Note

Iodobenzene diacetate as an efficient terminal oxidant in iron(III) porphyrin complex-catalyzed oxygenation reactions

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Abstract

An electron-deficient iron(III) porphyrin complex associated with iodobenzene diacetate (PhI(OAc) 2) afforded high yields of oxygenated products in catalytic oxygenations of olefins and alkanes when the reactions were carried out in the presence of a small amount of water. An oxoiron(IV) porphyrin cation radical intermediate was generated in the reaction of an iron(III) porphyrin complex and PhI(OAc) 2. These results demonstrate that PhI(OAc) 2, which is soluble in organic media, safe to use, and readily available, is an efficient oxygen atom donor that can be used as a substitute for polymeric iodosylbenzene (PhIO) in metalloporphyrin-mediated oxygenation reactions.

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1. Introduction

The reactions of iron(III) porphyrin complexes with various terminal oxidants have been extensively studied with the intention of elucidating the chemistry of cytochromes P450 [1]. Since Groves and co-workers discovered two decades ago that synthetic iron(III) porphyrin complexes associated with iodosylbenzene (PhIO) oxygenate hydrocarbons including olefins and alkanes [2], PhIO has been widely used as a single oxygen atom donor in catalytic oxygenation reactions as well as in mechanistic studies of oxygen transfer reactions [3]. However, polymeric PhIO is insoluble in most organic media and potentially explosive, and heating or extended storage at room temperature results in the disproportionation of PhIO to PhI and iodox-ybenzene (PhIO 2) [4].

Iodosylbenzene is prepared by the hydrolysis of iodobenzene diacetate, PhI(OAc) 2 [5]. PhI(OAc) 2, which is soluble in most organic solvents, safe to use, and commercially available, has been widely used as a starting material in the preparation of various hypervalent iodine(III/V) derivatives and as a mild and selective oxidant in non-catalytic organic reactions [4,6]. Despite such valuable oxidizing properties and broad applications in non-catalytic oxidative reactions, PhI(OAc) 2 has been less frequently used in metal complex-catalyzed oxidation reactions. It is very recent that Collman and co-workers used PhI(OAc) 2 as a terminal oxidant in competitive hydroxylation of alkanes by Fe(TPFPP)Cl (TPFPP = meso-tetrakis(pentafluorophenyl)porphinato dianion) [7]. Adam and co-workers reported a highly chemoselective oxidation of alcohols by Cr III(salen)X and PhI(OAc) 2 [8]. Che and co-workers also reported recently that PhI(OAc) 2 associated with NH 2R is an efficient amidating reagent in metalloporphyrin-mediated amidation of saturated C–H bonds [9]. Furthermore, Nishiyama and co-workers demonstrated that PhI(OAc) 2 is a better oxidant than PhIO in ruthenium-pyridine-2,6-dicarboxylate complex-catalyzed epoxidation of trans-stilbene [10]. In the present study, we report that PhI(OAc) 2 is an efficient oxidant in iron(III) porphyrin-catalyzed oxygenation of olefins and alkanes in the presence of a small amount of water in organic solvent. We also show that an oxoiron(IV)
porphyrin cation radical intermediate is generated in the reaction of an iron(III) porphyrin complex and Phl(OAc)₂.

2. Results and discussion

We have examined the ability of Phl(OAc)₂ as an oxygen atom donor in the catalytic epoxidation of olefins by Fe(TPFPP)Cl, an electron-deficient iron(III) porphyrin complex which has been used as an efficient and robust catalyst in various oxygenation reactions [11]. The reactions were carried out in the presence of a small amount of H₂O in a solvent mixture of CH₂CN and CH₂Cl₂ (1:1) at room temperature. The results in Table 1 show that the addition of Phl(OAc)₂ (1.5 equiv. with respect to olefins) converted olefins to the corresponding epoxide products. In the epoxidation of cyclooctene, cyclohexene oxide was yielded as a major product with the formation of small amounts of allylic oxidation products such as cyclohexenol and cyclohexanone. Cyclooctene oxide was the sole product detected in the epoxidation of cyclooctene. The epoxidation of cis- and trans-stilbene resulted in yielding the corresponding epoxide products without giving any isomerized oxide products (e.g. no formation of trans-stilbene oxide in the epoxidation of cis-stilbene), indicating that this catalytic system is highly stereoselective [12]. Interestingly, high yields of oxide products were obtained in the oxidation of less reactive terminal olefins such as 1-octene and 1-hexene. When the epoxidation by Fe(TPFPP)Cl and Phl(OAc)₂ was carried out in the absence of water, the reaction proceeded slowly (vide infra). In the absence of the iron porphyrin catalyst, no formation of cyclohexene oxide was detected in the epoxidation of cyclohexene by Phl(OAc)₂ alone.

Then, hydroxylation of alkanes by Fe(TPFPP)Cl and Phl(OAc)₂ was performed in the presence of a small amount of H₂O (Table 2). In the hydroxylation of cyclooctane and cyclohexane, alcohols were yielded as the major products with the formation of small amounts of ketone products, although the efficiency of the alkane hydroxylation was not as good as that of the olefin epoxidation. The ratio of alcohol to ketone was ~7. By carrying out the hydroxylation of cis- and trans-stilbene, the alkane hydroxylations were found to be highly stereoselective with >99% retention; no formation of isomerized alcohol products (e.g. the formation of trans-1,2-dimethylcyclohexanol in the hydroxylation of cis-1,2-dimethylcyclohexanol) was observed [13]. The high alcohol to ketone ratio and the stereoselectivity that we have observed in the hydroxylation of alkanes by Fe(TPFPP)Cl and Phl(OAc)₂ are the typical results of alkane hydroxylations by iron porphyrin catalysts and PhIO [13a]. As a conclusion, Phl(OAc)₂ was found to be an efficient oxygen atom donor that affords high yields of oxygenated products in the presence of H₂O (Scheme 1).

Since we have observed a significant water effect on the rate of epoxide formation, we followed the time course of cyclohexene epoxidation by Fe(TPFPP)Cl and Phl(OAc)₂, by carrying out the reactions in the presence and absence of H₂O. The results in Fig. 1 show that the epoxidation proceeded rapidly in the presence of water and completed within 15 min, whereas a slow formation...
of cyclohexene oxide was observed when the reaction was carried out in the absence of water and the completion of the reaction took 5 h.\(^1\) The fast formation of cyclohexene oxide in the presence of H\(_2\)O is rationalized with the generation of PhIO by the reaction of PhI(OAc\(_2\)) and H\(_2\)O (Eq. (1)), and the in situ generated PhIO may react fast with the iron(III) porphyrin catalyst.\(^2\)

\[
\text{PhI(OAc)}_2 + \text{H}_2\text{O} \rightleftharpoons \text{PhIO} + 2\text{AcOH} \quad (1)
\]

Finally, when PhI(OAc\(_2\)) was reacted with Fe(TMP)(CF\(_3\)SO\(_3\)) \((\text{TMP} = \text{meso-tetramesitylporphyrinato dianion})\) at \(-40^\circ\text{C}\), the color of the reaction solution turned to green. The UV–Vis spectrum of the green solution showed a weak Soret band at 407 nm and broad absorption bands around 550–750 nm, characteristic of a typical oxoiron(IV) porphyrin cation radical complex (Supplementary material, Fig. S1).\(^3\) This result demonstrates that PhI(OAc\(_2\)) can be used as a single oxygen atom donor in generating oxoiron(IV) porphyrin cation radical intermediates (Eq. (2)).

\[
[\text{Fe}^{III}(\text{Porp})]^+ + \text{PhI(OAc)}_2 \rightarrow [(\text{Porp})^+ \cdot \text{Fe}^{IV} = \text{O}]^+ \quad (2)
\]

In summary, we have shown here that iodobenzene diacetate is an efficient oxidant that can be used as a single oxygen atom donor in iron(III) porphyrin-catalyzed oxygenation reactions and in generating oxoiron(IV) porphyrin cation radical intermediates. These results demonstrate that PhI(OAc\(_2\)) can substitute for polymeric PhIO in metal complex-mediated oxygenation reactions.

\(^1\) Although the rate of the epoxide formation was markedly influenced by the presence of water, the product yields and distributions were not affected by the presence and absence of H\(_2\)O.

\(^2\) When PhIO was used instead of PhI(OAc\(_2\)) in the epoxidation of cyclohexene, the epoxidation was completed within 15 min and the yield of the cyclohexene oxide product was the same as that obtained in the reaction of PhI(OAc\(_2\)). This result may support the formation of PhIO as an oxidant in the reaction of PhI(OAc\(_2\)) and H\(_2\)O.

\(^3\) We have shown recently that the reaction of Fe(TMP)(CF\(_3\)SO\(_3\)) with PhIO dissolved in CH\(_2\)OH generates an oxoiron(IV) porphyrin cation radical complex, [(TMP)]\(^+\) (please refer to Eq. (2) for (Porp) + Fe\(^{IV} = \text{O}\)]\(^+\): [14].

3. Experimental

3.1. Materials and methods

Dichloromethane (anhydrous) and acetonitrile (anhydrous) were obtained from Aldrich Chemical Co. and dried with CaH\(_2\) prior to use. All chemicals obtained from Aldrich were the best available purity and used without further purification unless otherwise indicated. PhIO was prepared from PhI(OAc\(_2\)) by a literature method [15]. Fe(TPFPP)Cl and Fe(TMP)Cl were purchased from Aldrich and Mid-Century Chemicals, respectively. Fe(TMP)(CF\(_3\)SO\(_3\)) was prepared by stirring equimolar amounts of Fe(TMP)Cl with AgCF\(_3\)SO\(_3\) followed by filtering through a 0.45-\(\mu\)M filter.

Product analyses for the epoxidation of \textit{cis}- and \textit{trans}-stilbene were performed on Orom Vintage 2000 HPLC equipped with a variable wavelength UV-200 detector. Detection was made at 215 and 254 nm. Products were separated on Waters Symmetry C18 reverse phase column (4.6 \(\times\) 250 mm). Product analyses for the epoxidation of cyclohexene, cyclooctene, 1-octene, and 1-hexene and for the hydroxylation of alkanes were performed with a Hewlett-Packard 5890 II Plus gas chromatograph equipped with a FID detector using 30-m capillary column (Hewlett-Packard, HP–5). UV–Vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer equipped with Optoscan\(^\text{TM}\) variable-temperature liquid-nitrogen cryostat (Oxford Instruments).

3.2. Catalytic oxygenation reactions

All reactions were run at least in duplicate, and the data reported represent the average of these reactions. Since the epoxidation and hydroxylation reactions were
not affected by molecular oxygen, all the reactions presented in this study were performed in air. In general, PhI(OAc)$_2$ (0.3 mmol for olefin epoxidations and 0.05 mmol for alkane hydroxylations) was added to a reaction solution containing Fe(TPFPP)Cl (1/C$_2$/10/C$_2$/3 mmol), H$_2$O (5 ml), and organic substrates (0.2 mmol) in a solvent mixture (0.5 ml) of CH$_2$Cl$_2$ and CH$_3$CN (1:1). The reaction mixture was stirred for 30 min at room temperature and directly analyzed by GC or HPLC. The yields of products were determined by comparison with standard curves prepared with known authentic samples. UV–Vis spectra of reaction solutions were taken before and after the addition of the oxidant to reaction solutions, in order to determine the degree of the destruction of the iron porphyrin catalyst.

4. Supplementary material

Figure S1 displaying UV–Vis spectra of Fe$^{III}$((TMP)(CF$_3$SO$_3$) and [(TMP)$^{+}$$^{+}\cdot$Fe$^{IV}$=O]$^{+}$ is available from the authors on request.

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