Alkane Hydroxylation Catalyzed by A Nickel Complex Supported by Non-innocent Ligand

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Abstract: Efficient catalytic hydroxylation of inert alkanes including methane has been achieved by using a nickel(II) complex supported by a redox non-innocent diphenolate ligand as a catalyst and *m*-chloroperbenzoic acid (*m*-CPBA) as an oxidant. Mechanistic studies have suggested that a nickel-oxyl type intermediate is involved as a reactive oxidant, which is supported by DFT calculations.

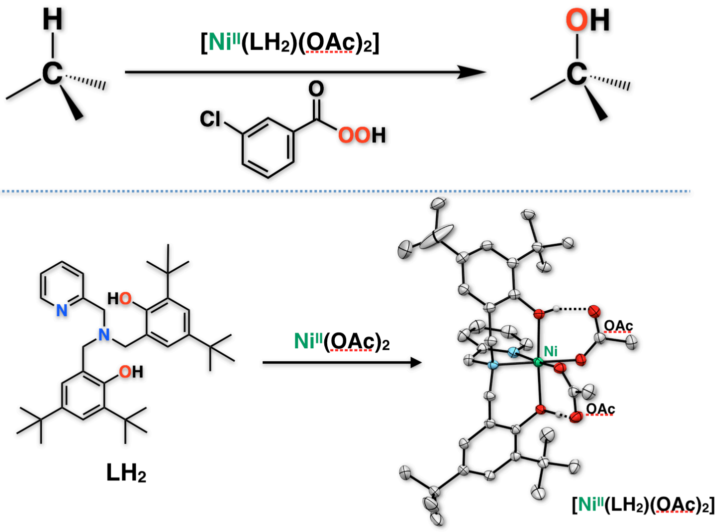
Keywords: Catalytic alkane hydroxylation, Nickel catalyst, *m*-CPBA.

1. Introduction (11-point boldface)

Direct hydroxylation of hydrocarbons, especially sp^3 C–H bond, is one of the most important chemical transformation reactions not only in synthetic organic chemistry but also in several biological oxidation reactions. Such a reaction can be achieved by using high-valent transition-metal complexes with a terminal oxo group, that can be generated from the corresponding lower-valent transition-metal complexes and active-oxygen donors. Such a high-valent transition-metal complexes with terminal oxo group are well known for early transition-metal elements from group 5 to 8, among which iron(IV)-oxo and iron(V)-oxo complexes both in the heme and non-heme systems have been studied most extensively due to their strong relevance to the biological oxidation and oxygenation reactions.

On the other hand, transition-metal complexes with terminal oxygen atom of group 9, 10, and 11 have been less explored due to the existence of a so-called 'oxo-wall' between group 8 and group 9 elements. Thus, on the right side of the oxo-wall, it is believed that the terminal oxygen complexes have an oxyl-radical form having a single bond character between the metal ion and the oxygen atom. This is due to the existence of d-electrons in the anti-bonding π*-orbitals generated by the interaction between the d_{xz} and d_{yz} orbitals of the metal ion having an octahedral geometry and the p orbitals of the terminal oxygen atom. Thus, we are interested in exploring the reactivity of such oxyl radical speceis.

In this study, we have examined the reaction of a nickel(II) complex supported by a redox non-innocent supporting ligand containing two phenol donor groups (LH_2) and *m*-chloroperbenzoic acid (*m*-CPBA) to



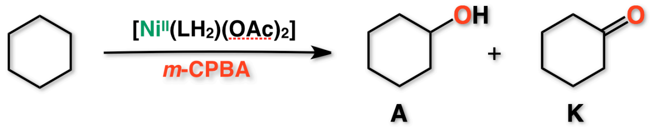
find formation of a nickel-oxyl radical type intermediate, the formation of which has been supported by DFT calculation. Then, catalytic hydroxylation of various alkane substrates including methane has been developed by using the nickel complex as the catalyst and *m*-CPBA as the oxidant. Mechanistic details of the catalytic hydroxylation reaction has also been discussed on the basis of DFT calculations.

2. Experimental (or Theoretical)

Ligand LH_2 was prepared according to the reported procedures.[1] Treatment of LH_2 with $Ni(OAc)_2$ gave a nickel(II) complex with an octahedral geometry, where two acetate ligands occupy the equatorial positions and two phenol groups of LH_2 exist at the axial positions, making hydrogen bonding interaction with the acetate oxygen atoms. Hydroxylation of various alkanes with *m*-CPBA was carried out in the presence of a catalytic amount of nickel complex in CH_2Cl_2/CH_3CN at room temperature. The yields of oxidation products were determined by GC and/or ^{1}H-NMR. Direct reaction of the nickel complex and m-CPBA was monitored by UV-vis, EPR, and resonance Raman spectra at a low temperature (below –70 °C).

3. Results and discussion

As shown in the right figure, the catalytic hydroxylation reaction of cyclohexane proceeded quite efficiently to give cyclohexanol as a major product together with a small amount of cyclohexanone. In this case, the turnover number (TON) of the catalyst reached 475 (98 % yield based on the oxidant), and high alcohol product selectivity was obtained after 2 h. Furthermore, we have obtained an appreciable amount of KIE, 2.6, by using perdeuterated substrate, suggesting that the C–H bond cleavage is involved in the rate-limiting step.



TON			A / K	Yield b)
A	K	Total a)		
397	39	475	10.3	98%

[Catalyst] = 0.36 mM, [*m*-CPBA] = 0.18 M, [Substrate] = 2.7 M, [DBU] = 0.36 mM in CH_2Cl_2/CH_3CN (3 : 1), at 30 °C, for 2 h, under N_2. a) A + 2K, b) Based on *m*-CPBA

In the case of adamantane as a substrate under the same experimental conditions, a high TON of the catalyst and a high alcohol product selectivity were also obtained. In this case, a high tertiary carbon selectivity against the secondary carbon oxidation was observed. This catalytic system could be applicable to catalytic oxidation of gaseous substrates such as butane, propane, and methane.

Spectroscopic examinations of direct reaction between the nickel complex and *m*-CPBA at low temperature suggested formation of a nickel-oxyl radical type intermediate, which was supported by DFT calculations. The generated oxyl radical intermediate induces alkane hydroxylation via hydrogen atom abstraction and oxygen rebound mechanism, which is supported by kinetic analysis and by DFT calculations.

4. Conclusions

We have succeeded to develop an efficient hydroxylation reaction using a nickel(II) complex as a catalyst and *m*-CPBA as an oxidant, where a nickel-oxyl radical type intermediate is suggested to be involved. The catalytic reaction has also been applied to direct oxidation of methane to methanol under very mild conditions.

References

1. T. Nagataki and S. Itoh, *Chem. Lett.* **36**, 748 (2007).