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A Complexation Promoted Organic N-Hydroxy Catalytic System for Selective Oxidation of Toluene

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Abstract: Complexation was innovatively utilized to design a novel catalytic system for the selective oxidation of toluene, which runs contrary to the traditional definition of organic metal complex catalysis. In the present system, an N-heteroaromatic ring-containing N-hydroxy compound acts as the catalytically active component. Through an electron-withdrawing effect produced by the occurring complexation with proper metal salts, which was characterized by real-time *in situ* Fourier transform infrared spectra, the activity of the organic molecule could be remarkably improved. The combination of copper(II) chloride with 6-hydroxy-pyrrolo[3,4-*b*]pyrazine-5,7-dione showed the best activity, and an inert hydrocarbon such as toluene could be efficiently transformed with 70.9% conversion and 93.5% selectivity to benzoic acid at 90 °C within 2 h.

Keywords: complexation; organic catalysis; oxidation; synthesis

The catalytic selective oxidation of hydrocarbons with molecular oxygen is of major industrial importance, and improving its efficiency and selectivity for the value-added products remains a challenge.[1] Efficient catalysts including homogeneous and heterogeneous catalysts have been developed for these reactions. Homogeneous catalysis has been studied for the past one hundred years at least, and it derives its predominance from its good activity and mild operation conditions. Organic metal complexes, one kind of homogeneous catalytic system being widely studied, have attracted much more attention for the flexible alteration of the active metal sites and organic ligands.[2] Complexation between these two parts plays an important role during the catalytic process, and the catalytic ability of active metal center could be obviously improved with the proper choice of organic ligand.[2c,d]

The catalytic system reported herein runs totally contrary to the traditional definition of an organic metal complex catalyst, in which a metal-free organic molecule acts as the catalytically active component while through complexation the metal ion acts as "ligand" to improve the catalytic ability of the organic molecule. Inert hydrocarbons such as toluene could be efficiently converted to, e.g., benzoic acid.

R_2NOH type organic molecules were found to be able to produce $R_2NO^{\bullet}$ radicals, which could act as an active intermediate to activate the hydrocarbon molecule through hydrogen abstracting behavior and then realize the oxygenation with molecular oxygen under moderate conditions.[3] *N*-Hydroxyphthalimide (NHPI) is such a good example to catalyze the oxygenation of C−H bonds and the production of PINO radicals is the key step affecting the catalytic efficiency.[3] To obtain more reactive PINO radical species different electron-withdrawing substitutes were usually introduced on the benzene ring to increase the hydrogen abstracting ability.[4] Inspired by the various homogeneous complex catalysts, which usually contain N-heterocyles to coordinate with metal ions, we designed and synthesized a series of N-heteroaromatic ring-containing R_2NOH type radical precursors. These compounds are *N*-hydroxyquinolinimide (NHQI), *N*-hydroxycinchomeronimide (NHCI), 6-hydroxypyrrolo[3,4-*b*]pyrazine-5,7-dione and (HPPDO), respectively, and the corresponding molec-
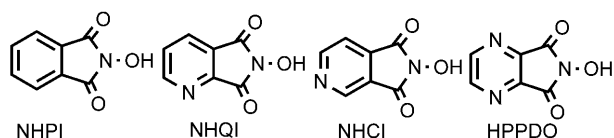
Scheme 1. Structure of N-heteroaromatic ring-containing R$_2$NOH derivatives

ular structures are shown in Scheme 1. When combined with metal ions, the complexation that takes place is expected to improve the hydrogen abstracting ability of the corresponding R$_2$NO$^{\bullet}$ radical through a strong electron-withdrawing effect, and then the conversion of the hydrocarbon could be improved.

Industrially, the oxidation of toluene to benzoic acid with O$_2$ is a key step for synthesizing ε-caprolactamine in the Snia–Viscose process, and merely 15% of the toluene is converted with 90% selectivity to benzoic acid under the optimal conditions.[5] Although many efforts have been made to improve the efficiency of toluene oxidation, a high efficiency could not be obtained under mild conditions without halogen ions, acidic solvents or powerful oxidant such as *t*-BuOOH.[3e,6] In the present work, the selective oxidation of toluene was chosen as a model reaction, and with O$_2$ as oxidant these N-heteroaromatic ring-containing R$_2$NOH type organic molecules showed encouraging results (Table 1).

NHPI, without a nitrogen atom in the aromatic ring, gave 5.8% conversion of toluene at 100 °C for 8 h. (entry 1). Benzaldehyde was the main product and the selectivity for benzoic acid was only 6.0%. By comparison, NHQI revealed a good catalytic activity

giving 9.7% conversion of toluene and selectivity for benzoic acid rose to 21.9% (entry 2), which are obviously higher than those obtained with NHPI. This result indicates that the catalytic ability of NHQI increased with the introduction of an N-heteroatom in the aromatic ring. The reason for this activity improvement should be ascribed to the electron-withdrawing effect of the N-heteroatom, which corresponds to the calculation results in the literature.[7] However, NHCI and HPPDO did not show higher efficiency (entries 3 and 4). For NHCI the poor solubility in the present solvent may affect its performance. For HPPDO two N-heteroatoms were introduced in the aromatic ring, the bond energy of R$_2$O−H should increase more than that in NHQI. The production of the corresponding R$_2$NO$^{\bullet}$ radical becomes more difficult, and a higher reaction temperature may be needed to realize its production. In fact, when the reaction was carried out at 120 °C the activity of HPPDO increased appreciably, and became comparable with that of NHQI (entries 1 and 2, Table S1, Supporting Information).

Our previous work showed that anthraquinone derivatives were a good kind of promoter for the NHPI-catalyzed oxidation of hydrocarbons.[8] However, 2-chloroanthraquinone (2-CAQ) did not show an obvious promotion effect for NHQI (entry 3, Table S1, Supporting Information). By comparison, when the metal salt cobalt acetate was used, amazing results were obtained. When we applied the NHPI/Co(OAc)$_2$ system in the reaction, it gave 15.3% conversion and 69.0% selectivity for benzoic acid at 100 °C for 2 h (entry 5). Compared with NHPI being used alone, the

Table 1. Catalytic oxidation of toluene by different catalytic systems.[a]

Entry	Catalyst	Additives	Conversion [%]	Selectivity [%][b]		
				−CHO	−OH	−COOH
1[c]	NHPI	none	5.8	73.9	19.1	6.0
2[c]	NHQI	none	9.7	63.0	13.6	21.9
3[c]	NHCI	none	4.0	77.9	17.6	3.2
4[c]	HPPDO	none	1.5	58.7	18.5	16.3
5	NHPI	Co(OAc)$_2$	15.3	22.3	8.2	69.0
6	NHQI	Co(OAc)$_2$	34.3	2.8	3.0	93.5
7	NHCI	Co(OAc)$_2$	7.2	63.8	15.0	14.7
8	HPPDO	Co(OAc)$_2$	12.7	41.7	11.6	46.1
9[d]	NHPI	pyridine/Co(OAc)$_2$	14.1	33.9	6.2	59.6
10[d]	NHQI	pyridine/Co(OAc)$_2$	7.7	56.4	6.1	37.5
11[d,e]	NHQI	CoTMPP	2.5	100	0	0
12[d,f]	HPPDO	Co(OAc)$_2$	41.4	10.4	1.0	88.6

[a] Toluene (2 mL, 18.8 mmol), organocatalyst (5 mol%), and additives (1.25 mol%) in 7 mL of acetonitrile with O$_2$ at 0.5 MPa, 100 °C for 2 h.

[b] −CHO, −OH, −COOH refer to benzaldehyde, benzyl alcohol, and benzoic acid, respectively.

[c] For 8 h.

[d] In the presence of pyridine (5 mol%).

[e] In the presence of cobalt tetramethoxyphenylporphyrin (CoTMPP).

[f] 2.5 mol% of metal salt was used.

conversion and selectivity of benzoic acid had increased by 9.5 and 63.0%, respectively. Under the same conditions NHQI/Co(OAc)$_2$ showed excellent activity, which is more than twice as much as that of NHPI/Co(OAc)$_2$. NHQI/Co(OAc)$_2$ gave 34.3% conversion and 93.5% selectivity for benzoic acid (entry 6). The addition of cobalt acetate realized 24.6 and 71.6% increases of conversion and selectivity for benzoic acid, respectively. Comparing these two results, it can be seen that the promotion effect of cobalt acetate is more effective for NHQI than NHPI.

For the NHPI/Co(OAc)$_2$ system, the utilization of Co(OAc)$_2$ was believed to promote the production of the PINO radical.[3] During the catalytic process, complexation of Co(II) with dioxygen could generate a labile cobalt(III)-oxygen complex. Reaction of NHPI with the cobalt(III)-oxygen complex would generate the PINO radical, which was considered as the most important step during the catalytic process.[3e] It seems that this explanation cannot be adopted for the present NHQI/Co(OAc)$_2$ system because the promotion effect of Co(OAc)$_2$ for NHQI is much more effective than that for NHPI. The one and only difference between the molecular structures of NHPI and NHQI is the existence of the N-heteroatom in the aromatic ring for NHQI, which is different from the nitrogen atom in the 5-member ring. It was reported that some complexation between N-hydroxysaccharin and Co(acac)$_3$ might occur, and the nitrogen atom in the 5-member ring may participate in this complexation.[3b] The N atom in the aromatic ring was usually used to coordinate with the metal ions to prepare some certain metal complexes.[9] For the present N-heteroatom in the aromatic ring its lone electron pair is freer than that of nitrogen atom in the 5-member ring, and the former N atom could show stronger potential participation in complexation once combined with transitional metal ions. It can also be acknowledged that, in the famous Gif system catalytic process or Shul′pin's reported works, a similar picolinic acid or pyrazine-2-carboxylic acid could coordinate with the metal species, and then the activity of the corresponding metal species could be apparently increased.[10] We speculate if there occurs some complexation behavior between NHQI and cobalt ions, which would exhibit an electron-withdrawing effect like but stronger than those of some special electron-withdrawing substitutes. To support this, a certain amount of pyridine was previously added to coordinate with cobalt ions, and it could be observed that the activity of NHPI/Co(OAc)$_2$ system remained almost the same (entry 9), while the activity of NHQI/Co(OAc)$_2$ system decreased noticably (entry 10). For the NHQI/Co(OAc)$_2$ system, the conversion of toluene decreased from 34.3 to 7.7% with the addition of pyridine, indicating that the complexa-

tion should happen between NHQI and Co(OAc)$_2$, which is a key factor for obtaining such a high activity. For further proof, tetramethoxyphenylporphyrin, a kind of cobalt complex being active for selective hydrocarbon oxidation,[11] was added in place of cobalt acetate. As a result, no complexation could happen and the conversion of toluene was only 2.5% under the present conditions (entry 11).

According to this speculation, HPPDO should show a higher activity than NHQI for possessing two complex sites on the premise that twice the amount of cobalt acetate were used. This expectation was realized with twice the amount of cobalt acetate being added, and the conversion of toluene increased from 1.5 to 41.4% (entry 12), which is nearly 28 times as much as that obtained with HPPDO being used alone. By comparison, more cobalt acetate could not show a positive effect for the NHQI/Co(OAc)$_2$ system (entry 7, Table S1, Supporting Information). In addition, Co(OAc)$_2$, pyridine/Co(OAc)$_2$, or pyridine-2,3-dicarboxylic acid anhydride/Co(OAc)$_2$ were also tested for the oxidation of toluene, respectively, and the above systems hardly exhibited any catalytic ability (entries 4–6, Table S1, Supporting Information). Then it could be affirmed that the active center is N−OH, which was indispensable for the oxidation of toluene under the present conditions.

Furthermore, other metal species were tried in combination with NHQI and the corresponding results are listed in Table 2. Like different organic ligands are able to modulate the activity of metal complex catalytic systems, different metal ions were assumed to be able to modulate the activity of the organic active center. It was reported that cobalt or manganese salts, CuCl, and Fe/MgO were effective co-catalysts for NHPI.[12] Among the tested metal salts in the present work, however, besides cobalt acetate, copper salts showed considerable activity for the oxidation of toluene (entries 1, 7–9, Table 2). And especially when CuCl$_2$ was combined with HPPDO, the best activity was obtained with 70.9% conversion of toluene and 93.5% selectivity for benzoic acid (Entry 9). This activity is much higher than that of the previous catalytic systems.[6]

We have tried to prepare a single crystal of the combined catalytic system, and it seems hardly to be obtained. Considering that the catalytic system should present as a solution form during the catalytic process, this would be different from its single crystal form. Much emphasis has been placed on *in situ* characterization. Through real-time *in situ* Fourier transform infrared (FTIR) spectral measurements the interaction between the catalytic components could be clearly observed and the corresponding results are listed in Figure 1. At the beginning NHQI was solely added into acetonitrile, with the background correction the spectra of NHQI was obtained (between A and B in

Table 2. Comparison of different metal salt on catalytic oxidation of toluene.[a]

Entry	Additives	Conversion [%]	Selectivity [%][b]		
			−CHO	−OH	−COOH
1	Cu(OAc)$_2$	29.1	17.0	1.1	80.2
2[c]	Mn(OAc)$_2$	5.4	63.6	15.4	20.6
3[c]	Fe$_2$(C$_2$O$_4$)$_3$	10.2	11.6	16.4	71.1
4	FeCl$_3$	11.6	32.2	trace	65.6
5	FeCl$_2$	10.4	15.3	trace	80.6
6	CoCl$_2$	2.6	35.7	17.7	39.5
7	CuCl	45.6	9.7	0.4	87.7
8	CuCl$_2$	63.6	2.1	trace	95.5
9[d]	CuCl$_2$	70.9	4.4	trace	93.5

[a] Toluene (5 mmol), NHQI (5 mol%), and metal additives (1.25 mol%) in 7 mL of acetonitrile with O$_2$ at 0.5 MPa, 90 °C for 2 h.
[b] −CHO, −OH, −COOH refer to benzaldehyde, benzyl alcohol and benzoic acid, respectively.
[c] At 100 °C.
[d] HPPDO combined with 2.5 mol% of CuCl$_2$.
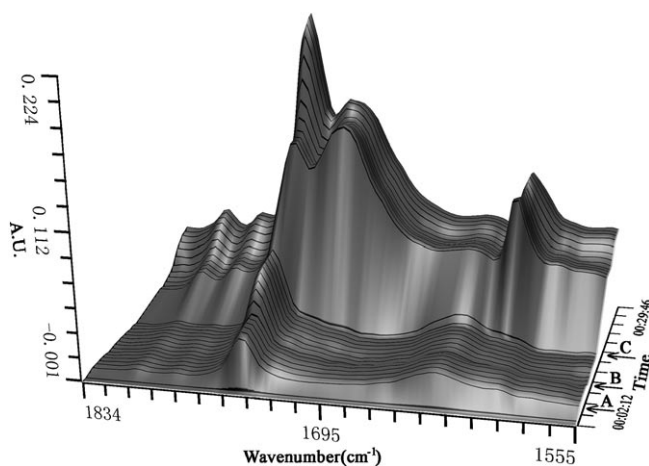

Figure 1. Real-time *in situ* FTIR for the catalytic system. A: NHQI; B: adding CuCl$_2$; C: start heating.

Figure 1). Typical bands associated with C=O stretching vibrations (at 1745 cm^{-1}) and pyridine ring vibrations (at 1630 cm^{-1}) were detected at ambient temperature. After the addition of the metal salt, besides a slight increase in absorption intensity there were no obvious changes for the spectra (between B and C in Figure 1). However, during the heating process to the reaction temperature (100 °C) significant changes occurred with new absorption bands (1716 and 1601 cm^{-1}) emerging (after C in Figure 1). The absorption band at 1716 cm^{-1} should be ascribed to the vibrational absorption of C=O, which manifests that one of the C=O bonds might participate in the coordination with metal ions and then splitting off of the C=O absorption band occurred. The almost disappearance of the pyridine ring absorption band at 1630 cm^{-1} and its red-shift to 1601 cm^{-1} indicate that pyridine ring may also participate into the complexation.[13] By comparison, NHQI itself could not show

these changes during the heating process. According to these characterization results the structure of the complex (B) was deduced as in the Scheme S1 (Supporting Information).

The production of a radical was considered as the most important step during the R$_2$NOH-catalyzed oxidation of hydrocarbons.[3] The intrinsic difference in the present process is that the corresponding radical should be produced through an intermolecular electron transfer process, which is believed to be more easy and effective. And then the subsequent hydrogen abstraction behavior occurred to realize the activation of toluene molecule, which could be facilitated by the strong electron-withdrawing effect of the occurring complexation. In the following the benzyl radical is readily trapped by dioxygen to provide the benzylperoxy radical followed by benzyl hydroperoxide and eventually the product benzoic acid is formed.[3]

In conclusion, a series of novel N-heteroaromatic ring-containing R$_2$NOH-type radical precursors were synthesized. Through complexation with metal salts they were found to be able to remarkably improve the activity of the organic metal-free catalyst, and toluene could be efficiently converted with this kind of catalytic system. This is the first report that a metal salt could improve the activity of metal-free organic molecule through complexation, which is contrary to the understanding of traditional organic metal complex catalysis. Further studies of the reaction mechanism and extensive application of this catalytic system for the other hydrocarbon oxidation are underway.

Experimental Section

The detailed synthesis procedures of NHQI, NHCl, and HPPDO can be found in the Supporting Information. The oxygenated products were identified by Agilent 6890N GC/

5973 MS detector and analyzed by gas chromatography using an Agilent model 4890D gas chromatograph with a flame ionization detector and a PEG-20M capillary column (50 m×0.32 mm×0.4um). Quantification of components was based on the internal standard technique using 1,2,4,5-tetramethylbenzene. Real-time *in situ* infrared spectra measurements were carried out on a Mettler toledo ReactIR™ 45 m equipped with an external AgX fiber conduit diamond ATR probe. ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker DRX-400FT using DMSO-d_6 as the solvent with TMS as an internal reference. Data are reported as follows: chemical shift in parts per million (δ, ppm), integration, multiplicity (s=singlet, br s=broad singlet, d=doublet, t=triplet, q=quartet, and m=multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Bruker DRX-400FT at ambient temperature. Chemical shifts are reported in ppm from DMSO-d_6 taken as 39.5 ppm.

Typical Procedure for the Oxidation

Catalytic reactions were performed in a 70-mL autoclave reactor with a teflon insert. Typically, toluene (2 mL, 18.8 mmol), NHQI (5 mol%) Co(OAc)$_2$·4H$_2$O (1.25 mol%), and acetonitrile (7 mL) were placed in the reactor. After the autoclave had been sealed, the air inside was replaced with O$_2$ for three times. Then the reactor was heated to the reaction temperature, while agitation was ensured by an external magnetic stirrer. Upon heating to the reaction temperature, the reactor was charged with 0.5 MPa of O$_2$ and O$_2$ was fed continuously to maintain a constant pressure. After the reaction, the mixture was cooled to room temperature, and analyzed by gas chromatography.

Acknowledgements

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