



Editor's choice paper

Metalloporphyrin-mediated aerobic oxidation of hydrocarbons in cumene: Co-substrate specificity and mechanistic consideration

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ABSTRACT

Selective aerobic oxidation of hydrocarbons by molecular oxygen to afford valuable oxygen-containing functional compounds is a key challenge in modern chemical industry. Herein, an efficient catalytic system including metalloporphyrins as ideal catalysts and cumene as a co-substrate was developed for the aerobic oxidation of hydrocarbons to afford products with high yields and excellent chemoselectivities. Notably, this biomimetic process was found to be similar to cytochrome P450 monooxygenase-catalyzed reactions according to Michaelis–Menten kinetics. Experimental results and *in situ* monitoring techniques including the kinetic study, *in situ* ultraviolet–visible spectroscopy, and *in situ* electron spin resonance spectroscopy indicated that *in situ* generated cumyl hydroperoxide acted as an actual oxidant. Its formation was possibly mediated by metalloporphyrins to generate numerous free-radical species, and the high-valent Mn^{IV}-oxo π -cation radicals were regarded as active species in the aerobic oxidation. Consequently, both the co-substrate specificity and the possible reaction mechanism were systematically investigated based on the control experiments and results obtained from our previous studies.

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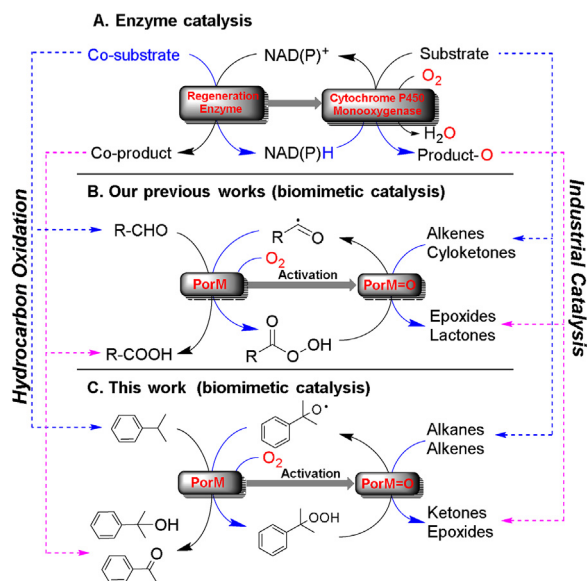
1. Introduction

Selective oxidation of hydrocarbons to produce valuable oxygen-containing functional compounds is a key challenge in modern chemical industry in terms of chemo, regio, and stereoselectivity [1–3]. Compared to the traditional oxidants including organic peracids (for *e.g.* meta-chloroperbenzoic acid [4]), hydrogen peroxide (H₂O₂) [5], and iodosylbenzene [6], molecular oxygen (O₂) is the most preferred oxidant in synthetic catalytic oxidation systems because of its ubiquitous and environmentally friendly nature (water as a sole by-product) [7]. Nowadays, utilization of O₂ together with several transition metal catalysts has been successfully applied in industrial oxidation processes, such as oxidation of cyclohexane [8], *p*-xylene [9], cumene [10] and so forth. However, considering its special nature of “difficult-to-activation”, the aerobic oxidation of organic substrates remains an ongoing challenge and thus a key research hot topic.

It is universally acknowledged that the life goes through a series of oxidation processes at every moment in the presence of O₂ as the primary oxidant, which is a very successful example of the activation of O₂ [11]. The activation of O₂ is important because of its central role in the functioning of metalloenzymes, which utilize O₂ to perform a number of challenging reactions including the highly selective oxidation of various substrates. Accordingly, inspired by metalloenzyme catalysis in the nature, it was found that the cytochrome P450 (CYP450) monooxygenases as a typical metalloenzyme could be widely applied for the oxyfunctionalization of hydrocarbons through a series of electron and hydrogen transfer processes [12,13]. This enzyme-catalyzed process exhibits high efficiency and unprecedented chemoselectivity, as well as can be performed under mild conditions [14]. Scheme 1A provides an overview of the general property of CYP450 monooxygenase system from the perspective of enzyme catalysis. Clearly, the high-valent metal–oxygen intermediate acts as the catalytically active species, which is obtained *via* a sequence of electron transfer in the presence of co-substrate (hydrogen donor), regeneration enzyme, and the reduced nicotinamide cofactor (NAD(P)H) [13]. Furthermore, the cofactor regeneration consumes another substrate (co-substrate) and produces a stoichiometric co-product.

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Scheme 1. (A) An overview on the general property of CYP450 monoxygenase system on the basis of enzyme catalysis; (B) Our previous works on hydrocarbon oxidation using organic aldehydes as co-substrates over metalloporphyrins on the concept of biomimetic catalysis; (C) This work using cumene as co-substrate in alkene epoxidation or alkane oxidation over metalloporphyrins.

Nevertheless, it is difficult to optimize the complicated electron transport chains.

From the academic point of view, *in situ* generation of H₂O₂ reported by Hollmann and coworkers is a more efficient route to promote peroxxygenase-catalyzed oxyfunctionalization of hydrocarbons [15,16]. Furthermore, our group reported the aerobic epoxidation of alkenes [17–19] and the Baeyer–Villiger oxidation of cycloketones [20,21], catalyzed by various metalloporphyrins based on the concept of biomimetic catalysis. These processes required a stoichiometric amount of organic aldehyde as co-substrate (sometimes called co-reductant) originated from the *in situ* generation of organic peracids (Scheme 1B). However, the above-mentioned strategies, in general, brought about the following three main drawbacks, leading to the difficulty in industrialization: (1) the co-substrate (aldehyde) is often expensive than the corresponding co-product (carboxylic acid), thus making the oxidation process cost ineffective; (2) the oxidation process often exhibits high reaction rate due to highly active acyl radical species, thereby arising a series of safety problems; and (3) the reaction requires acetonitrile or dichloromethane as the additional non-green solvent to achieve the catalytic cycle because the presence of solvent could decrease the concentration of the generated acyl radicals, probably enhancing the chemoselectivity toward products. Therefore, the development of the inexpensive and easy-to-available as well as appropriate co-substrate becomes increasingly important in the future studies.

In chemical industry, cumene obviously acts as a co-substrate capable of carrying out the aerobic epoxidation of propylene to produce propylene oxide through the Sumitomo process [22]. The *in situ* generation of cumyl hydroperoxide (CHP) from autooxidation of cumene could promote the occurrence of oxidation process. Therefore, we envisioned that the metalloporphyrins (models for CYP450)-catalyzed aerobic oxidation of hydrocarbons could smoothly be performed in the presence of cumene as a co-substrate without the addition of any additional organic solvents. Herein, a biomimetic catalytic system using metalloporphyrin as an efficient catalyst and cumene as a co-substrate was developed for the aerobic oxidation of hydrocarbons including alkanes and alkenes to obtain the corresponding ketones and epoxides

(Scheme 1C) in good yields. A series of experimental results such as the kinetic study, and *in situ* monitoring techniques including *in situ* ultraviolet–visible (UV–vis) spectroscopy and *in situ* electron spin resonance (ESR) spectroscopy indicated that the high-valent Mn^{IV}–oxo π -cation radicals (denoted as Mn^{IV} = O⁺) were the active species, generated by the heterolysis of O–O bond within active transition states. Finally, the co-substrate specificity was investigated in detail and the possible reaction mechanism was also proposed based on the control experiments and the results obtained from our previous studies.

2. Experimental section

2.1. Materials and methods

CHP, alkanes, alkenes, ketones, and epoxides were purchased from J&K Scientific Ltd. Various metalloporphyrins were obtained from Sigma-Aldrich Co. LLC. The *in situ* ESR spectra were recorded using a JEOL electron spin spectrometer equipped with X-band microwave unit. The *in situ* UV–vis spectroscopy was performed using an Ocean optics UV–vis spectrometer.

2.2. General procedure for the aerobic oxidation of hydrocarbons

Liquid oxidation reactions were performed in a two-necked flask (20 mL) attached with a magnetic stirrer, a reflux condenser, and an oil bath. Substrate (1.0 mmol), cumene (5 mL), and catalyst (if used) were taken into the flask, the reaction mixture was sonicated for 5 min, and then heated rapidly to the preconcerted temperature under O₂ bubbling with a constant flow rate. The conversions and yields were determined using biphenyl as an internal standard and measurement was performed using a GC2010 gas chromatograph (GC, Shimadzu) equipped with the capillary column (Rtx-5, 30 m \times 0.32 mm \times 0.25 μ m) and the flame ionization detector. The CHP concentration was calculated according to the standard iodometric method after the reduction reaction with triphenylphosphine [23], and the products were also analyzed by GC or GC–MS.

2.3. In situ electron spin resonance experiments

The ESR spectra were recorded using a Wilmad WG-810-A quartz-flat cell with 500 μ L reactant solution from mixture containing diphenylmethane (1.0 mmol), CHP (5 mL), and MnTPPCI (0.7 mol%) under nitrogen atmosphere. The amount of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as radical scavenger was about 60 mM. The ESR analysis was carried out at microwave frequency of 9.05 GHz at 353 K and the corresponding spectra were collected at the rate of one spectrum every 2 min.

3. Results and discussion

3.1. Aerobic oxidation of alkenes and alkanes

Initially, the aerobic oxidation of alkenes was conducted to investigate and describe the catalytic performance. The alkenes were catalyzed by metalloporphyrins using cumene as co-substrate and *cis*-cyclooctene (**1a**) as a representative model as summarized in Table 1. The reaction did not proceed without catalyst by using cumene as a sole solvent at 90 °C when the stream of O₂ was bubbled through the reaction (Table 1, entry 1). When metalloporphyrins bearing different metal centers including cobalt (CoTPP), iron (FeTPPCI), and manganese (MnTPPCI) were employed as catalyst, the catalyst MnTPPCI exhibited the superior catalytic activity with the conversion of 98% compared to that by the catalyst CoTPP

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