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Copper(II) Catalyzed Oxidation of Cyclohexane by *tert*-Butyl Hydroperoxide[1]

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Cicloexano pode ser facilmente oxidado por *ter*-butil-hidroperóxido, à temperatura ambiente, utilizando cloreto de cobre(II) como catalisador e piridina como solvente. O produto principal da oxidação é cicloexeno, mas cicloexanona e uma pequena quantidade de cicloexanol também são formados. A eficiência em relação ao oxidante é alta (78%). Embora a reação seja lenta (4 h), a quantidade de produtos acumulados em 4 reações corresponde a uma concentração de 0,52 mol/L. Sob atmosfera de argônio a 70 °C, a reação é muito mais rápida, com cerca de 82% dos produtos formados após os primeiros 5 min. Após 1 h obtém-se a mesma eficiência observada após 4 h a 28 °C. Sob atmosfera de oxigênio a 70 °C, ciclohexanona e cicloexanol são formados em maior quantidade. Após 1 h, a eficiência relativa ao oxidante é superior a 100%, mostrando a participação do oxigênio molecular no processo. Após 6 acumulações, obtém-se uma concentração de produtos oxidados igual a 1,02 mol/L em apenas 1 h de reação.

Cyclohexane can be easily oxidized at room temperature by *tert*-butyl hydroperoxide, using copper(II) chloride in pyridine as a catalyst. Cyclohexene is the main product but cyclohexanone and some cyclohexanol are formed as well. The efficiency with respect to the oxidant is high (78%). The reaction is slow (4 h) but in four accumulations a final concentration of 0.52 mol/L of oxidized products can be obtained. At 70 °C under an argon atmosphere, the reaction is faster. After 5 min, 82% of the oxidation products are already formed and after 1 h the efficiency is the same as observed at 28 °C in 4 h. At 70 °C under an oxygen atmosphere more cyclohexanone and cyclohexanol are produced, and after 1 h the efficiency with respect to the oxidant is above 100%, showing that molecular oxygen participates in the oxidation. By accumulation of 6 reactions under these conditions a 1.02 mol/L solution of the oxidation products is obtained in only 1 h of reaction time.

Keywords: *cyclohexane oxidation, Gif system,* tert-*butyl hydroperoxide, copper(II) catalyst*

Introduction

The oxidation of cyclohexane is considered to be the least efficient of all major industrial chemical processes. However, it is an extremely important commercial reaction, since approximately 10^6 tons per year of cyclohexanone and cyclohexanol are made worldwide for conversion to Nylon-6 and Nylon-6,6[2]. In Brazil, cyclohexane is commercially oxidized by Nitrocarbono S.A. using the DSM process, in the presence of a soluble cobalt(II) salt at approximately 160 °C and 15 bar of air. The conversion of cyclohexane (ane) is limited to 4% in order to achieve a selectivity for cyclohexanol (ol) and cyclohexanone (one) of 80%. The remainder (20%) consists of by-products such as n-butyric, n-valeric, succinic, glutaric and adipic acids[3].

Enzymes are capable of oxidizing cyclohexane to cyclohexanol at room temperature with very high selectivity[4]. However, the mechanisms of enzymatic oxidations are known in considerably less detail than those of other biological reactions[5]. One very important approach to gaining a deeper understanding of these biological processes consists of using model compounds to imitate enzymatic activity. Barton *et al.*[6] have developed a family of chemical systems which allows the oxidation and functionalization of saturated hydrocarbons under mild conditions and have grouped them under the name Gif systems. These systems are able to quantitatively convert saturated hydrocarbons to ketones (and a small amount of alcohol) in conversions ranging between 20 and 30%[7]. More surprisingly, the oxidation of the hydrocarbons takes place even in the presence of different, more easily oxidizable, compounds[8].

We found that the Gif^{IV} [using iron(II), oxygen (from air) and zinc dust] and $GoAgg^{II}$ [using iron(III) and hydrogen peroxide] systems are the most practical and we opti-

mized them for cyclohexane oxidation[9,10]. A major drawback of the Gif^{IV} system is that, during the oxidation, radical reactions become more important, causing over-oxidation and coupling of the products with pyridine[11]. Using the GoAgg^{II} system and picolinic acid to accelerate the oxidation, we are able to accumulate the oxidation products one + ol to a concentration similar to that obtained in the industrial process in only 60 min of reaction time and without the formation of any by-products[12]. However, pyridine is an essential solvent for the reaction; its substituition by *tert*-butanol, acetone or acetonitrile gives much lower concentrations of products and low efficiency with respect to hydrogen peroxide[13]. A comparison of cyclohexane oxidation by the classical process and the Gif systems and an evaluation of its possible substitution was published in two recent review articles[14,15].

An interesting feature of Gif chemistry is that the iron salt can be substituted by a copper salt[16]. We studied cyclohexane oxidation by hydrogen peroxide in the presence of copper(II) salts (GoChAgg^{I} system) and found that this system was less efficient than the GoAgg^{II} system although more selective for cyclohexanone[17]. Futhermore, the presence of acetic acid is not necessary. In cumulative reactions, the concentration of the oxidation products (one + ol) obtained after 120 min is slightly lower than that obtained with the GoAgg^{II} system after 60 min[18].

One of the major drawbacks of the GoAgg^{II} and GoChAgg^{I} systems is the water formed during the oxidation process which causes hydrolysis of the catalyst (GoAgg^{II} system)[12] or phase separation (GoChAgg^{I} system)[18]. Substitution of hydrogen peroxide by *tert*-butyl hydroperoxide, which is cheap and industrially produced by air-oxidation of isobutane, is an interesting alternative. The *tert*-butanol formed during the reaction is soluble in most solvents and should not interact with the catalyst. Barton *et al.*[19] recently showed that *tert*-butyl hydroperoxide in the presence of an iron(III) salt (GoAgg^{IV} system) gives similar results to the GoAgg^{II} system in the oxidation of saturated hydrocarbons. However, *tert*-butyl hydroperoxide in the presence of a copper(II) salt (GoChAgg^{II} system) mostly forms the corresponding olefin, supporting a metal-dependent reaction pathway for the oxidation[20]. We wish to report here our results on the oxidation of cyclohexane by *tert*-butyl hydroperoxide in the presence of copper(II) chloride.

Experimental Details

All reagents and solvents used were of analytical grade. Cyclohexane was purified by washing with conc. sulfuric acid, water, 5% sodium hydroxide solution and water, and then distilled. A solution of *tert*-butyl hydroperoxide (82.8%) in cyclohexane was obtained from Nitrocarbono S.A.

The oxidation reactions were performed in a closed 125 mL Erlenmeyer under an argon atmosphere, using 28 mL of pyridine, 1.48 g of cyclohexane and 170 mg (1 mmol) of cupric chloride. The reaction flask was placed in a water bath with thermostat at 28 °C, the mixture was magnetically stirred at 500 rpm, and the reaction was initiated by addition of 1.1 g (10 mmol) of the solution of *tert*-butyl hydroperoxide. The cyclohexane added to this solution brought the total amount to 20 mmol. The reaction flask was closed with a septum to avoid evaporation of cyclohexane and the mixture typically reacted for 4 h. In the kinetic measurements, 0.5 mL of the solution was taken out of the reaction mixture every hour for quenching with phosphoric acid and subsequent analysis. In the cumulative reactions at 28 °C, 100 mmol of cyclohexane were used and a new portion of 1.1 g (10 mmol) of *tert*-butyl hydroperoxide was added every 4 h. All reactions were stopped after the indicated time by additition of 0.3 mL (4.4 mmol) of phosphoric acid (85%). Kinetic measurements were also performed at 70 °C under argon as well as under an oxygen atmosphere. At this temperature, 0.5 mL of the solution was taken out of the reaction mixture at the times indicated and quenched as previously described. In the cumulative reactions at 70 °C under an oxygen atmosphere, 100 mmol of cyclohexane was used and a new portion of 1.1 g (10 mmol) of *tert*-butyl hydroperoxide was added every 10 min.

The reaction mixture was analyzed with a CG-37 gas chromatograph equipped with a 4 m packed columm of 15% Carbowax 20M on Chromosorb W-HP and coupled to a flame ionization detector. After 20 min at 115 °C, the temperature was programmed at 10 °C/min to 170 °C. Cyclooctane was added as an internal standard and the observed retention times were: cyclohexane (ane, 2.1 min), cyclohexene (ene, 2.6 min), cyclooctane (oct, 5.4 min), cyclohexanone (one, 16.4 min) and cyclohexanol (ol, 21.0 min). The mass balance (m.b.) represents the percentage related to the initial cyclohexane, of the products from the reaction: unreacted cyclohexane, cyclohexene, cyclohexanone and cyclohexanol. The efficiency with respect to *tert*-butyl hydroperoxide was calculated taking into account that 1 mol of *tert*-butyl hydroperoxide is needed to produce 0.5 mol of cyclohexanone, 1 mol of cyclohexanol or 1 mol of cyclohexene, respectively (equations 1 to 3)

$$C_6H_{12} + 2\,C_4H_9OOH \rightarrow \underset{\text{(one)}}{C_6H_{10}O} + 2C_4H_9OH + H_2O \quad (1)$$

$$C_6H_{12} + C_4H_9OOH \rightarrow \underset{\text{(ol)}}{C_6H_{11}OH} + C_4H_9OH \quad (2)$$

$$C_6H_{12} + C_4H_9OOH \rightarrow \underset{\text{(ene)}}{C_6H_{10}} + C_4H_9OH + H_2O \quad (3)$$

Results and Discussion

The results obtained for the oxidation of cyclohexane under standard conditions for the cupric chloride/hydrogen

peroxide ($GoChAgg^{I}$) and cupric chloride/*tert*-butyl hydroperoxide ($GoChAgg^{II}$) systems are shown in Table 1. The $GoChAgg^{I}$ system is approximately 8 times more rapid than the $GoChAgg^{II}$, but much less efficient. A similar result was already observed for the $GoAgg^{II}$ system where the addition of picolinic acid accelerated the reaction by 40 times, but reduced the efficiency from 91% to 53% [15]. This shows clearly that Gif systems are more efficient in transfering active oxygen to the saturated hydrocarbons if the reaction is slow. The $GoChAgg^{I}$ system is very selective, forming only cyclohexanone[18]. As already reported by Barton *et al.*[20], cyclohexene is the main product of the $GoChAgg^{II}$ system, but cyclohexanone and small amounts of cyclohexanol are formed as well. However, the quantity of cyclohexanone produced by the $GoChAgg^{II}$ system is higher than the total amount of products obtained with the $GoChAgg^{I}$ system. This shows the higher efficiency of the $GoChAgg^{II}$ system, which allows a turnover number 3.6 times higher than the $GoChAgg^{I}$ system. However, the mass balance does not close for the $GoChAgg^{II}$ system, the remaining 4% (0.8 mmol) being over-oxidation products, mainly 2-cyclohexenone, and chlorinated products, mainly chlorocyclohexane and 2-chlorocyclohexanone, which were identified by GC/MS analyses. The formation of the chlorinated products shows that the $GoChAgg^{II}$ system may be used for ionic substitution reactions of saturated hydrocarbons, as described by Barton *et al.*[21,22] in two recent papers.

In the $GoChAgg^{II}$ system, the color of the reaction mixture, which is initially light blue, changes to dark green during the course of the reaction. This indicates that the active copper species suffers modifications during the reaction. We therefore investigated the reaction kinetically and the results are shown in Table 2. During the first hour, the $GoChAgg^{II}$ produces only cyclohexene. With the color change, cyclohexanone and some cyclohexanol are formed as well. The total amount of oxidized products increases almost linearly during the first 4 h and then stays constant, showing that the reaction is finished after this time. The efficiency with respect to the oxidant reaches 78% and the mass balance gives 96% throughout the reaction.

We then tried to accumulate the oxidation products by adding 10 mmol of *tert*-butyl hydroperoxide every 4 h to the reaction mixture. The results are shown in Table 3. The

Table 1. Reaction time, selectivity, turnover number, efficiency and mass balance as a function of the oxidant (20 mmol of cyclohexane, 1.0 mmol of cupric chloride, 28 mL of pyridine, 10 mmol of the oxidant, 28 °C, argon atmosphere).

oxidant	time (h)	one (mmol)	ol (mmol)	ene (mmol)	turnover number	effic. (%)	m.b. (%)
H_2O_2	0.5	1.65	–	–	1.6	33	100
C_4H_9OOH	4	2.00	0.17	3.63	5.8	78	96

Table 2. Time dependence of selectivity, turnover number, efficiency, and mass balance (20 mmol of cyclohexane, 1.0 mmol of cupric chloride, 28 mL of pyridine, 10 mmol of *tert*-butyl hydroperoxide, 28 °C, argon atmosphere).

time (h)	one (mmol)	ol (mmol)	ene (mmol)	ene/one	turnover number	effic. (%)	m.b. (%)
1	0	0	1.92	∞	1.9	19.2	96
2	0.68	0.08	2.49	3.6	3.2	39.3	97
3	1.16	0.09	3.06	2.6	4.4	54.7	95
4	2.00	0.17	3.63	1.8	5.8	78.0	96
5	1.95	0.17	3.65	1.9	5.8	77.2	96
6	2.08	0.19	3.63	1.7	5.8	79.8	97

Table 3. Turnover number, efficiency, mass balance and concentration of products (one + ol + ene) in cumulative reactions (100 mmol of cyclohexane, 1.0 mmol of cupric chloride, 28 mL of pyridine, 28 °C, argon atmosphere, every 4 h: 10 mmol of *tert*-butyl hydroperoxide).

time (h)	one (mmol)	ol (mmol)	ene (mmol)	ene/one	turnover number	effic. (%)	m.b. (%)	conc. (mol/L)
4	0.70	0.17	3.06	4.3	3.9	46.0	98	0.14
8	1.60	0.27	6.42	4.0	8.3	50.2	96	0.29
12	2.16	0.40	8.98	4.2	11.6	47.3	97	0.39
16	2.86	0.56	12.74	4.4	16.2	48.3	98	0.52
20	2.74	0.61	13.02	4.7	16.5	38.2	95	0.50
24	2.80	0.57	12.84	4.5	16.2	30.2	93	0.49

total amount of oxidized products increases almost linearly during the first four accumulations, giving a final concentration of 0.52 mol/L. This concentration is higher than that obtained in the commercial cyclohexane oxidation process (0.32 mol/L)[14] and that obtained in the cumulative reactions using the $GoAgg^{II}$ system (0.36 mol/L)[12]. However, the total reaction time (16 h) is very long. The selectivity for the three oxidation products stays approximately constant during the reaction course. After 4 accumulations, the catalyst loses its activity as the quantities of the oxidized products stay constant and cyclohexane is not further consumed. The reason for the deactivation of the catalyst is not yet understood.

The oxidation of cyclohexane by the $GoChAgg^{II}$ system is faster at 70 °C, as shown in Table 4. After 5 min of reaction time, 82% of the oxidation products are already formed. With longer reaction times, the quantities of the products increase only slowly, reaching a maximum after 60 min. The product distribution stays approximately constant during the reaction course and is similar to that obtained in the reaction at 20 °C (Table 2). The total efficiency of the oxidation (77%) and the mass balance (96%) are the same as observed in the reaction at 20 °C, within experimental error. This result is somehow surprising, as the efficiency of the $GoChAgg^{I}$ system at 60 °C was only 60% of that observed at 28 °C.

We have also studied the oxidation of cyclohexane by the $GoChAgg^{II}$ system at 70 °C under an atmosphere of oxygen. The results are shown in Table 5. After 5 min of reaction time, the amount of cyclohexene produced is approximately the same as that obtained under an argon atmosphere. The amounts of cyclohexanone and cyclohex-

Table 4. Selectivity, turnover number, efficiency and mass balance as a function of reaction time (20 mmol of cyclohexane, 1.0 mmol of cupric chloride, 28 mL of pyridine, 10 mmol of *tert*-butyl hydroperoxide, 70 °C, argon atmosphere).

time (h)	one (mmol)	ol (mmol)	ene (mmol)	ene/one	turnover number	effic. (%)	m.b. (%)
5	1.37	0.30	3.30	2.41	5.0	63.4	96
10	1.40	0.33	3.50	2.50	5.2	66.3	93
20	1.44	0.35	3.68	2.55	5.4	69.1	90
30	1.50	0.37	3.82	2.51	5.6	71.9	95
40	1.55	0.39	3.85	2.48	5.8	73.4	97
50	1.63	0.42	3.90	2.40	5.9	75.8	92
60	1.66	0.38	4.00	2.41	6.0	77.0	96
120	1.64	0.40	3.94	2.40	5.9	76.2	95
180	1.63	0.41	4.10	2.51	6.1	77.8	92
240	1.65	0.37	3.90	2.36	5.9	75.7	94
300	1.66	0.39	3.98	2.40	6.0	76.9	97

Table 5. Selectivity, turnover number, efficiency and mass balance as a function of reaction time (100 mmol of cyclohexane, 1.0 mmol of cupric chloride, 28 mL of pyridine, 10 mmol of *tert*-butyl hydroperoxide, 70 °C, oxygen atmosphere).

time (h)	one (mmol)	ol (mmol)	ene (mmol)	ene/one	turnover number	effic. (%)	m.b. (%)
5	2.14	0.76	3.31	1.55	6.2	83.5	68
10	2.20	0.81	3.87	1.76	6.8	90.2	62
20	2.29	0.87	3.94	1.72	7.6	94.3	65
30	2.33	0.75	4.03	1.73	7.2	94.2	60
40	2.44	0.79	4.07	1.67	7.3	97.4	63
50	2.68	0.79	3.96	1.48	7.4	100.1	64
60	2.79	0.96	3.83	1.37	7.5	103.7	69
120	2.82	1.02	3.89	1.38	7.7	105.5	62
180	2.84	0.91	3.59	1.26	7.3	101.4	63
240	2.66	1.13	3.86	1.45	7.6	103.1	62
300	2.65	1.09	3.62	1.37	7.3	100.1	61
360	2.61	0.98	3.59	1.38	7.1	97.9	59

anol produced in 5 min are considerably higher, resulting in an increase of 25% in the oxidation products. As observed for the reaction under an argon atmosphere, the total amount of oxidized products only increases slowly after 5 min, reaching a maximum after approximately 2 h. This maximum is unexpected as it represents an efficiency with respect to *tert*-butyl hydroperoxide of 105%. This high efficiency can only be explained if the molecular oxygen participates in the oxidation reaction, either by directly oxidizing cyclohexane or by reoxidizing *tert*-butanol to *tert*-butyl hydroperoxide. Similar results have been recently reported by Barton *et al.*[23] for the iron(III) nitrate/*tert*-butyl hydroperoxide in pyridine system, and for iron(III) or copper(II) chelates/*tert*-butyl hydroperoxide in cyclohexane. The mass balance of the reaction is poor due to evaporation of cyclohexane, as an open oxygen atmosphere was used. Over-oxidation is also observed under these conditions, as the total amount of the oxidized products is reduced after 2 h of reaction time.

We tried to accumulate the oxidation products at 70 °C under an oxygen atmosphere by adding 10 mmol of *tert*-butyl hydroperoxide every 10 min to the reaction mixture. The results are shown in Table 6. The concentration of oxidized products increases almost linearly during the accumulation reactions. After 2 accumulations (20 min) it is already higher than that obtained in the commercial cyclohexane oxidation process after 40 min. After 6 accumulations, the concentration of oxidized products is 1.02 mol/L (10%), which is three times higher than in the commercial process. Furthermore, the number of accumulations could be further increased as the system is still active. Interestingly, the ene/one ratio, which is around 2 at the beginning, increases with further accumulations, showing that under these reaction conditions the active species stabilizes, becoming more and more selective for cyclohexene formation. This means that the catalyst could be used for more cumulative reactions. After 60 min the turnover number reaches 34.7, showing that this catalyst is very reactive under these reaction conditions. The oxidation efficiency is good (70%) and the mass balance closes within 5%, showing that few by-products are formed which do not increase during the course of the reaction. The reaction conditions described here seem to be optimized as the catalyst is very reactive and selective, producing the oxidized products in high concentration.

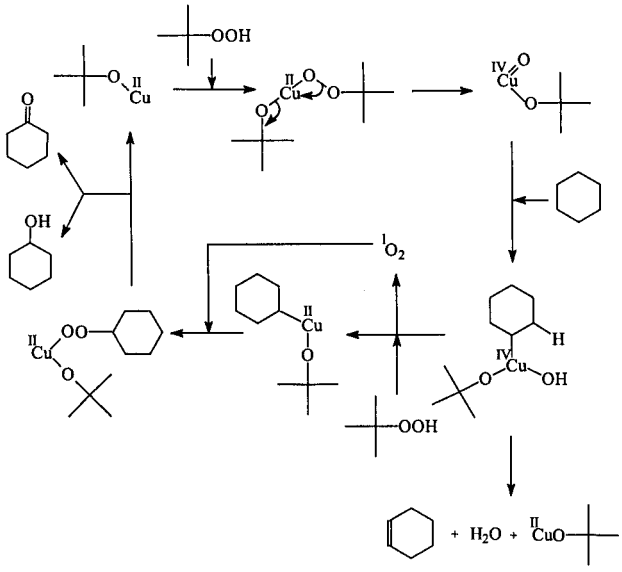
Proposed Reaction Mechanism

The mechanistic pathway of the GoChAgg^{II} system is considered to be similar to that proposed for other Gif systems[7, 24]. The copper(II) salt reacts with *tert*-butyl hydroperoxide to form, *via* a copper(II) peroxide, a copper(IV) oxenoid species, in which *tert*-butyloxy remains coordenated to the copper, explaining the different selectivity of this system. The copper(IV) oxenoid species then reacts with cyclohexane to form a cyclohexyl copper(IV) hydroxy complex, which under reaction conditions preferentially decomposes to cyclohexene, water and the original copper(II) complex. It is also reduced by an excess of *tert*-butyl hydroperoxide to a cyclohexyl copper(II) complex with the formation of molecular oxygen, which we believe to be singlet oxygen[14], as already proposed by Sawyer *et al.*[25] in the reaction of bis(picolinate)iron(II) with hydrogen peroxide. This cyclohexyl copper(II) complex then inserts the singlet oxygen into the copper-carbon bond, forming a cyclohexylperoxy copper(II) complex, which decomposes to cyclohexanone with some cyclohexanol and the initial copper(II) complex. The proposed mechanism is shown in Scheme I.

The oxenoid copper(IV) species, which corresponds to the oxenoid iron(V) species found as a reactive intermediate in methane monooxygenases[26], activates saturated hydrocarbons by the cleavage of a C-H bond. The cyclohexyl copper(IV) hydroxide species thus formed is sterically rather crowded if a *tert*-butyloxy group is bound to it. It, therefore, suffers easy elimination of cyclohexene and water, giving the unusual selectivity of the GoChAgg^{II} system. In the GoChAgg^{I} system (which uses hydrogen peroxide) this elimination reaction is not observed. The formation of the cyclohexylperoxy copper(II) species occurs in both systems with approximately the same efficiency and decomposes mostly to cyclohexanone independent of the oxidant used. The superiority of the GoChAgg^{II} system lies in the possibility of forming additional cyclohexene by the elimination reaction, which gives

Table 6. Selectivity, turnover number, efficiency, mass balance and concentration of products (one + ol + ene) in cumulative reactions (100 mmol of cyclohexane, 1.0 mmol of cupric chloride, 28 mL of pyridine, 70 °C, oxygen atmosphere, every 10 min: 10 mmol of *tert*-butyl hydroperoxide).

time (h)	one (mmol)	ol (mmol)	ene (mmol)	ene/one	turnover number	effic. (%)	m.b. (%)	conc. (mol/L)
10	1.85	0.56	3.76	2.03	6.2	80.2	96	0.21
20	3.06	1.22	6.63	2.16	10.9	69.9	95	0.36
30	3.96	1.42	11.71	2.95	16.0	70.1	96	0.55
40	5.41	2.25	16.40	3.03	24.0	73.7	97	0.75
50	6.52	2.75	19.45	3.03	28.7	70.5	94	0.87
60	7.24	2.81	24.67	3.40	34.7	70.0	95	1.02



Scheme 1. Proposed reaction mechanism.

a much better efficiency to this system and allows for obtaining the oxidation products in very high concentration. The cyclohexene is easily transformed with 95% selectivity into additional cyclohexanone, by oxidation with palladium and copper chloride in ethanol under mild conditions[27].

Conclusions

The GoChAgg^{II} system (copper(II) chloride and *tert*-butyl hydroperoxide in pyridine) under an oxygen atmosphere at 70 °C is efficient and rapid, giving oxidation products in very high yields. Furthermore, molecular oxygen may participate under certain conditions in the oxidation. This makes the GoChAgg^{II} system a very good candidate for substitution of the classical cyclohexane oxidation process. For this purpose, the pyridine has to be replaced, as it is not appropriate for industrial use. We believe that the oxidation could be performed in pure cyclohexane using a soluble copper complex. Furthermore it should be possible to find reaction conditions under which the molecular oxygen reoxidizes the *tert*-butyl hydroperoxide, which would allow its use in catalytic amounts. Cyclohexane would be oxidized by molecular oxygen at 70 °C with high velocity and selectivity, which certainly would be a major advance with respect to the classical process.

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