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Catalytic Cyclohexane Oxidation | *Very Important Paper* |

VIP

One-Pot Conversion of Cyclohexane to Adipic Acid Using a μ_4-Oxido-Copper Cluster as Catalyst Together with Hydrogen Peroxide

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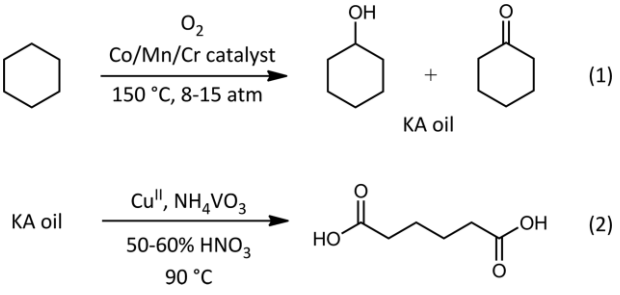
Abstract: The production of nylon-6.6 is one of the largest scale syntheses in industrial chemistry. The standard procedure is based on an energy consuming low-level conversion of cyclohexane to yield adipic acid in two steps that is converted to nylon-6.6 in a separate step. Therefore, there is a strong intent to optimize the synthetic route in an economic and ecologic matter. In this work, we present a one-pot oxygenation of cyclohexane with hydrogen peroxide and a μ_4-oxido-copper cluster catalyst to yield dicarboxylic acids with adipic acid as the main product.

Introduction

Oxidation reactions are crucial in chemical industry to provide basic chemicals as well as specialized pharmaceutical products. An important and well-known example is the production of adipic acid that is a precursor for the synthesis of nylon-6,6.[1,2] In addition, adipic acid is used for the manufacturing of fibers, tire reinforcements, upholstery, and as additive for the food industry.[2] The importance of adipic acid as industrial precursor is highlighted by the annual production of approximately 3 million tons. Starting from cyclohexane, adipic acid is produced via a two-step synthesis that is established on an industrial scale for more than 75 years. First, cyclohexane is reacted catalytically with dioxygen and a cobalt or manganese catalyst at high temperatures (150 °C) and pressures (8 to 15 bar) to yield a mixture of cyclohexanol and cyclohexanone, the so called KA oil [Scheme 1, (1)].[3]

In a second step, the KA oil is converted to adipic acid [Scheme 1, (2)] via nitric acid oxidation.[4] In total, the yield of adipic acid is determined by the conversion level of cyclohexane to KA oil, which has to be maintained at a low level (4 %-15 %) to promote selectivity.[5] The main disadvantages, however, are the high consumption of nitric acid at high temperatures that causes corrosion and emission of nitrous oxide (35 % of the exhaust gas) as an ozone decomposing greenhouse gas.[6,7] Hence, there is a strong intend to optimize the process. Potential improvements aim at feasibility at moderate reaction conditions, higher yields, lower costs, and the reduction of hazardous chemicals. Several lab scale routes to prepare adipic acid at mild conditions while using less toxic and expensive catalysts have been described in the literature. Examples include the HNO_3-free one-pot conversion of cyclohexane to adipic acid via ozone oxidation and UV-irradiation. This route led to high conversions and a selectivity of 70–90 %.[8] Another example is the catalytic synthesis via an iron(II) scorpionate complex.[9] Additionally, an alternative "green" route to adipic acid has been reported by Noyori and co-workers using hydrogen peroxide and cyclohexene as starting materials. An unresolved issue of this route, however, is the considerably low availability of cyclohexene.[10]



Scheme 1. Reaction scheme for the industrial production of adipic acid: (1) oxygenation of cyclohexane to KA oil, (2) oxidation of KA oil to yield adipic acid.

Our groups are interested in selective oxidation reactions of organic substrates catalyzed by copper complexes.[11,12] Simple copper compounds have a wide range of applications in organic and inorganic syntheses such as oxygenation, cyclization or coupling reactions.[13–17] The use of copper compounds on an industrial scale offers advantages such as a relative high nat-

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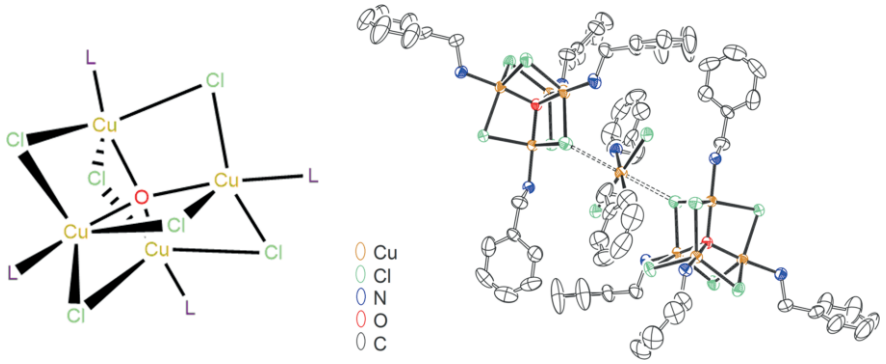


Figure 1. Schematic drawing of the central μ_4-oxido core (*left*) and molecular structure of cluster I $\{[Cu_4OCl_6(BnNH_2)_4]_2[CuCl_2(BnNH_2)_2]\}$[18] (*right*). Solvent molecules and hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50 % probability.

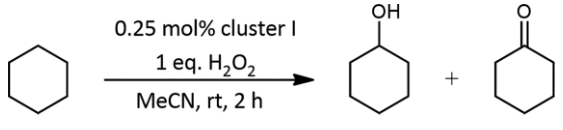
ural abundance, i.e. low catalyst costs, and a low toxicity in comparison to other 3d metal catalysts such as cobalt or chromium(VI) catalysts.[18] An additional improvement to lower the catalyst load in homogeneously catalyzed reactions comprises the use of multinuclear species because they have the advantage to transfer more than one electron per molecule, a concept that is commonly used in nature in active sites of multinuclear metalloenzymes.[19]

More recently, we reported the multinuclear copper cluster "cluster I" that exhibited interesting redox properties.[20] Cluster I $\{[Cu_4OCl_6(BnNH_2)_4]_2[CuCl_2(BnNH_2)_2]$, $BnNH_2$ = benzylamine$\}$ belongs to the family of μ_4-oxido-copper compounds that are distinguished by their central $[Cu_4OCl_6]$ core (Figure 1) and have been reported first by Bertrand et al. in 1966.[21]

Cluster I comprises two individual μ_4-oxido copper clusters $[Cu_4OCl_6(BnNH_2)_4]$ that are bridged via a mononuclear $[Cu(BnNH_2)_2Cl_2]$ complex.[20] During our investigations concerning such cluster systems, we additionally synthesized and characterized a variety of μ_4-oxido-copper solvento clusters (Figure 1, L = MeOH, DMF, DMSO, MeCN).[22,23] Furthermore, we could show that the presence of a base causes an immediate formation of solvento clusters if $CuCl_2{\cdot}2H_2O$ is dissolved in a coordinating solvent.[23] Preliminary investigations have shown that among these clusters, cluster I was able to catalyze the oxygenation of cyclohexane to cyclohexanol and cyclohexanone with hydrogen peroxide as oxidant with moderate yields (in total 18 %).[20] Driven by this finding, we investigated the potential of μ_4-oxido clusters in the oxygenation reaction of cyclohexane in more detail and found a one-pot synthesis for adipic acid at room temperature and atmospheric pressure.

Results and Discussion

We compared the catalytic activity of cluster I to that of the solvento clusters and evaluated their suitability as potential catalysts for the first reaction step in the industrial production of adipic acid according to Scheme 2. In analogy to our preliminary experiments we reacted hydrogen peroxide with cyclohexane and a copper catalyst in different solvents to initially yield cyclohexanol and cyclohexanone.[18] The conversion was determined and quantified via GC/MS. Here, the use of internal standards allowed a thorough calibration for the substrate as well as the products cyclohexanol and cyclohexanone. In addition, the products were isolated to carry out a complete characterization (vide infra).



Scheme 2. Catalytic oxygenation of cyclohexane with cluster I and H_2O_2.

Solvento clusters rapidly undergo ligand exchange reactions with other solvent molecules, thus, the solvent used had to match the solvent molecules coordinated to the μ_4-oxido copper core of the solvento clusters. Comparative studies have been carried out with cluster I to investigate the solvent influence. In addition, several test reactions with simple $CuCl_2{\cdot}2H_2O$ as sole catalyst and test reactions without any catalyst were performed. The results of this study are summarized in Table 1.

Table 1. Cyclohexane oxygenation with 1 equiv. H_2O_2. The conversion has been averaged over three individual reactions. The quantity used of $CuCl_2{\cdot}2H_2O$ is increased by nine times compared to cluster I to yield the same amount of copper ions in solution. (CyOH = cyclohexanol; CyO = cyclohexanone).

Entry	Catalyst	Solvent	CyOH [%]	CyO [%]	Total conv. [%]
1	–	all solvents	–	–	–
2	$CuCl_2{\cdot}2H_2O$	MeCN	traces	–	2
3	$CuCl_2{\cdot}2H_2O$	MeOH	2	–	–
4	$CuCl_2{\cdot}2H_2O$	DMF	–	–	–
5	$[Cu_4OCl_6(MeCN)_4]$	MeCN	5	2	31
6	$[Cu_4OCl_6(MeOH)_4]$	MeOH	traces	traces	19
7	$[Cu_4OCl_6(DMF)_4]$	DMF	traces	–	6
8	Cluster I	MeCN	8	2	28
9	Cluster I	MeOH	traces	traces	14
10	Cluster I	DMF	traces	traces	5

As expected, reacting cyclohexane with hydrogen peroxide without a catalyst did not lead to any conversion (entry 1). Minor conversion was obtained when using simple $CuCl_2{\cdot}2H_2O$ as catalyst. Here, a maximum conversion of 2 % was observed when performing the reaction in methanol (entry 3). Performing the reaction in either acetonitrile or DMF did not lead to any observable or only small traces of products (entries 2 and 4).

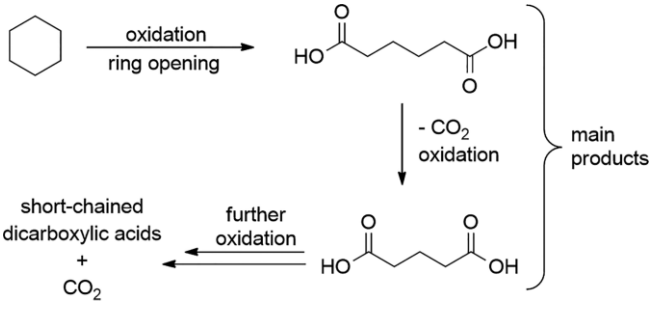
Similarly, only traces of cyclohexanol and cyclohexanone could be observed when using the solvento clusters as catalysts (entries 5–7). However, the total conversion of cyclohexane increased to 31 % and 19 % when applying the solvento cluster $[Cu_4OCl_6(MeCN)_4]$ and $[Cu_4OCl_6(MeOH)_4]$, respectively, indicating that additional products must have been formed (vide infra).

Using cluster I as catalyst led to similar results (as partly observed previously[20]): a maximum conversion of 28 % was reached when performing the reaction in acetonitrile (entry 8), however, only minor amounts of cyclohexanol and cyclohexanone were observed. The total conversion decreased when changing the solvent to methanol (14 %, entry 9) and DMF (5 %, entry 10), thus following the trend already observed for the solvento clusters. In summary, $[Cu_4OCl_6(MeCN)_4]$ and cluster I led to the highest conversion of cyclohexane.

However, the striking difference between the amount of converted cyclohexane and the amount of oxygenation products observed remained a puzzling detail. E.g. the catalytic oxygenation of cyclohexane with cluster I led to 28 % total conversion, but only to 8 % and 2 % of cyclohexanol and cyclohexanone, respectively (Table 1, entry 8). Evaporation of any substrate from the reaction flask could be excluded through constant cooling. Therefore, it was obvious that side products that cannot be detected by standard GC/MS procedures such as carboxylic acids had formed. To test this hypothesis, we performed an in situ esterification of all potential carboxylic acids formed by adding a 1.6 M solution of (trimethylsilyl)diazomethane in hexane to the reaction solution after completion of the reaction. We were able to successfully detect and quantify several dicarboxylic acids that included adipic acid, glutaric acid and succinic acid. A postulated reaction scheme for the formation of these products is presented in Scheme 3. In line with the industrial process, we propose a ring opening oxidation of cyclohexanone to yield adipic acid. Further oxidation leads to a chain shortening with simultaneous loss of CO_2 and subsequent oxidation. We were able to qualitatively detect evolving CO_2 during this reaction, which supports this hypothesis.

Having identified the side products, we sought to improve the overall conversion of the oxygenation reaction. For this purpose, we focused on cluster I as the sole catalyst. That is because solvento clusters decompose quickly in the presence of moisture and thus, turned out not to be suitable for subsequent experiments.

First, we used a higher concentrated hydrogen peroxide solution (50 % instead of 30 %). That is because μ_4-oxido copper clusters are sensitive towards moisture. The protonation of the central oxide anion usually leads to decomposition and formation of basic copper hydroxides and thus, deactivation of the catalyst. Even though cluster I is stable at atmospheric conditions and consequently tolerates small amounts of water, reacting cluster I with aqueous solutions still leads to deactivation of the catalyst over time. Attempts to completely avoid water by using other peroxide oxidants such as *m*CPBA, *tert*-butyl hydroperoxide or urea hydrogen peroxide were not successful. They either led to a significantly lower conversion or to the deactivation of the catalyst through formation of a yet unidentified precipitate. After identifying hydrogen peroxide as most suitable oxidant (50 % aqueous solution), we further tuned the reaction conditions by adding hydrogen peroxide constantly and slowly via a syringe pump over a time span of four hours. This procedure avoids a huge amount of water at the reaction start and thus, the immediate deactivation of the catalyst. In addition, the amount of hydrogen peroxide added was varied. An overview of all reaction conditions as well as a quantitative analysis of the formation of adipic and glutaric acid is reported in Table 2. The formation of dicarboxylic acids increased with the number of equivalents of hydrogen peroxide added. A maximum of 45 % adipic acid and 23 % glutaric acid (total conversion of 95 %) can be achieved by adding four equivalents of hydrogen peroxide over a time range of four hours (entry 14). Based on the observed evolution of CO_2 during this reaction, we propose that in addition to succinic acid further short-chained dicarboxylic acids such as oxalic acid might be formed that undergo subsequent oxidation to form ultimately CO_2 (see Scheme 3). This conversion might contribute to the difference between quantified products (in total 78 %) and the total conversion of 95 %.



Scheme 3. Postulated reaction scheme for the formation of dicarboxylic acids through initial oxygenation of cyclohexane.

Table 2. Conversion of cyclohexane with 1–4 equiv. of 50 % H_2O_2 added (addition rate: 1 equiv. H_2O_2/h; i.e., the number of equivalents added is consistent with the reaction time in hours).

Entry	Equiv. H_2O_2 added	Conv. CyOH [%]	Conv. CyO [%]	Conv. Adipic Acid [%]	Conv. Glutaric Acid [%]	Total Conv [%]	TON
11	1	8	3	6	2	32	128
12	2	12	6	16	6	56	224
13	3	9	5	24	11	77	308
14	4	5	5	45	23	95	380

In general, the reaction conditions are critical in achieving this high conversion, specifically the addition rate of the hydrogen peroxide solution and the reaction time itself. If the hydrogen peroxide solution is added too slowly, water contained in the solution will deactivate the catalyst and consequently reduce the conversion. In turn, if the peroxide solution is added too fast, a rapid decomposition of cyclohexane to CO_2 and short-chained dicarboxylic acids are observed via qualitative GC/MS.

Additionally, the reaction time itself influences the product range. In line with our postulated reaction scheme a decrease in the yield of adipic acid was observed with increasing reaction time, presumably due to further chain shortening reactions/CO_2 elimination. Accordingly, the highest yield of adipic acid could be monitored directly after the addition of the peroxide solution and further stirring of 15 minutes with trimethlylsilyldiazomethane. Further indication for our proposed reaction scheme derives from the observation that the yield of cyclohexanol and cyclohexanone stayed nearly constant in all reactions performed, indicating that the substrate will be further oxidized to dicarboxylic acids. We are currently focusing on understanding the mechanism of the reaction; however, the evolution of molecular oxygen as well as carbon dioxide has hampered detailed mechanistic studies so far. The addition of hydrogen peroxide to the cluster I suspension causes an immediate color change from green to red and evolution of gas. Kirillova et al. previously proposed a mechanism for the reaction of tetranuclear copper(II) clusters with hydrogen peroxide. Here, in a Fenton type reaction, the copper(II) centers are reduced to copper(I) and hydroxyl radicals as well as molecular oxygen are formed.[24] It is likely that activation of cluster I with hydrogen peroxide proceeds via a similar mechanism. The detection of a yet unidentified copper(I) species and the evolution of oxygen during the reaction are in line with this finding.

As cyclohexyl-hydroperoxide might be formed in significant amounts during the oxygenation of cyclohexane,[24] we tested the reaction solutions for this hydroperoxide by adding PPh_3 after completion of the reaction. However, we neither observed an increase in the formation of cyclohexanol, the degradation product of cyclohexyl-hydroperoxide, nor cyclohexanone (see SI). Additionally, only small amounts of $O{=}PPh_3$ could be detected, which are probably formed through oxidation by remaining H_2O_2 in the reaction mixture. Thus, even though cyclohexyl-hydroperoxide is likely to occur as intermediate, it is not accumulated as product.

In summary, we found a facile one-pot oxidation of cyclohexane to yield adipic acid in good yields. Clear benefits of this reaction are the moderate reaction conditions at room temperature and atmospheric pressure, as well as the renounce of nitric acid. Glutaric acid as well as other dicarboxylic acids is formed as side-product that complicates the separation and thus, purification of the products. Whereas the industrial workup is achieved through fractionated distillation, the dicarboxylic acids can only be separated via preparative HPLC. Recrystallization with activated carbon allowed to obtain a pure sample of crystalline adipic acid (Figure 2) that could be fully characterized by $^1H/^{13}C$-NMR, single-crystal X-ray diffraction (CCDC 1956886), ESI-MS, and elemental analysis, see SI.

Figure 2. Purified, colorless, crystalline adipic acid that was obtained via catalytic oxygenation of cyclohexane.

Conclusions

We report a facile one-pot synthesis for adipic acid and glutaric acid based on cyclohexane using the μ_4-oxido-copper cluster I as catalyst and hydrogen peroxide as oxidant. In contrast to established procedures, the reaction can be performed at room temperature and atmospheric pressure. In line with the industrial production of adipic acid, the reaction presumably proceeds via initial oxygenation of cyclohexane to yield cyclohexanol and cyclohexanone. Further oxidation leads to dicarboxylic acids such as adipic and glutaric acid. A maximum conversion of 95 % of cyclohexane to cyclohexanol (5 %), cyclohexanone (5 %), adipic acid (45 %), glutaric acid (23 %), and other dicarboxylic acids (17 %) was achieved when adding four equivalents of hydrogen peroxide. The mechanistic details of the reaction remain unclear so far. Mechanistic investigations as well as experiments to improve the selectivity of the product range are ongoing.

Experimental Section

Materials and Methods: All chemicals used were of p.a. quality and were purchased from either Acros Organics, or Sigma Aldrich. Dry purchased solvents for air sensitive synthesis were redistilled under argon. The preparation and handling of air sensitive compounds were performed in a glovebox or under standard Schlenk-techniques. Electrospray-ionization MS (ESI-MS) measurements were performed on a Bruker microTOF mass spectrometer. The conversions of the catalytic reactions were determined via gas chromatography (GC) and gas chromatography coupled with a mass spectrometer (GC/MS). For the quantitative determination, a calibration line was created with 100 µL of toluene as an internal standard. For NMR measurements a Bruker Avance II 400 MHz (AV II 400) was used for all samples. Elemental analysis was performed by a Thermo Scientific FlashEA 1112. Analytical HPLC was performed by a Dionex Ultimate 3000, with a Kanuer Eurospher II C18H 100–5 4 × 250 mm column.

μ_4-Oxido-Copper Cluster Catalysts: Cluster I and $[Cu_4OCl_6(MeOH)_4]$ were prepared according to published procedures.[20] Other solvento clusters were prepared in situ in a glove box by adding the amount of $[Cu_4OCl_6(MeOH)_4]$ to the respective solvent (MeCN and DMF). The corresponding solvent cluster forms immediately through ligand exchange reactions.

Oxygenation of Cyclohexane (reaction conditions according to Table 1): 1.1 mL of cyclohexane (0.84 g, 10 mmol) and 25 μmol of cluster I were suspended in 10 mL of acetonitrile. A hydrogen peroxide solution (50 %, 0.56 mL, 10 mmol) was added to the solution. To prevent the evaporation of the substrate, the flask was put in a water bath and was sealed with a septum (see SI). A cannula was plugged through the septum to enable pressure equalization. After the addition, the reaction was stirred for 1 hour in a water bath before adding the internal standard for GC analytics (see SI). Afterwards, the reaction solution was filtered with a PTFE syringe filter to remove solid residues of copper oxides from catalyst decomposition. The samples were analyzed immediately via GC. The oxygenation reactions catalyzed by solvento clusters were performed accordingly, however, the solvent was chosen to match the coordinating ligand. I.e., when using $[Cu_4OCl_6(MeOH)_4]$ as catalyst, the reaction was performed in methanol instead of acetonitrile, etc. In addition, the reactions were carried out under inert conditions and in dry solvents to prevent hydrolysis of the solvento clusters.

Oxygenation of Cyclohexane (reaction conditions according to Table 2): 1.1 mL of cyclohexane (0.84 g, 10 mmol), 25 μmol of cluster I, and the internal standard were suspended in 10 mL of acetonitrile. The reaction vial was put in a water bath and equipped with a cannula pierced through the septum. Then, a 50 % H_2O_2 solution was added via a syringe pump. The flow rate was set to 0.5–0.6 mL per hour, which corresponds to an addition rate of appr. 1 equivalent H_2O_2 per hour. The number of H_2O_2 equivalents added was varied according to Table 2. After completion of H_2O_2 addition, the reaction was additionally stirred for one hour. After that, the reaction was cooled to 0 °C in an ice bath and 1.6 M trimethylsilyldiazomethane solution was added in excess. The reaction solution was stirred for another 15 min at room temperature. Then, the solution was filtered through a PTFE syringe filter to remove solid precipitates. The samples were analyzed immediately via GC.

Purification and Isolation of Adipic Acid: After the reaction, the solution was filtered and purified via preparative HPLC (see SI). For additional purification, adipic acid was re-crystallized with activated carbon in water.

CCDC 1956886 (for adipic acid) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: Copper · Cluster compounds · Homogeneous catalysis · Cyclohexane oxidation · Synthesis design

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