



Efficient and region-selective conversion of octanes to epoxides under ambient conditions: Performance of tri-copper catalyst, $[\text{Cu}_3^{\text{I}}(\text{L})]^{+1}$ (L=7-N-Etppz)

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In this paper, is described the conversion of the octane group of hydrocarbons into industrially important epoxides using tri-copper catalyst, $[\text{Cu}_3^{\text{I}}(\text{L})]^{+1}$ (L=7-N-Etppz). The role of hydrogen peroxide as a sacrificial oxygen donor during catalytic conversion to epoxides has been investigated. The performance of the catalyst has been evaluated in terms of turnover numbers (TON) and turnover frequencies (TOF) reported in this article.

Keywords: Epoxidation, region-selectivity, ambient conditions, tri-copper catalyst

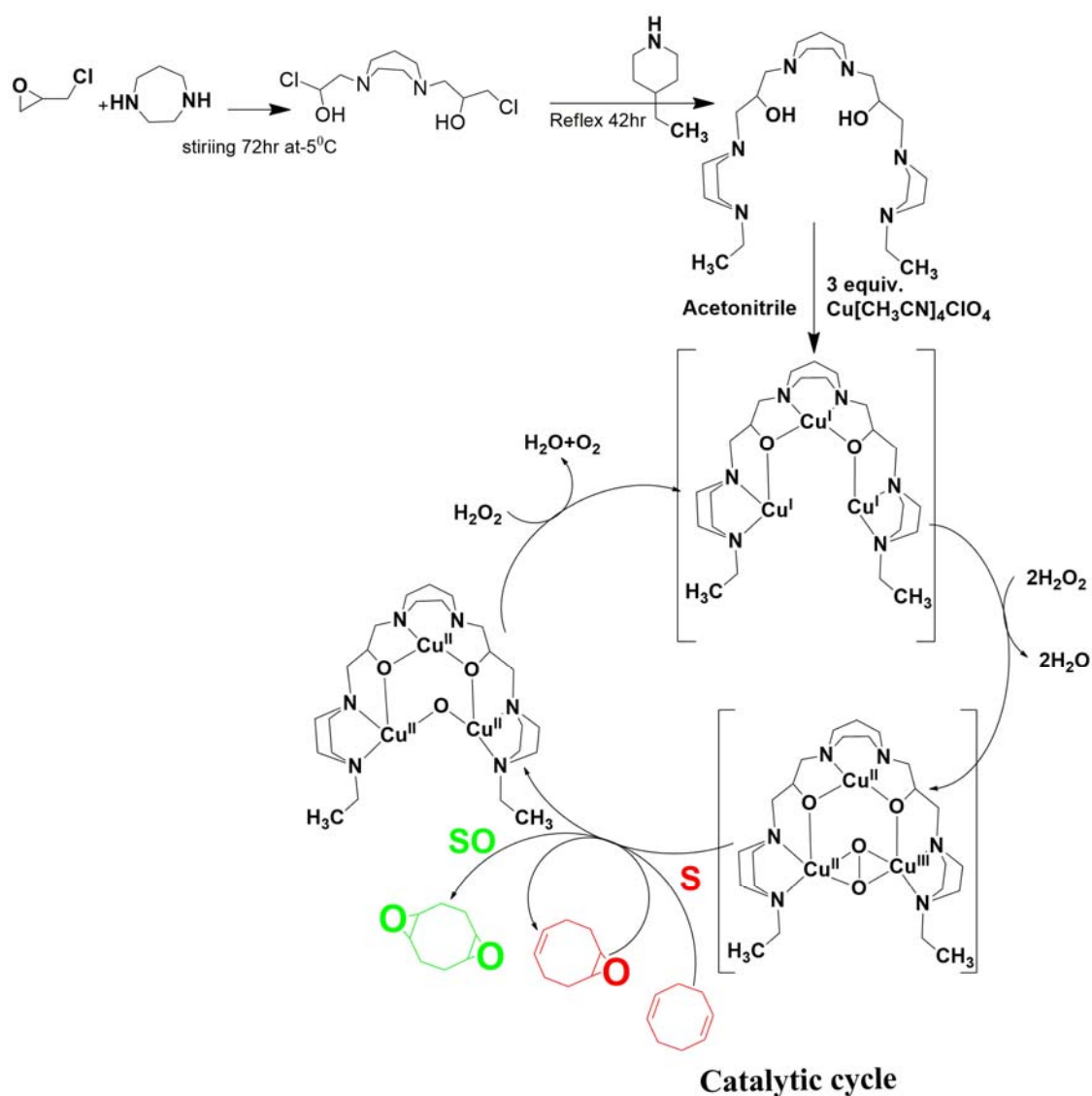
Oxidation of hydrocarbons is a complicated and uncontrolled process during the synthesis of epoxides. Epoxides are one of the most important building blocks for developing various industrial products starting from drugs and pharmaceuticals to paints and adhesives by using synthetic chemistry approaches¹. The oxidation of alkenes by using cost-effective, efficient and eco-friendly H_2O_2 is the most widely reported synthetic route for epoxides preparation¹⁻⁵. Recently, a tri-copper cluster complexes have shown biomimetic properties of methane monooxygenase (pMMO) for methane to methanol conversion and similar reactions at ambient conditions⁵⁻¹². The enzyme pMMO identified in methanotrophic bacteria and this enzyme can perform the facile conversion of methane (CH_4) to methanol (CH_3OH) at ambient conditions. Based on structural elucidation of the enzyme reports that the multi-coppers centers with an active $\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ tri-copper cluster. This cluster undergoes oxygen activation to produce a mixed-valency transient copper cluster $[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\mu\text{-O})_2\text{Cu}^{\text{III}}]^{+1}$, which can harnesses extremely reactive "singlet oxene" to reorganize C=C and C-H bonds during oxidation or epoxidation of alkenes^{9,10}. In recent studies we have reported that Cu_3 -copper cluster in combination with oxidizing agents (H_2O_2) convert a wide range of hydrocarbons to the corresponding oxidized products such as like cyclohexane, styrene, benzene, benzil, 2,3-butanedione and styrene have been described

for $[\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}(\text{L})]^{+1}(\text{X})$, (L= 7-Ethppz, 7-Morph, 7-Mehppz, 7-Me, 7-Et and 7-Thio, X = perchlorate (ClO_4) tri-copper complexes under ambient conditions¹³⁻¹⁵. In this study, we report the first time, the performance of tri-copper complex for efficiently and regio-selectively converting octane group of hydrocarbons to epoxides in the presence of oxygen source. H_2O_2 is a facile oxidant which generates oxygen to participate in heterogeneous/homogeneous catalysis. The organic compounds are easily oxidized with H_2O_2 with an efficiency of about 50% and the by-product is water. In this study, the role of H_2O_2 to improve the tri-copper catalysis induced oxidation of the octane group of hydrocarbons to epoxides under ambient conditions has been reported (Scheme I). In this report, we have chosen three octane family substrates (i) n-octane with 18 C-H only sigma bonds, (ii) cyclooctene is the smallest cycloalkene with an 8-membered ring containing 14 C-H orthogonal allylic and one double bond and (iii) 1,5 cyclooctadine is an organic compound with 12 C-H bonds with two double bonds at 1 and 5 positions. According to the Gas Chromatograph (GC) hyphenated with mass spectrometer analysis of reaction products indicate that the yield of products was the combination of 2-octanol, 4-octanol, 2-octanone and 4-octanone when the n-octane was used as the substrate. While cyclooctene substrate was used, the product epoxy-cyclooctane was formed as the major fraction (about 85%) and other products were 5-hydroxy-1-cyclooctene

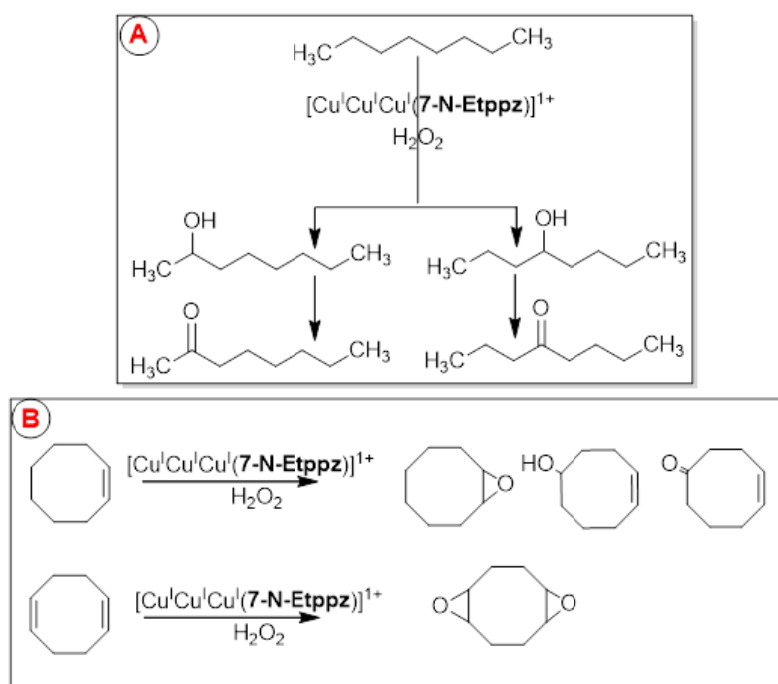
and cyclooct-4-ene. When cyclooctadiene was used as the substrate, only bis-epoxide was formed and there were no other by-products (Scheme II). The products formation in these catalytic reactions depends on the quantity of H_2O_2 used in the reaction. The kinetics of the reaction is an important parameter of the study. The experimental results have shown that the reaction complete within 30 min and in due course of time the oxidant H_2O_2 was consumed.

It can be assessed that the catalyst initially works on activation of C–H aliphatic bond to produce alcohol and ketone as depicted in Scheme II. Initial activation of tri-copper cluster step involves oxygen-atom transfer from the mixed-valence of $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}(\mu-$

$\text{O})_2\text{Cu}^{\text{III}}(7\text{-N-Etppz})]^{1+}$ complex to harnesses vastly reactive “singlet oxene.” The oxidation of cyclooctene mediated by the catalyst in the presence of H_2O_2 at room-temperature produces region-selectively only epoxide (*cis*-9-oxabicyclo (6.1.0) nonane) and no other product was found in GC peaks. This is an evidence for confirmation of activation required for aromatic nucleus much easier than the aliphatic σ -bond¹⁵. Similarly, substrate 1,5-cyclooctadiene produce bis-epoxide the only product and there was no by-product such as mono-epoxide formation. Meunier *et al.*^{19,20} reported alkene epoxidation in the presence of H_2O_2 catalyzed with molybdenum porphyrins¹⁸ and PhIO–iron porphyrin systems^{19,20} to produce selectively



Scheme I — Synthesis of ligand and complex and the proposed catalytic cycle for the oxidation of octane group of hydrocarbons to epoxide



Scheme II — Oxidation of the various (A=n-octane and B= cyclooctene and 1,5-cyclooctadiene) substrates by $[\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}(\text{7-N-Etppz})]^{1+}$ and H_2O_2 in acetonitrile solvent

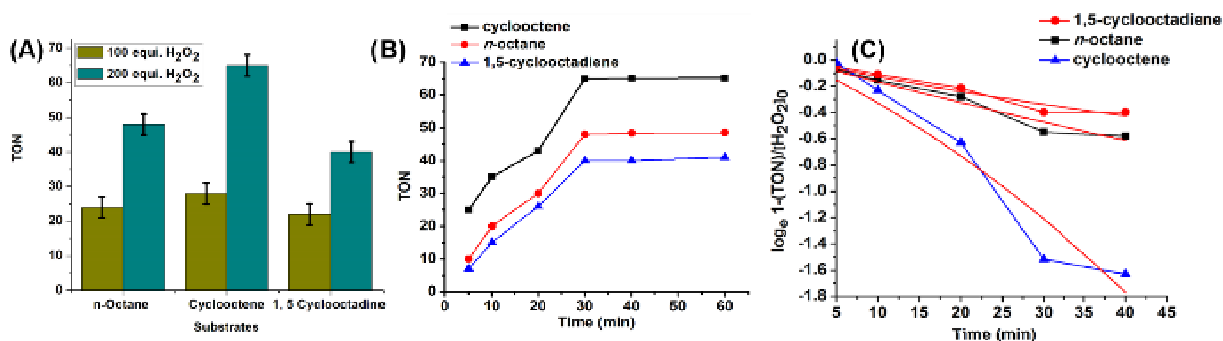


Figure 1 — (A) TON of selected substrates with various H_2O_2 concentrations (100 and 200 equiv.) (B) Time course experiments and product formation in the catalytic turnover during the oxidation of C_8H_{18} , C_8H_{14} and C_8H_{12} to their corresponding epoxides, alcohols, ketones by 200 equiv. of H_2O_2 at the start and (C) The time course of selected substrates oxidation; inset: pseudo-first-order kinetic plot with rate constant (k_1) with the best straight-line fit to the data.

mono-epoxide. In our study, very precisely the substrate 1,5-cyclooctadiene with 200 equiv. H_2O_2 formed bis-epoxide without any by-products such as w mono-epoxide. The rate of product formation could be determining the rate of utilization of the H_2O_2 as a function of time.

TOF is a measurement of the rapid efficiency of a selected catalyst and calculation was driven by TON of the catalytic cycle with respect of the time. Plots of time *versus* the logarithm $\{1-(3) (\text{TONs})/([\text{H}_2\text{O}_2]_0)\}$ were close to linearity. The kinetic

data from experimentations were plotted and depicted in Figure 1 (C). The TOF and the confine primary slope of $\sim 3\text{k}3$ [catalyst], could be calculated for every experiment. The slopes were resultant for 3 selected octane family substrates n-octane, cyclooctene and 1,5 cyclooctadiene by catalyst Cu_3 -complex by taking H_2O_2 200 equiv. yield k_3 of $1.15 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}$, 3.0×10^{-2} and $9.11 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}$ respectively. We also obtain TOFs $1.5 \times 10^{-2} \text{ s}^{-1}$, $4.8 \times 10^{-2} \text{ s}^{-1}$ and $4.3 \times 10^{-3} \text{ s}^{-1}$ for the substrates n-octane, cyclooctene and 1,5 cyclooctadiene respectively, at $[\text{H}_2\text{O}_2]_0$ of 200 equiv.

The hydrocarbon substrate was excess the catalytic reaction and the product formation by activation of Cu₃-complex is the rate-limiting step. The initial oxidation of each of these hydrocarbons was mediated by the activated Cu₃-catalyst regardless of the ligand used to assemble the catalyst. Of course, subsequent transfer of “singlet oxene” to the substrate depends on the affinity of the substrate for the activated catalyst Cu₃-complex which would explain the products formed with a Cu₃-catalyst. The significance of the present work is the reaction takes place region- selectively. Octane group with 8 membered ring having single and double bonds especially in 1,5 cyclooctadine substrate with two double bonds at opposite sides of the ring is undergo very selective oxidation and forms a selective compound with dual epoxides namely 5,10-Dioxatricyclo[7.1.0.0(4,6)] at 1 and 5 positions without disturbing single bonds of the same ring with retention time at 4.9 in GC (Figure S3). In the case of n-octane with long chain structure forms multi-products at different positions due to long chain structure can react/binds randomly to dioxygen containing catalyst and forms alcohols and ketones at different positions. We strongly believe that this catalyst [Cu₃^I(L)]⁺ (L=7-N-Etppz) is doing neat and clean chemistry with single and double bonds within 30 min.

Controls experiments with the complex [Cu(ACN)₄]ClO₄ without ligand (copper complex with our ligand) as a catalyst, low levels of substrate oxidation are observed and also reporting the blank experiments performed under similar conditions but without the Cu₃-catalyst show no formation of products. The results are supporting that without a doubt, the oxidation of each of these hydrocarbons are mediated by the activated tri-copper cluster regardless of the ligand used to assemble the catalyst. A detailed synthesis of ligand, complex and reaction conditions has given in supporting information (SI). Oxidation reaction of selected substrates n-octane (C₈H₁₈) cyclooctene (C₈H₁₄) and 1,5 cyclooctadine (C₈H₁₂) have given in supporting information with retention time (Figure S1-S3). Synthesis of ligand, preparation [Cu^ICu^ICu^I(7-N-Etppz)]⁺ complex and physical measurements of catalyst, EPR spectra of [Cu^{II}Cu^{II}(μ-O)Cu^{II}]¹⁺ and reaction conditions were already reported in our previous publications^{12,15}.

Supplementary Information

Supplementary information is available in the website <http://nopr.niscair.res.in/handle/123456789/60>.

Acknowledgments

Authors contribution statement: NB conceived the idea and conceptualized the research work. NB also prepared the catalyst, few experiments and prepared the original draft. PSP conducted experiments related to catalytic conversion of octane group of hydrocarbons to epoxides and GC-MS studies. RJK KRC No.: CSIR-NEERI/KRC/2018/MARCH/EMD/1.

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