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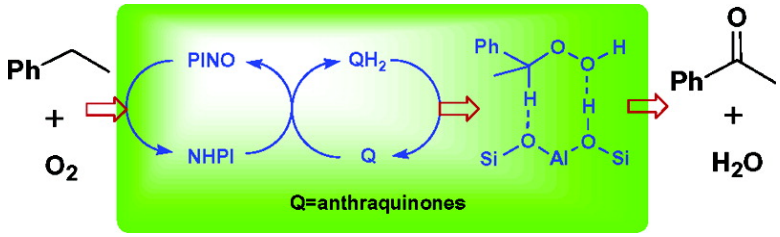

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Biomimetic Catalytic System Driven by Electron Transfer for Selective Oxygenation of Hydrocarbon

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Selective oxyfunctionalization of hydrocarbons is a crucial industrial process and remains a challenge.[1] Molecular oxygen, which is environmentally benign and economic, would be an ideal ultimate oxidant for oxygenation of hydrocarbons. However, most current processes require elevated temperatures and often show lower selectivity. Mimicry for biological oxygenation may be an inspirational approach for selective oxyfunctionalization of hydrocarbon with O_2, because biological oxygenation exhibits high selectivity under mild conditions.

On the evolution of enzyme mimicry,[2] the biomimetic oxygenation model should encompass three elementary factors: a redox center, a one-electron transfer chain, and multiple binding sites similar to the surrounding protein environment of the enzyme.

A large number of oxidoreductases contain redox centers, which can be organic radicals or metallic compounds.[3] Biological oxygenations of C−H bonds stem from the abstraction of hydrogen from organic compounds by the redox centers.[4] It is known that electrophilic radicals can readily abstract hydrogen atoms.[5] The phthalimide *N*-oxyl radical (PINO) is highly electrophilic and can efficiently promote hydrocarbon oxyfunctionalization with O_2, as demonstrated by recent intensive studies.[6] PINO can be generated from *N*-hydroxyphthalimide (NHPI) by donating both an electron and a proton and can convert to NHPI by abstracting a hydrogen atom from hydrocarbons. Therefore, PINO can be a nonmetalic redox center in catalytic hydrocarbon oxygenation.

The action of the redox center in biologic oxygenation relies on a chain of one-electron transfers, resulting in formation of radicals.[7] A ubiquitous quinone derivative (i.e., coenzyme) is often one of the units of the electron-transfer chain.[8]

Indeed, the essence of biosynthesis is the control of selectivity by some noncovalent binding of the substrate to the enzymatic protein domain. This suggests that porous zeolites could be used as host materials for host−guest composites with sequestered organic molecules, analogous to enzyme−substrate complexes in biooxidation, and enhance molecular orientation for chemical reactions.[9]

It is tempting to suggest that the quinones can make NHPI convert to PINO via one-electron transfer and subsequently facilitate hydrocarbon autoxidation, in which zeolite is used to promote reaction selectivity. Such a biomimetic system could be applied for selective oxygenation of hydrocarbons by O_2 under moderate conditions. The present study examined this biomimetic system with anthraquinone derivatives (Q) as electron-transfer mediators and ethylbenzene (**1**) as a probe molecule.

Oxygenation of **1** was performed by employing different Qs in this biomimetic catalytic system using a 70 mL Teflon-lined autoclave with O_2 (0.30 MPa) at 80 °C in acetonitrile for 10 h. When 2.5 mol % 1,4-diamino-2,3-dichloro-anthraquinone (DACAQ) was used, in combination with 10 mol % NHPI and 2.0 w % zeolite HY (HY), 66.2% of **1** was oxygenated. In comparison, only 10.9, 2.7, or 0.7% of **1** was oxygenated when NHPI, DACAQ, or HY was used individually. Results (Table 1) clearly show that the biomimetic system can significantly promote oxygenation of **1**.

Table 1. Catalytic Oxygenation of **1** by O_2[a]

		selectivity (%)[c]			conversion[c]	yield[d] of **3**
entry	feed catalysts[b]	3	4	2	(%)	(%)
1	AQ/NHPI/HY	92.8	3.8	3.4	37.3	33.2
2	EAQ/NHPI/HY	91.8	3.1	5.0	36.9	32.5
3	CAQ/NHPI/HY	92.9	5.8	1.3	41.7	36.5
4	DACAQ/NHPI/HY	95.8	4.2	0	66.2	61.1
5	AQ/NHPI	32.5	14.8	52.7	41.2	12.5
6	DACAQ/NHPI	73.5	13.1	13.4	67.9	48.4
7	DACAQ	21.5	30.8	47.7	2.7	e
8	NHPI	0	12.5	87.5	10.9	e
9	HY	96.5	2.5	1.0	0.7	e
10		1.2	3.4	95.4	1.0	e

[a] Reaction conditions: **1** (2 mL), Q (2.5 mol %), NHPI (10 mol %), HY (2.0 w %), acetonitrile (7 mL), 80 °C, O_2 (0.3 MPa), 10 h. [b] AQ, EAQ, CAQ, and DACAQ represent anthraquinone, 2-ethylanthraquinone, 2-chloroanthraquinone, and 1,4-diamino-2,3-dichloroanthraquinone, respectively. [c] GC results. [d] Isolated yields of **3**. [e] Too little to be accurately isolated.

1-Phenylethyl hydroperoxide (**2**) is an initial product from **1** autoxidation, and considerable quantities always exist in the mixture of products. Some of **2** may further convert into a variety of byproducts following a random radical mechanism.[10] When mixtures of these products were analyzed by GC, according to literature methods,[10] it was surprising to find that 95.8% selectivity of acetophenone (**3**) could be obtained. GC-MS measurements showed that **3**, 1-phenylethanol (**4**), and **2** were produced. Such high selectivity of **3** without any appreciable amount of over-oxidation byproducts and aromatic hydroxylated products clearly demonstrated that our biomimetic oxygenation system had a high product orientation.

The action of Qs and NHPI was investigated in the absence of HY. When anthraquinone (AQ) and NHPI were employed, conversion of **1** reached 41.2%. In comparison to the results in the presence of HY, the selectivity of **3** decreased to 32.5%; **2** and **4** increased to 52.7 and 14.8%, respectively. When HY alone was employed, the conversion was 0.7% with a selectivity of **3** up to 96.5%. This showed that Qs and NHPI were coupled as a catalytic system for efficient oxygenation of **1** mainly to **2**, as expected. Even though HY cannot catalyze oxygenation, it can selectively catalyze the cleavage of **2** to **3**.

The interaction between NHPI and 2-ethylanthraquinone (EAQ) was investigated by a special liquid in situ FTIR system, composed of a flow-through liquid cell, a peristaltic pump, and a water bath (see "Supporting Information"). Spectra are shown in Figure 1. When the same molar amounts of NHPI and EAQ in acetonitrile were heated at 80 °C, broad peaks at 3632 and 3544 cm^{-1} appeared in the spectrum (Figure 1C) and were assigned to the −OH stretching vibration of 2-ethylanthracenediol. Correspondingly, the

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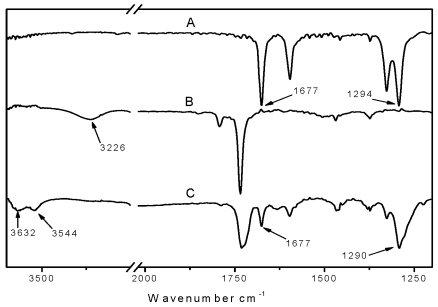
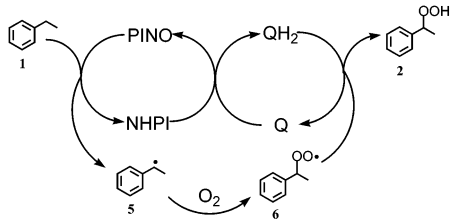


Figure 1. Liquid in situ FTIR study of NHPI and EAQ interactions. This was performed with 0.063 M NHPI and 0.063 M EAQ in acetonitrile in a special in situ system at 80 °C. The same concentrations of NHPI and EAQ were measured by the same method. Spectra of EAQ (line A), NHPI (line B), and a mixture of NHPI and EAQ (line C) were obtained by subtracting the spectral background of acetonitrile.

Scheme 1. Redox Cycle for Oxidation of **1** by the Q/NHPI System



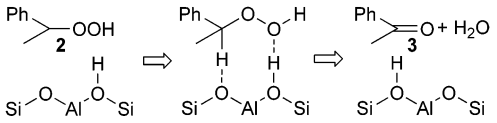
carbonyl peak of EAQ in the region of 1677 cm^{-1} decreased, and the 3226 cm^{-1} peak belonging to the stretching vibration of −OH of NHPI (Figure 1B) disappeared (Figure 1C). A strong peak also appeared at 1290 cm^{-1} (Figure 1C), which was not the peak of EAQ at 1294 cm^{-1} (Figure 1A). It may be assigned to the stretching vibration of NO bond of PINO since its vibration often shows a broad and strong peak at this frequency region.[11] These changes indicated that PINO was formed from NHPI by reacting with EAQ, while EAQ was converted to 2-ethylanthracenediol.

It can be concluded that there is a coupling redox transformation between Q/anthracenediols (QH_2) and NHPI /PINO via a one-electron transfer. The actions of Qs resemble the redox activity of quinones in biological processes. The formed PINO abstracts a hydrogen atom from **1** to produce 1-phenylethyl radical (**5**) and then reverts to NHPI. **5** interacts with O_2 and converts to 1-phenylethylperoxyl radical (**6**). After further H-abstraction from QH or QH_2, **6** converts to **2**; QH or QH_2 transforms to Q at the same time. The redox cycle of the oxidation of **1** is created (Scheme 1, QH is not shown).

The hydroxyl groups bridging Si and Al in the lattice of HY are responsible for its Brønsted acidity, leading to its fundamental application as a solid acid catalyst in various reactions. To investigate whether only the Brønsted acidity of HY catalyzes ketonic cleavage of **2**, benzoic acid (1.0 w%) was used (instead of HY) in combination with EAQ and NHPI at the same reaction conditions. The resulting 64.1% selectivity of **2** showed that this was not the case. It is known that HY catalysis involves not only the protic sites but also the surrounding framework.[12] In fact, 60.5% of **2** was obtained when 2.0% zeolite NaY (the same framework as HY but with no acidic proton) was employed with EAQ and NHPI. Such results imply that the framework and the acidic proton of HY act together in catalysis for ketonic cleavage of **2**.

It is known that some compounds possessing active protons (such as water and alcohol) can assist the migration of protons between the framework oxygen of HY, and that hydrocarbons can also have a similar function at elevated temperatures.[13] These exchanges occur between acidic protons of HY and active protons of absorbed molecules. It is suggested that the weaker acidic 1-H of **2** can also participate in proton exchange with HY.

Scheme 2. Suggested Mechanism of Ketonic Cleavage of **2** through an Adsorbed Transition State on HY



The mechanism of ketonic cleavage of **2** in the presence of HY is proposed (Scheme 2). During the reaction, **2** comes into contact with HY. The adsorption complex, acting as a cleavage transition state, was formed by O of the hydroxyl of **2** coordinating to the acidic proton on the HY surface and 1-H coordinating to the neighboring framework oxygen. Afterward, the complex synergetically decomposes, resulting in proton exchange on HY, dehydrolysis, and ketonization of **2**. This nonradical mechanism can suppress random radical cleavage of **2** and orient toward **3** generation, so that the selectivity of **3** increases greatly.

In summary, the Qs, NHPI, and HY three-component biomimetic system can efficiently catalyze oxygenation of **1** by O_2 under moderate reaction conditions. NHPI acts as a nonmetallic redox center and Qs as redox-active cofactors, and both contribute to a redox catalytic cycle. HY catalyzes nonradical cleavage of **2** to **3**. The high selectivity of **3** without any appreciable over-oxidation byproducts suggests the application of this catalytic system for methylene ketonization of hydrocarbons.

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Supporting Information Available: Detailed experimental procedures; GC measurement method; description of liquid in situ FTIR system; and original IR spectra of EAQ, NHPI, and EAQ/NHPI interaction in acetonitrile solution (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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