



REGULAR ARTICLE

# Rhenium-containing compound(PyHReO<sub>4</sub>): synthesis, characterization and catalytic application in olefin epoxidation and baeyer-villiger oxidation

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**Abstract.** A novel compound based on catalytic functional metal rhenium, pyridinium perrhenate(PyHReO<sub>4</sub>) was synthesized and characterized. The pyridinium perrhenate was used as catalyst in two types of reactions. One is the epoxidation of cyclooctene, the other is the Baeyer-Villiger oxidation of cyclic ketones to lactones. The effects of catalyst, oxidant, solvent, reaction time and temperature were investigated, which confirmed the optimum reaction conditions of the catalyst system. Both types of catalytic reactions exhibit high yields and high selectivity.

**Keywords.** Rhenium; Catalysis; characterization; Olefin epoxidation; Baeyer-Villiger.

## 1. Introduction

Rhenium has no independent ore and is extremely rare in associated ore, so it is one of the rarest elements in the earth's crust. Nowadays, rhenium and its compounds have been widely studied for their excellent performances in chemical catalysis.<sup>1–5</sup> Re-based compounds have been reported to catalyze various types of reactions, including olefin oxidation,<sup>6,7</sup> olefin metathesis,<sup>8</sup> arene oxidation,<sup>9</sup> aldehyde olefination,<sup>10,11</sup> Baeyer-Villiger oxidation,<sup>12</sup> and metal carbonyl oxidation.<sup>13,14</sup> Prompted by the evident versatility of Re-based catalyst, a rhenium compound catalyst has been prepared and thoroughly investigated with the objective of catalytic behaviour.

The epoxidation reaction is the introduction of oxygen atoms into the double bond of alkene to form 1, 2-epoxide compounds.<sup>15</sup> The epoxidation of olefins can be employed to produce various crucial intermediates and fine chemicals, so it stands out as essential application value in petrochemicals and fine chemicals industries.<sup>16–21</sup> The catalyst of epoxidation processes normally utilized molybdenum-based compounds<sup>22–25</sup> and rhenium-based compounds.<sup>26</sup> The

most renowned of which is methyltrioxorhenium(VII) (MTO).<sup>27–30</sup> The disadvantages of MTO are low stability and difficult recovery, so it is particularly crucial to develop green and recyclable catalysts.

Baeyer-Villiger oxidation (BVO) of cyclic ketones is a commonly used reaction for the synthesis of lactones are utilized, i.e., as monomers in the polymer industry, in the synthesis of fragrances, pharmaceuticals or solvents.<sup>31</sup> For the past few years, researchers have developed a variety of BVO processes such as direct/indirect H<sub>2</sub>O<sub>2</sub> method, inorganic/organic peroxyacid method, biological enzyme method.<sup>32</sup> The disadvantages of the peroxy acid approach are toxic waste acid and safety issues. Baeyer-Villiger monooxygenases (BVMOs) have been intensively researched for oxygenation of multifarious ketone to prepare corresponding lactones, which has led to possible alternative of using them as safe and green catalysts. Nevertheless, their high cost and low substrate conversion limit their use.<sup>33,34</sup>

Herein, a rhenium-based catalyst, pyridinium perrhenate(PyHReO<sub>4</sub>) was designed and synthesized. We demonstrated that the PyHReO<sub>4</sub> may catalyze two different types of oxidation reactions. A novel

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approach for catalyzing epoxidation of cyclooctene and Baeyer-Villiger oxidation reaction was accomplished, which is stable, high efficiency and easy to recover.

## 2. Experimental

### 2.1 Materials

Rhenium powder (RG) was bought from Hunan rhenium alloy material Co., Ltd. (Hunan, China). Pyridine(AR), ether (AR), methanol (AR), acetonitrile (AR), ethyl acetate (AR), hydrogen peroxide (AR), urea hydrogen peroxide (RG), cyclohexene (RG), cyclooctene (RG), cyclopentene(RG), 1-hexene(RG), styrene(RG), 2-adamantanone (RG) and epoxy cyclooctane (GC) were purchased Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

### 2.2 Synthesis of pyridinium perrhenate (PyHReO<sub>4</sub>)

All reactions were carried in gas atmosphere (Argon) with standard Schlenk techniques. Solvents were dried following standard procedures and kept under Argon. Rhenium powder and AgNO<sub>3</sub> were mixed in an acidic environment. Then a white crystallizing solid AgReO<sub>4</sub> was well prepared after filtrating, washing and drying.

A solution of AgReO<sub>4</sub> in CH<sub>3</sub>CN was added a quantitative amount of SiMe<sub>3</sub>Cl, then pyridine was added drop by drop whilst stirring at 45 °C. After 2 h, the yellow solution was concentrated under an oil pump vacuum, and the light yellow precipitate was collected by filtration, washed with diethyl ether and dried under reduced pressure. The synthesis process is shown in Scheme 1.

### 2.3 Characterization of pyridinium perrhenate (PyHReO<sub>4</sub>)

The pyridinium perrhenate (PyHReO<sub>4</sub>) was characterized by FTIR, Raman, <sup>1</sup>HNMR spectroscopy and EMI-MS. In addition, single-crystal X-ray structure

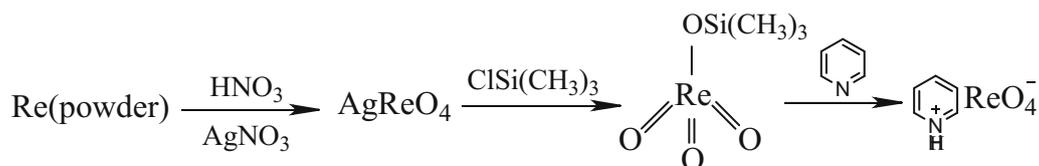
was determined. FTIR spectra were conducted on a Nicolet 5700 FT-IR spectrometer. PyHReO<sub>4</sub> FTIR  $\nu_{\max}/\text{cm}^{-1}$ : 1556 [ $\nu(\text{C}=\text{C})$ ], 1627 [ $\nu(\text{C}=\text{N})$ ], 3433[ $\nu(\text{N}-\text{H})$ ], 913 [ $\nu_{\text{s}}(\text{ReO}_4^-)$ ], 844 [ $\nu_{\text{as}}(\text{ReO}_4^-)$ ]. The results of FTIR are in good consistent with literature.<sup>35</sup>

<sup>1</sup>HNMR spectra were obtained on nuclear magnetic resonance (Mercury-vx300NMR): <sup>1</sup>HNMR (300 MHz, DMSO) spectrum of PyHReO<sub>4</sub>:  $\delta = 3.361 \sim 3.416$ (1H, NH), 7.921 ~ 8.166 (2H, CH), 8.450 ~ 8.642 (1H, CH), 8.735 ~ 8.914 (2H, NCH).

ESI-MS of PyHReO<sub>4</sub> was characterised by an Agilent 1100 ion trap spectrometer. ESI-MS (acetonitrile, m/z): 251.0[M-H]<sup>-</sup>, 181.2[2M+Na]<sup>+</sup> (Calcd. for PyHReO<sub>4</sub>, 330.31). The Raman data was collected by a Raman spectrometer(RM2000) produced by Renishaw UK. The Raman signal was recorded over the wavenumber range 150–1500 cm<sup>-1</sup>, the characteristic peak of pyridine appeared at 1005.81cm<sup>-1</sup>.<sup>36</sup> The characteristic peak of ReO<sub>4</sub><sup>-</sup> (Re=O) was an acute peak at 329cm<sup>-1</sup> and 962 cm<sup>-1</sup>, which is basically agreement with the literature values of 331 cm<sup>-1</sup> and 971 cm<sup>-1</sup>. A small amount of displacement is due to steric hindrance between ReO<sub>4</sub><sup>-</sup> and pyridine.<sup>37</sup> The small peak at 420 cm<sup>-1</sup> just comes from the remaining contribution of the Raman scatter peak of ReO<sub>4</sub><sup>-</sup>.

Single-crystal X-ray structure of pyridinium perrhenate (0.24×0.22×0.18 mm) was determined on a Bruker smart 1000 CCD diffractometer with graphite-monochromated utilizing Mo K $\alpha$ ( $\lambda = 0.71075\text{\AA}$ ) by  $\omega$ -2 $\theta$  method at 113 K. 18604 measured reflections were collected in the range of 2.4 <  $\theta$  < 30.1°, of which 2178(R<sub>int</sub> = 0.125) independent reflections. The coordinates of non-hydrogen atoms were solved by direct methods, and anisotropic refinement on F<sup>2</sup> Least-squares matrix using the SHELXTL package.

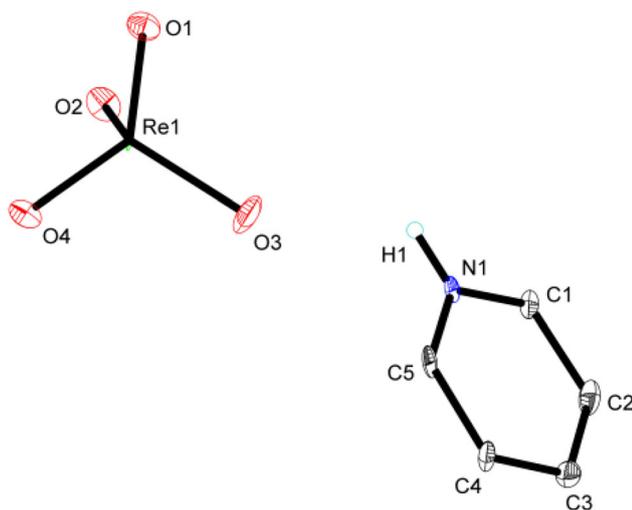
Empirical formula of pyridinium perrhenate is C<sub>5</sub>H<sub>6</sub>NO<sub>4</sub>Re, M<sub>r</sub> = 330.31, crystal system belongs to the orthorhombic, space group Pbca. Unit cell dimensions: a = 7.230(1)Å, b = 12.1070(15)Å, c = 17.0420(18)Å, V = 1491.7(3)Å<sup>3</sup>, Z = 8, D<sub>c</sub> = 2.941 Mg/m<sup>3</sup>,  $\mu = 16.26 \text{ mm}^{-1}$ , F(000) = 1200; H atoms treated by a mixture of independent and constrained refinement, and structure deviation factor R = 0.046, wR = 0.121, S = 1.13.  $w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + 19.3911P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ ; the maximum



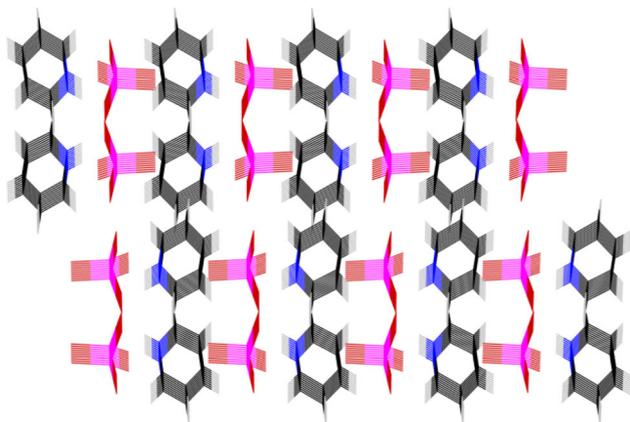
**Scheme 1.** The synthesis of rhenium-based compound.

peak of residual electron density is located at  $3.81 \text{ e}\text{\AA}^{-3}$  and the minimum peak is  $-6.16 \text{ e}\text{\AA}^{-3}$  [ $(\Delta\rho)_{\text{max}} = 3.81 \text{ e}\text{\AA}^{-3}$ ,  $(\Delta\rho)_{\text{min}} = -6.16 \text{ e}\text{\AA}^{-3}$ ,  $(\Delta/\sigma)_{\text{max}} = 0.001$ ].

Figures 1 and 2 are schematic diagrams of molecular structure and packing diagram of pyridinium perrhenate respectively. Selected bond lengths and bond angles listed in Table 1, and data of hydrogen bond are in Table 2. The  $\text{ReO}_4^-$  fragment has a tetrahedral geometry, where O-Re-O angles range from  $109.0(2)^\circ$  to  $110.1(3)^\circ$ . The Re-O bond lengths are around  $1.7 \text{ \AA}$ , which is consistent with the Re-O bond distance in some known organorhenium (VII) oxide.<sup>38</sup> The N-H in the pyridine group interacts with the two oxygens in  $\text{ReO}_4^-$  by hydrogen bonding. The hydrogen bond lengths  $d(\text{H}(1)\cdots\text{O}(3))$  and  $d(\text{H}(1)\cdots\text{O}(2))$  are  $2.20 \text{ \AA}$  and  $2.13 \text{ \AA}$ , respectively. The bond angles  $\angle\text{N}(1)\text{H}(1)\text{O}(3)$  and  $\angle\text{N}(1)\text{H}(1)\text{O}(2)$  are  $125^\circ$  and  $144^\circ$ , respectively. Molecules interact through



**Figure 1.** Molecular structure of  $\text{PyHReO}_4$ .



**Figure 2.** Packing diagram of the unit cell of  $\text{PyHReO}_4$ .

**Table 1.** Selected Bond Lengths ( $\text{\AA}$ ) and Bond Angles ( $^\circ$ ) of Compound 4

Bond	Dist.	Bond	Dist.
Re1—O4	1.715 (5)	O4—Re1—O1	109.0 (2)
Re1—O1	1.730 (6)	O4—Re1—O2	110.1 (3)
Re1—O2	1.740 (5)	O1—Re1—O2	109.2 (2)
Re1—O3	1.745 (5)	O4—Re1—O3	109.3 (3)
N1—C1	1.345 (8)	O1—Re1—O3	109.5 (3)
N1—C5	1.347 (9)	O2—Re1—O3	109.7 (3)
N1—H1	0.8800	C1—N1—C5	122.4 (6)
		C1—N1—H1	118.8
		C5—N1—H1	118.8

**Table 2.** Data of Hydrogen-bond in compound ( $\text{\AA}$ ,  $^\circ$ )

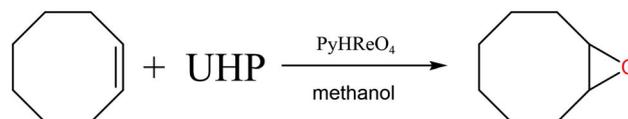
D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O3	0.88	2.20	2.800 (8)	125
C5—H5...O4 <sup>i</sup>	0.95	2.60	3.517 (9)	163
N1—H1...O2 <sup>ii</sup>	0.88	2.13	2.887 (8)	144
C5—H5...O4 <sup>i</sup>	0.95	2.60	3.517 (9)	163

hydrogen bonds to form a one-dimensional ordered molecular arrangement. On this basis, the dislocation arrangement is formed through the weak interaction of C—H...O.

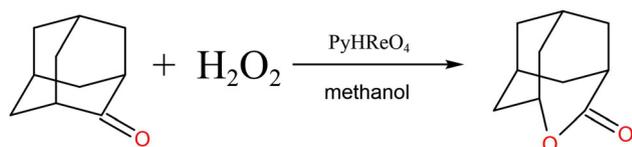
#### 2.4 General procedure of catalytic system

The catalytic reaction was carried out in a self-made glass reactor: The solvent, catalyst and oxidant were added in turn to the reactor and stirred until they were fully dissolved. They were followed by the addition of the substrate. The reaction was connected to a condensation reflux unit and stirred in a water bath at a specific temperature. Afterwards, the reaction products were analyzed by gas chromatography (GC). Figures 3 and 4 are the reaction equations for epoxidation and Baeyer-Villiger oxidation, respectively.

GC analysis was carried out in the following experimental condition. The carrier gas was passed at a constant flow rate of  $60 \text{ mL/min}$ . A sample volume of  $1 \mu\text{L}$  was used and the column temperature was programmed to  $50 \text{ }^\circ\text{C}$  with an increasing temperature of  $20 \text{ }^\circ\text{C/min}$  to  $185 \text{ }^\circ\text{C}$  for cyclooctene epoxidation.



**Figure 3.** Reaction equation of catalyst for epoxidation of cyclooctene.



**Figure 4.** Reaction equation of catalyst for Baeyer-Villiger oxidation of 2-adamantanone.

The column temperature was programmed to 80 °C with an increasing temperature of 15 °C/min to 280 °C for Baeyer-Villiger oxidation.

### 3. Results and Discussion

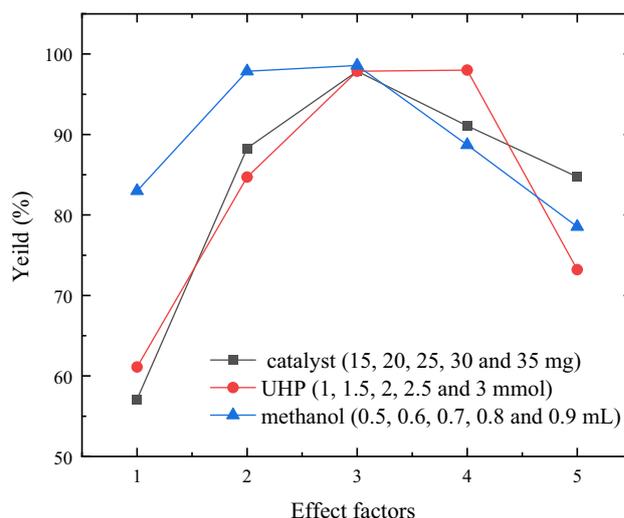
#### 3.1 Catalytic performance of pyridinium perrhenate in the epoxidation of olefins

H<sub>2</sub>O<sub>2</sub> is the most commonly used oxidant in the epoxidation of olefins, which is economical and easy to obtain. The oxidation capacity and oxidation efficiency of the commonly used 30% hydrogen peroxide solution are low due to its small concentration, so it is frequently necessary to add activating substances to improve the efficiency of the reaction. In the two-phase reaction system, H<sub>2</sub>O<sub>2</sub> could not thoroughly contact the substrate, resulting in low oxidation efficiency. As a solid form of H<sub>2</sub>O<sub>2</sub>, urea peroxide (UHP) with good stability and high H<sub>2</sub>O<sub>2</sub> content (36.2%), which makes the reaction simpler to carry out. Using UHP and H<sub>2</sub>O<sub>2</sub> as oxidants for parallel comparison, UHP can obtain a higher yield and avoid creating H<sub>2</sub>O as a byproduct during the use of H<sub>2</sub>O<sub>2</sub>.

The catalytic system is a homogeneous reaction, where the solubility of catalyst in solvent directly could affect the catalytic effect. In some organic solvents, the yield increases with the dissolution rate. In comparison, the yield in methanol with greater polarity was higher, which can reach 97.86% after 3 h. Several ionic liquids, EMISE, [Smim]BF<sub>4</sub> and [Smim]PF<sub>6</sub> were used as reaction carriers for the catalytic system, but the catalytic efficiency was not satisfactory (Table 3).

**Table 3.** Influence of different solvents

Solvent	Time/h	Yield/%
Methanol	3	97.86
Acetonitrile	3	72.66
Ethyl acetate	6	5.60
EMISE	6	10.16
[Smim]BF <sub>4</sub>	6	6.38
[Smim]PF <sub>6</sub>	6	57.56

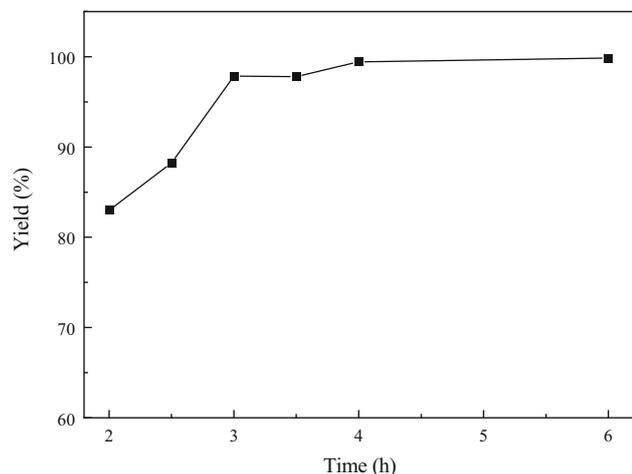


**Figure 5.** Effect of amount of catalyst, oxidant and solvent on cyclooctene epoxidation.

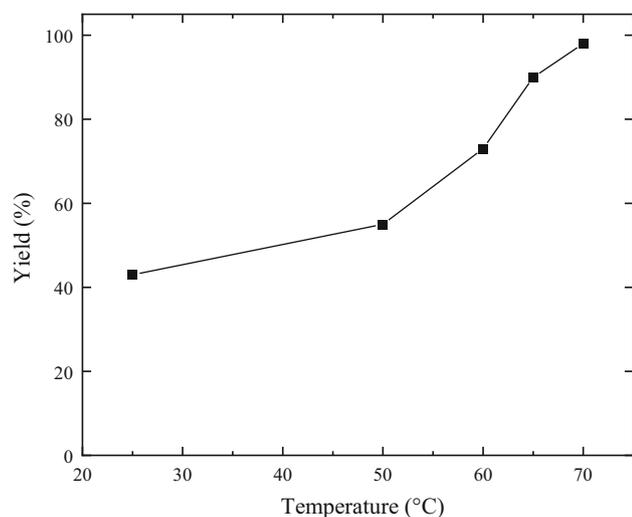
Univariate analysis was carried out for the purpose of exploring the effects of experimental variables. The results (Figure 5) showed that when the amount of catalyst, UHP and methanol increased, the epoxidation product increased at first and then decreased gradually. The concentration of catalyst in the system increased with the increasing of catalytic dose, which was beneficial to accelerate the reaction rate. However, when the concentration of catalyst increased to the saturation state, it had little effect on the reaction rate and yield. Even more than necessary catalyst (> 25 mg) would lead to ring-opening reaction of epoxy cyclooctane, thus reducing the selectivity of the reaction. The yield increased with the increasing UHP dosage. Whereas, excessive UHP could not dissolve sufficiently, thus destroying the homogeneous reaction environment. According to the results, the yield was positively correlated with the concentration of the system. When the solvent amount was 0.5 mL, the catalyst and oxidizer could not be completely dissolved, which reduced the catalytic activity. When the amount of solvent was increased to 6–7 mL, the optimum reaction concentration and the highest yield (> 97%) were achieved.

Cyclooctene epoxidation reactions with increasing time as indicated (Figure 6). Catalytic efficiency increased over time owing to the material being fully mixed. The epoxide yields basically completed conversion in 3 h, with a longer reaction time there was no significant change in yield.

Change in yield as a function of reaction temperature was shown in Figure 7. Some common catalytic olefin epoxidation systems have low results at room temperature.<sup>39,40</sup> According to the experiment, the



**Figure 6.** Effect of reaction time on cyclooctene epoxidation.



**Figure 7.** Effect of reaction temperature on cyclooctene epoxidation.

epoxide yield was not high at room temperature due to the low activity of the reaction system. Catalytic activity increased with the increasing temperature, consequently, the yield kept increasing. Considering the boiling point of methanol, the reaction temperature should not be further increased.

We optimized a series of experiments by univariate analysis to achieve the optimal catalytic reaction conditions: cyclooctene, 1 mmol; PyHReO<sub>4</sub>, 25 mg; UHP, 2.0 mmol; methanol, 0.6 mL; reaction temperature, 70 °C; reaction time, 3 h. The highest yield of cyclooctene epoxidation catalyzed by PyHReO<sub>4</sub> was 97.86%. The turnover number (TON) could reach 12.93 mol of cyclooctene epoxidation per mol.

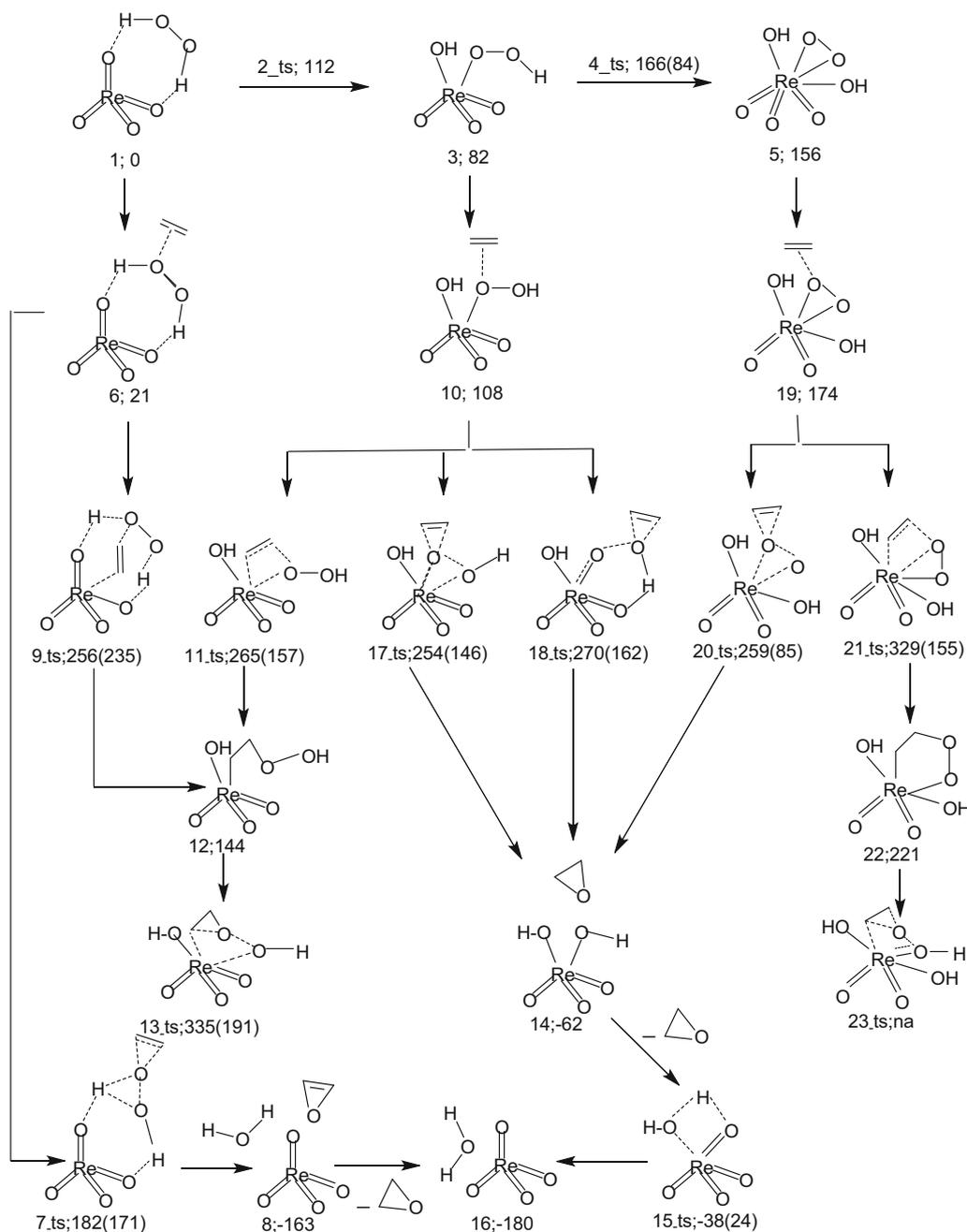
PyHReO<sub>4</sub> also had an estimable catalytic effect on other olefins. Supporting information is listed in Table 4. In order of catalytic efficiency, was

**Table 4.** Results of different substrates on epoxidation

Substrate	Temperature (°C)	Time (h)	Yield (%)
	70	3	97.86
	55	6	74.92
	35	6	88.72
	55	9	34.67
	70	8	11.00

cyclooctene>cyclopentene>cyclohexene>1-hex-ane>styrene. This trend could be attributed to spatial effects. The electron cloud on the olefin double bond has high density and affinity, therefore it is leisure to take place epoxidation reaction.<sup>41</sup> The double bonds of cyclic alkenes are more easily oxidized than those of terminal alkenes. For the reason that the double bond of cyclic alkenes is formed between two secondary carbons, which is more reactive than the double bond of terminal alkenes is connected by primary and secondary carbons.<sup>42</sup> Cyclooctene and cyclopentene tend to generate more stable octatomic ring and hexatomic ring, while the six-membered ring structure of cyclohexene is stable and difficult to undergo ring-opening reaction, so the catalytic efficiency is lower than that of cyclooctene and cyclopentene. Styrene had the lowest yield owing to the spatial effect of the benzene ring prevented the double bond from contacting the activation center. In contrast, the spatial effect of butyl groups bonded to double bonds in 1-hexene were less impeding, and was therefore relatively easy to oxidize.

In the previous work, our research group<sup>43</sup> discussed the epoxidation mechanism of olefin catalyzed by perrhenate through spectral experiments. Additionally, we examined various possible transition states(ts), and the activation energy (kJ mol<sup>-1</sup>) of the reaction was calculated by Density Functional Theory (DFT) (Figure 8). Herein, UHP was used as H<sub>2</sub>O<sub>2</sub> source in the catalytic system, the two hydrogen atoms of H<sub>2</sub>O<sub>2</sub> attacked the two Re = O bonds, respectively to form intermediate state 1. There were two other possible intermediate states 3 and 5, which interacted with the double bond during oxygen atom transfer to produce large activation energy (254 kJ mol<sup>-1</sup>, 259 kJ mol<sup>-1</sup>). Then the labelling experiment of catalyst <sup>17</sup>O was carried out, and after 24 h the product still had no



**Figure 8.** Mechanism of the cyclooctene epoxidation catalysed by  $\text{PyHReO}_4$ .

signal in ONMR. This result indicated that the oxygen atom in the epoxidation product is provided by UHP, and oxygen did not interact directly with the central Re atom, therefore we thought there was only one intermediate state 1.

Path 1→6→7→8 required the lowest activation energy of all the reactions that could occur by direct oxidation of intermediate state 1. The activation energy of transition state 7<sub>ts</sub> is 171 kJ mol<sup>-1</sup> higher than that of intermediate state 6, and  $\text{ReO}_4^-$  group can be formed without opening the second double bond. In intermediate state 8, the perrhenate is coordinated with

water molecules through oxygen atoms, which is similar to the catalytic process of MTO.<sup>44,45</sup>

Intermediate state 8 is easy to form, but its reverse activation energy is 355 kJ mol<sup>-1</sup>, which is not easy to occur. Intermediate state 6 directly inserted into the double bond to form intermediate state 9 requires high activation energy (256 kJ mol<sup>-1</sup>), so it is difficult to achieve. The reaction pathway with thermodynamic advantage is 1→6→7→8.

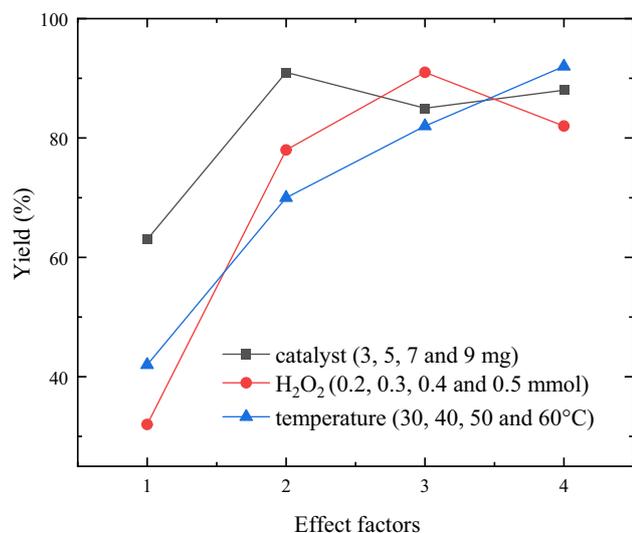
Furthermore, the reusability of the catalyst was investigated. After the catalytic reaction, 200-mesh silica gel was used as the stationary phase and the

volume ratio of 3:1 n-hexane-ethyl acetate was used as the eluent to separate the reaction mixture by silica gel column chromatography, and the epoxidation product and the catalyst could be separated successfully. In order to test the performance of the recovered catalyst, another catalytic experiment was carried out under the optimal conditions obtained in previous experiments. The results showed that neither yield nor selectivity has changed much, indicating that the rhenium catalyst synthesized in this paper had good repeatability.

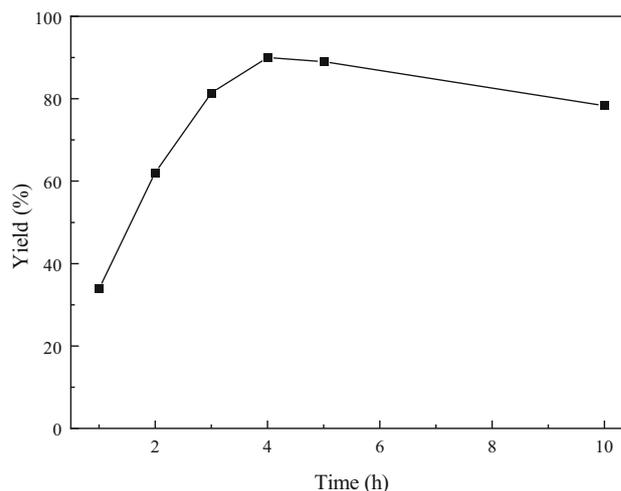
### 3.2 Catalytic performance of pyridinium perrhenate in Baeyer-Villiger oxidation reaction

The oxygen source of Baeyer-Villiger oxidation is initially highly toxic peroxy acid which is replaced by green hydrogen peroxide or oxygen now. Hydrogen peroxide has the advantage of being inexpensive, secure, and environmentally friendly with only water as a byproduct. Correspondingly, the oxygen source is abundant and safe, in line with the environmental protection requirements of green chemistry. In this section, the H<sub>2</sub>O<sub>2</sub> (30 wt%) solution was used as the oxidant.

Univariate analysis was carried out for the purpose of exploring the effect of experimental variables (Figure 9). First of all, the influence of reaction temperature (30, 40, 50 and 60 °C) was followed. The temperature dependence of the catalytic activity of PyHReO<sub>4</sub> is pronounced. Considering the low boiling point of methanol, 60 °C was chosen as the optimal reaction temperature. Then, different amounts of catalyst (3, 5, 7 and 9 mg) and oxidant (0.2, 0.3, 0.4 and



**Figure 9.** Effect of amount of catalyst, oxidant and temperature on Baeyer-Villiger oxidation.



**Figure 10.** Effect of reaction time on Baeyer-Villiger oxidation.

0.5 mmol) were selected to investigate. The experimental results illustrated that the more catalyst and oxidation dosage, the more favorable the BV reaction generally. Whereas the yield began to decline when the amount of oxidant was excessive (> 0.4 mmol) on account of the over-decomposition of H<sub>2</sub>O<sub>2</sub> leading to hydrolysis of the product lactone. Similarly, an excessive catalyst caused catalyst deactivation while insufficient catalysts caused the incomplete catalytic reaction.

Reaction time is an important index to measure the activity of catalyst. The catalytic reaction could achieve a high yield (90.02%, Selectivity > 99%) in a short time (4 h). When the reaction time was extended to 10 h, the yield decreased slightly. GC detection demonstrated that byproducts were generated at this time, and the selectivity of the reaction was reduced (Figure 10).

The optimum conditions for Baeyer-Villiger oxidation catalyzed by PyHReO<sub>4</sub> were detailed as follows: 2-adamantanone, 0.2 mmol; PyHReO<sub>4</sub>, 5 mg; 30 wt% H<sub>2</sub>O<sub>2</sub>, 0.4 mmol; methanol, 6 mL, reaction time, 4 h; reaction temperature, 60 °C. The highest yield of the Baeyer-Villiger oxidation reaction catalyzed by PyHReO<sub>4</sub> was 90.02% with a TON of 11.89.

## 4. Conclusions

In summary, pyridinium perrhenate (PyHReO<sub>4</sub>) based on catalytic functional metal rhenium has been developed by a new catalyst. The properties and structure of which were studied employing <sup>1</sup>HNMR, IR, MS, Raman. Besides the single-crystal X-ray analysis was performed in order to investigate the crystalline structure of the title compound. The

synthesized PyHReO<sub>4</sub> was then used to catalyze different types of reactions. To begin with, PyHReO<sub>4</sub> exhibit excellent catalytic activity in the epoxidation of cyclooctene with the conversion and selectivity of cyclooctene oxide was more than 97%. The catalytic performance in the epoxidation of other alkenes was also estimable. Subsequently, we discussed the mechanism and alternative reaction pathways of olefin epoxidation. Furthermore, PyHReO<sub>4</sub> demonstrated catalytic activity in Baeyer-Villiger oxidation of 2-adamantanone with great yields (90.02%) using 30% H<sub>2</sub>O<sub>2</sub> as an oxidant. Consequently, the system with PyHReO<sub>4</sub> as a catalyst provided an easy separation, effective, mild and convenient method for catalyzing different types of reactions, and the pyridinium perrhenate (PyHReO<sub>4</sub>) will have broad industrial application prospects.

### Supplementary Information (SI)

Figures S1-S7 are available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

### Acknowledgements

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