form H_2O_2 on the cathode's surface under the controlled cathode potential electrolyses. Then the H_2O_2 in situ generated can selectively oxidize cyclohexene to epoxycyclohexane upon catalysis by Q_3 . Mn^{III} via undergoing a pathway of forming a key intermediate $Q_3Mn^V = O$ [9].

Conclusion

In summary, an electrochemical control technique combined with Q_3Mn^{III} complexes has been developed as an

efficient method for epoxidation of cyclohexene with molecular oxygen. The established method has the following advantages: (1) utilization of more cost-effective and green molecular oxygen and water-acetone as the oxidant and solvent, respectively; (2) good catalytic efficiency and high epoxidation selectivity and (3) facile operation. It is anticipated that this method will have competitive potential for the selective oxidation of alkenes and alcohols by molecular oxygen if its oxidation efficiency is further improved.

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