Chinese Chemical Letters 24 (2013) 447–449

Contents lists available at SciVerse ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Solvent effects on oxygen atom transfer reaction between manganese(V)-oxo corrole and alkene

Lan Yu [a], Qi Wang [a], Lu Dai [a], Wei-Ying Li [a], Rong Chen [a], Mian HR Mahmood [a], Hai-Yang Liu [a,*], Chi-Kwong Chang [b,*]

[a] *Department of Chemistry, South China University of Technology, Guangzhou 510640, China*
[b] *Department of Chemistry, Michigan State University, E. Lansing, MI 48824, USA*

ARTICLE INFO

Article history:
Received 16 January 2013
Received in revised form 28 February 2013
Accepted 3 March 2013
Available online 19 April 2013

Keywords:
Corrole
Mn(V)-oxo corrole
Oxygen atom transfer reaction
Solvent effect

ABSTRACT

Pseudo-first order reaction rate constants of 5,10,15-tris(pentafluorophenyl)corrole Mn(V)-oxo (F_{15}CMn(V)-oxo), 5,15-bis(pentafluorophenyl)-10-(phenyl)corrole Mn(V)-oxo (F_{10}CMn(V)-oxo), 5,15-bis(phenyl)-10-(pentafluorophenyl)corrole Mn(V)-oxo (F_5CMn(V)-oxo) and 5,10,15-tris(phenyl)corrole Mn(V)-oxo (F_0CMn(V)-oxo) with a series of alkene substrates in different solvents were determined by UV–vis spectroscopy. The results indicated that the oxygen atom transfer pathway between Mn(V)-oxo corrole and alkene is solvent-dependent.

1. Introduction

Many biological reactions involve oxygen atom transfer (OAT) from a transition metal active center to the substrates [1]. High-valent metal–oxo complexes are critical to a large class of metalloenzymes involved in OAT reaction [2,3]. Manganese(V)-oxo porphyrins have long been recognized as an active species in OAT reactions [4]. Corrole is an aromatic 18-π electron macrocycle that bears a close resemblance with porphrin [5]. Compared to the transient Mn(V)-oxo porphyrin [6], Mn(V)-oxo corrole is more stable and thus provides an ideal mechanistic probe for the catalytic oxidation of organic substrates.

The first synthesis of manganese(V)-oxo was achieved by oxidation of manganese 5,10,15-tris(pentafluorophenyl)corrole [(TPFC)Mn(III)] with iodosylbenzene (PhIO) or ozone as an oxidant [7], albeit laser flash photolysis may also be used [8]. Electron-deficient perfluorinated Mn(V)-oxo corrole was found to be more reactive towards a cyclooctene substrate [9], and the presence of an axial ligand also enhanced the reactivity of Mn(V)-oxo corrole [10]. The direct evidence of OAT between Mn(V)-oxo and alkene came from the ^{18}O-labeling experiments using a highly bulky Mn(V)-oxo corrole complex [11]. DFT calculations indicated that the reactivity of β-brominated Mn(V)-oxo corrole is more related to the spin state changes [12]. It is well-known that solvent plays important role in the catalytic oxidation reactions [13] and solvent effects have previously been observed in chromium-oxo corroles [14] and molybdenum-oxo corroles [15] Herein, we wish to report the solvent effects on the OAT reaction between manganese(V)-oxo corroles and alkenes. The investigated manganese(V)-oxo corrole species are shown in Scheme 1.

2. Experimental

Mn(III) corroles were prepared according to our previously reported procedure [16]. The corresponding Mn(V)-oxo corroles were also prepared according to reported method [7,9]. Typically, iodosobenzene (PhIO) was added to a solution of Mn(III) corrole ($\sim 3.0 \times 10^{-5}$ mol/L) (Mn(III) corrole/PhIO molar ratio is 1:10), and the solution color turned into red gradually. After reaction, superfluous PhIO was removed by flash chromatography on basic alumina. It is noteworthy that Mn(V)-oxo corroles could not be prepared by the same method in THF or DMSO.

3. Results and discussion

Mn(V)-oxo corroles are unstable and will gradually decompose and finally return to the corresponding Mn(III) corrole in general. However, the more electron-rich F_5CMn(V)-oxo and F_0CMn(V)-oxo will gradually change to Mn(IV) corrole in toluene and

---

[*] Corresponding authors.
E-mail addresses: chhyliu@scut.edu.cn (H.-Y. Liu), changc@msu.edu (C.-K. Chang).

1001-8417/$ – see front matter © 2013 Hai-Yang Liu, Chi-Kwong Chang. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.
http://dx.doi.org/10.1016/j.cclet.2013.03.029

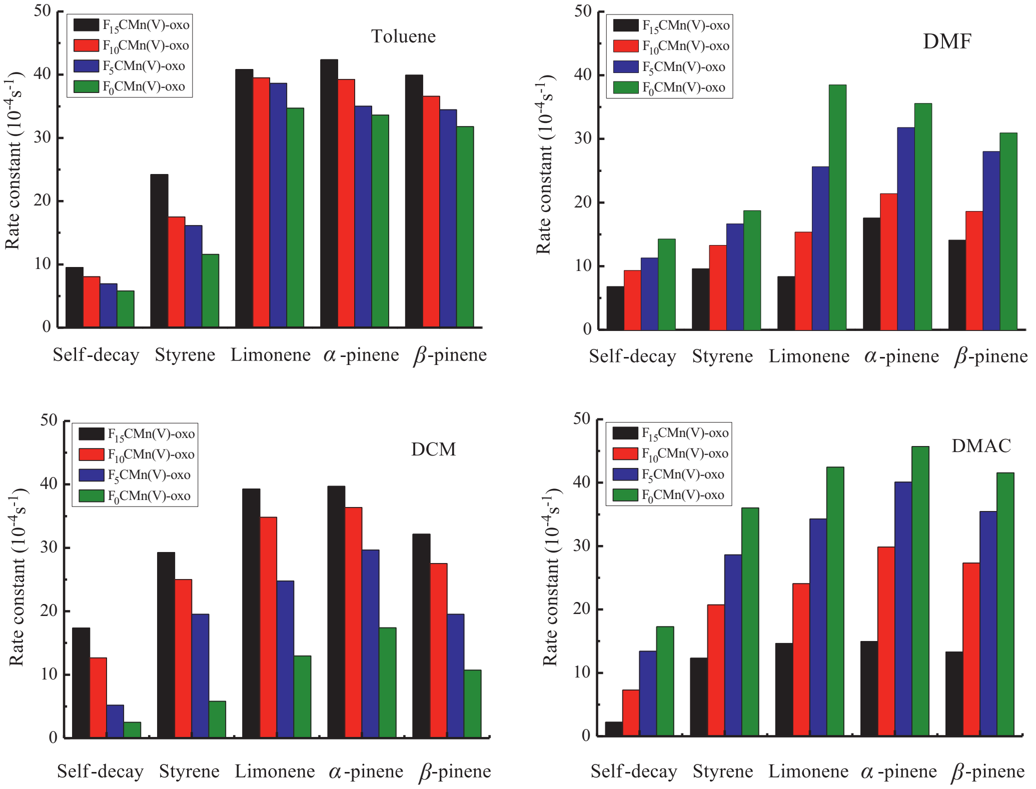
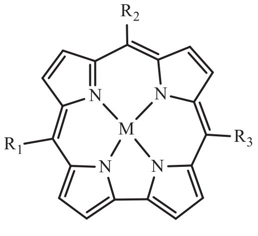


Fig. 1. Self-decay and *pseudo*-first-order reaction rate constants of manganese-oxo corroles with substrates (25.0 °C ± 0.1 °C) in different solvents.

dichloromethane (DCM), as indicated by UV–vis spectra. These two Mn(V)-oxo species could only return to Mn(III) corrole in DMF or DMAc solutions, which may be related to the stability of electron-rich Mn(III) corrole in these solvents. It was also observed that these electron-rich Mn corroles prefer to exhibit Mn(IV) complex in DCM [17]. The self-decay rate constants (k) of Mn(IV) corroles were determined by monitoring the absorption maximum of Soret band (left arm) at (25.0 ± 0.1) °C and the data are shown in Fig. 1. It can be seen that in toluene and DCM, the self-decay rate constants follow the order: F_{15}CMn(V)-oxo > F_{10}CMn(V)-oxo > F_5CMn(V)-oxo > F_0CMn(V)-oxo. In contrast, self-decay rate constants follow a reversed order: F_{15}CMn(V)-oxo < F_{10}CMn(V)-oxo < F_5CMn(V)-oxo < F_0CMn(V)-oxo in DMF, DMAc. This indicates that solvent has a significant effect on the self-decay process of Mn(V)-oxo corroles.

Pseudo-first order reaction rate constants (k_{obs}) between Mn(V)-oxo corroles and alkene substrates in different solvents are also shown in Fig. 1. Here, k_{obs} was measured by the reaction of Mn(V)-oxo corrole and a large excess of substrates ([substrate]/[Mn-oxo] = 1000). In all these cases, the addition of alkene substrate was found to accelerate the decay of Mn(V)-oxo corrole significantly. This is caused by the OAT reaction between Mn-oxo corrole and alkene. The rate constants of limonene, α-pinene and β-pinene are much larger than that of styrene due to the presence of more electron-rich alkene double bond (Fig. 1). The difference in rate constants between limonene, α-pinene and β-pinene are consistent with the enhanced reactivity of Mn(V)-oxo triphenylcorrole towards the less-substituted and electron-rich alkene [11]. In toluene and DCM, *pseudo*-first order rate constants (k_{obs}) follow the order: F_{15}CMn(V)-oxo > F_{10}CMn(V)-oxo > F_5CMn(V)-oxo > F_0CMn(V)-oxo. This is in accordance with the electronic demand of Mn(V)-oxo corroles. As the OAT reaction between Mn(V)-oxo corrole and alkene is an electrophilic reaction, it is expected that more electron-deficient Mn(V)-oxo corroles would be more reactive. This means a direct OAT reaction between Mn(V)-oxo corrole and alkene substrates could have occurred in this case. Interestingly, in DMF and DMAc, the *pseudo*-first order rate constants (k_{obs}) follow a reversed order: F_{15}CMn(V)-oxo < F_{10}CMn(V)-oxo < F_5CMn(V)-oxo < F_0CMn(V)-oxo. This is contradictory to the reactivity of Mn(V)-oxo corroles based on electronic demand. Similar phenomenon was also observed by Mn(V)-oxo corroles generated by laser flash photolysis [8]. It was rationalized by the generation of a higher valent Mn(VI)-oxo species *via* a disproportionation process of the Mn(V)-oxo corrole. The more electron-rich Mn(V)-oxo corroles undergo the disproportionation reaction more easily. In DMF and DMAc, electron-rich F_0CMn(V)-oxo exhibited the largest reaction rate constants to all examined substrates, and the k_{obs} of alkene with electron-rich double bonds are also much higher. This indicates the formation of new reactive F_0CMn-oxo species in these solvent systems. These observations also suggested that OAT reaction of Mn(V)-oxo corrole and alkene substrates may proceed *via* different mechanisms in different solvents.



	R_1	R_2	R_3
F_{15}C	C_6F_5	C_6F_5	C_6F_5
F_{10}C	C_6F_5	C_6H_5	C_6F_5
F_5C	C_6H_5	C_6F_5	C_6H_5
F_0C	C_6H_5	C_6H_5	C_6H_5

Freebase M= 3H
Mn(III) corrole M= Mn
Mn(V)-oxo corrole M= Mn≡O

Scheme 1. Structures of free base corroles and their Mn complexes.

4. Conclusion

In conclusion, we report the first observation of solvent effect on the OAT reaction between Mn(V)-oxo corroles and alkene substrates. The reaction may proceed either through a direct OAT between Mn(V)-oxo and alkene or through a high-valent Mn-oxo species generated *via* a disproportionation process, and is strongly solvent-dependent. Further investigations on how the solvent affects the reactivity of Mn(V)-oxo corroles in OAT reactions are underway.

Acknowledgment

The financial support from the National Natural Science Foundation of China (Nos. 20971046 and 21171057) is gratefully acknowledged.

References

[1] J. McMaster, C.D. Garner, E.I. Stiefel, Hydrogen, carbon, and sulfur metabolim, in: I. Bertini, H.B. Gary, E.I. Stiefel, et al. (Eds.), Biological Inorganic Chemistry, Structure and Reactivity, University Science Books, Sausalito, California, 2007, pp. 443–555.

[2] Y. Mishina, C. He, Oxidative dealkylation DNA repair mediated by the mononuclear non-heme iron AlkB proteins, J. Inorg. Biochem. 100 (2006) 670–678.

[3] M. Dekker, Metals ions in biological system, in: A. Sigel, H. Sigel (Eds.), Molybdenum and Tungsten: Their Roles in Biological Processes, vol. 39, CRC Press Inc., New York, 2002.

[4] K.A. Prokop, H.M. Neu, S.P. de Visser, et al., A manganese(V)-oxo β-cation radical complex: influence of one-electron oxidation on oxygen-atom transfer, J. Am. Chem. Soc. 133 (2011) 15874–15877.

[5] C. Erben, S. Will, K.M. Kadish, Metallocorroles: molecular structure, spectroscopy and electronic states, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 2, Academic Press Inc., San Diego, CA, 2000, pp. 233–295.

[6] R. Zhang, M. Newcomb, Laser flash photolysis formation and direct kinetic studies of manganese(V)-oxo porphyrin intermediates, J. Am. Chem. Soc. 125 (2003) 12418–12419.

[7] Z. Gross, G. Golubkov, L. Simkhovich, Epoxidation catalysis by a manganese corrole and isolation of an oxomanganese(V) corrole, Angew. Chem. Int. Ed. 39 (2000) 4045–4047.

[8] R. Zhang, D.N. Harishchandra, N. Newcomb, Laser flash photolysis generation and kinetic studies of corrole-manganese(v)-oxo intermediates, Chem. Eur. J. 11 (2005) 5713–5720.

[9] H.Y. Liu, T.S. Lai, L.L. Yeung, et al., First synthesis of perfluorinated corrole and its $\mathrm{Mn{=}O}$ complex, Org. Lett. 5 (2003) 617–620.

[10] H.Y. Liu, H. Zhou, L.Y. Liu, et al., The effect of axial ligand on the reactivity of oxomanganese(V) corrole, Chem. Lett. 36 (2007) 274–275.

[11] H.Y. Liu, F. Yam, Y.T. Xie, et al., A bulky bis-pocket manganese(V)-oxo corrole complex: observation of oxygen atom transfer between triply bonded $\mathrm{Mn^{V}{\equiv}O}$ and alkene, J. Am. Chem. Soc. 131 (2009) 12890–12891.

[12] C. Zhu, J. Liang, B. Wang, et al., Significant effect of spin flip on the oxygen atom transfer reaction from (oxo)manganese(v) corroles to thioanisole: insights from density functional calculations, Phys. Chem. Chem. Phys. 14 (2012) 12800–12806.

[13] T. Michel, D. Betz, M. Cokoja, et al., Epoxidation of alpha-pinene catalyzed by methyltrioxorheniurn(VII): influence of additives, oxidants and solvents, J. Mol. Catal. A: Chem. 340 (2011) 9–14.

[14] R.S. Czernuszewicz, V. Mody, A. Czader, et al., Why the chromyl bond is stronger than the perchromyl bond in high-valent oxochromium(IV,V) complexes of tris(pentafluorophenyl)corrole, J. Am. Chem. Soc. 131 (2009) 14214–14215.

[15] V.V. Mody, M.B. Fitzpatrick, S.S. Zabaneh, et al., Solvent effects on the electronic and vibrational properties of high-valent oxomolybdenum(V) 5,10,15-triphenylcorrole probed by UV–visible and resonance Raman spectroscopy, J. Porphyrins Phthalocyanines 13 (2009) 1040–1052.

[16] P. Lian, H.Y. Liu, L. Chen, et al., Demetalation of manganese corroles, Chin. J. Inorg. Chem. 25 (2009) 1420–1425.

[17] H.Y. Liu, M.H.R. Mahmood, S.X. Qiu, C.K. Chang, Recent developments in manganese corrole chemistry, Coordin. Chem. Rev. 257 (2013) 1306–1333.