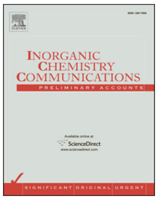
Inorganic Chemistry Communications 82 (2017) 27–30

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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



Short communication

Visible-light photolysis of corrole-manganese(IV) nitrites to generate corrole-manganese(V)-oxo complexes

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ARTICLE INFO

Article history:
Received 24 March 2017
Received in revised form 21 April 2017
Accepted 2 May 2017
Available online 10 May 2017

Keywords:
Manganese(V)-oxo
Corroles
Visible light
Oxidation
Kinetics

ABSTRACT

Photolysis of highly photo-labile corrole-manganese(IV) nitrites by visible light was studied in three corrole systems with different electronic environments. As observed in all three systems, homolytic cleavage of O—N bond of nitrite ligand resulted in one-electron photo-oxidation to generate manganese(V)-oxo corroles, as determined by their distinct UV–vis spectra and kinetic behaviors. The spectral and kinetic results are rationalized by a multiple oxidation model, where the electron-demand Mn^V-oxo species may serve as direct two-electron oxidant for oxygen atom transfer reactions and less electron-demand systems undergo a disproportionation reaction to form a putative manganese(VI)-oxo corrole as the true oxidant.

In enzymatic and synthetic catalytic oxidations, most commonly, a high-valent transition metal-oxo intermediate is formed as the active oxidant for oxygen atom transfer (OAT) reaction [1–4]. The spectroscopic detection and physical studies of the active metal-oxo transients, however, are still challenging in view of their high reactivities and/or low concentrations. Furthermore, a high valent metal-oxo species detected in a reaction might not be the true oxidant but a precursor to the true oxidant that is formed in small, undetectable amounts [5,6]. In this context, 19-membered metallocorroles have garnered considerable attention in their catalytic properties due to their similarity to metalloporphyrins [7–10]. In general, corrole-metal-oxo species are inherently more stable than the porphyrin-metal-oxo analogues because corrole ligands are trianionic as opposed to dianionic porphyrin ligands. For examples, the relatively stable and well-characterized manganese(V)-oxo corroles, abbreviated as Mn^V(Cor)O, serve as important mechanistic probes to understand metal-catalyzed oxidation reactions [11–13]. Electronic effects were found to be important factors in controlling the reactivity of Mn^V-oxo corroles. Gross and co-workers have suggested that highly electron-demanding corroles-manganese(V)-oxo species directly transfers oxygen atom, while relatively less electron-demanding corroles-manganese(V)-oxo complexes undergo disproportionation reaction to generate corrole-manganese(VI)-oxo as the active oxidant [14]. Our recent kinetic and spectral studies also illustrated that the photo-generated manganese(V)-oxo corroles may oxidize the substrate through different oxidation pathways, depending on the nature of corrole ligand and the solvent [15].

The first isolation and characterization of an electron-deficient corrole-manganese(V)-oxo complex by oxidation of Mn^{III} precursor with ozone was reported by Gross and co-workers [16]. Chang and co-workers also reported the synthesis of a perfluorinated and a very bulky Mn^V(Cor)O with chemical oxidants [17,18]. Later, lash flash photolysis producing corrole-manganese(V)-oxo species were achieved [19]. A significant advantage for forming the oxidizing metal-oxo species by photochemical rather than chemical methods is that the kinetics of the generated intermediates is not convoluted with the rate constants for formation of the reactive transients by reaction of the sacrificial oxidant with the low-valent metal species [20] In this regard, we have utilized photo-induced ligand cleavage reactions to produce a variety of *trans*-dioxoruthenium(VI) porphyrins [21,22] as well as the putative ruthenium(V)-oxo species [23]. Very recently, we communicated a photo-induced entry to iron(IV)-oxo porphyrin radical cations (compound I models) or iron(IV)-oxo porphyrin (compound II models) as controlled by the electronic nature of porphyrin ligands [24]. In this work, we report our ongoing progress in the development of a new phtoto-generation of manganese(V)-oxo corroles by visible light irradiation of manganese(IV) nitrite precursors in three corrole systems (Scheme 1).

As shown in Scheme 1, three corrole systems, 5,10,15-triphenylcorrole(TPC) [25], 5,10, 15-tris(4-trifluoromethylphenyl)corrole(4-CF$_3$TPC) [25] and 5,10, 15-tripentafluorophenyl corrole(TPFC) [26], were studied in this work. All three manganese(III) corroles including Mn^{III}(TPC) (**1a**), Mn^{III}(4-CF$_3$TFC) (**1b**) and Mn^{III}(TPFC) (**1c**) were known and synthesized according to the reported procedure [16,19].

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http://dx.doi.org/10.1016/j.inoche.2017.05.001
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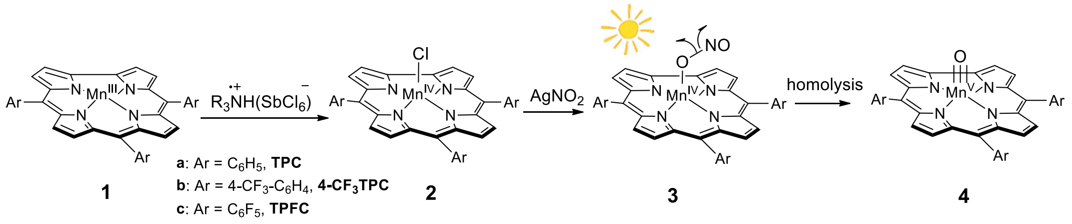

Scheme 1. Photochemical formation of corrole-manganese(V)-oxo complexes by visible light irradiation of corrole-manganese(IV) nitrites.

According to a known method described by Gross and co-workers, oxidation of the neutral triarylcorrole–manganese(III) species **1a** with tris(4-bromophenyl)ammoniumyl hexachloroantimonate gave the corrole–manganese(IV) chloride salts **2a** [11]. Facile exchange of the chloride counterion in **2a** with 1.5 equivalent of $AgNO_2$ gave the corresponding nitrite salt **3a** with a distinct observation of AgCl precipitate. The formation of **3a** was further indicated by the UV–vis spectra (Fig. 1A). These species **3** were highly photolabile and thus, immediately used for photochemical reactions after preparation.

Irradiation of nitrite complex **3a** in anaerobic CH_3CN with visible light from a SOLA engine (output power 60 W) resulted in formation of corrole-manganese(V)-oxo species **4a** (Fig. 1B). These time-resolved UV–vis absorption spectra show decay of photo-labile precursor (**3a**) and growth of the oxo product (**4a**) with clean isosbestic points at 316, 414,496 and 567 nm. As evident by UV–vis spectra, species **4a** displayed split Soret bands that are distinct with a strong blue-shifted from the Soret band of manganese(IV) nitrites, matching that from chemical oxidation of corresponding manganese(III) precursor **1a** (see Fig. S1 in the Supplementary material). The use of the non-coordinating solvents such as CH_2Cl_2 gave similar results (data not shown). However, no formation of **4a** was observed in CH_3OH solution. Clearly, the relatively weak nitrite ion bound to manganese metal can be readily disassociated by the strong coordinating solvent.

As expected, the transformation of **3a** to **4a** was more rapid using more intensive visible light (120 W). In a fashion similar to that described for the generation of **4a**, another sterically unhindered Mn^V(4-CF$_3$TPC)O (**4b**) and highly electron-demanding Mn^V(TPFC)O (**4c**) were also generated (see Fig. S2 and Fig. S3), demonstrating the generality of this photochemical method. It is noticed that the formation rate of species **4** follows TPC > 4-CF$_3$TPC > TPFC, reflected by the expected oxidation potential of corrole ligands. Control experiments showed that no species **4** was formed in the absence of light. As monitored by UV–vis spectroscopy, we did not observe significant photo-degradation of the complexes used in all studies under visible light irradiation.

The generation of the three manganese(V)-oxo species **4** upon visible light irradiation of nitrate **3** can be explained by photo-induced homolytic cleavage of O—N bonds in the nitrite counterion, which results in one-electron photo-oxidation reactions as expected. The same homolysis manifold was previously observed in porphyrin-Mn^{III}(ClO_3), corrole-Mn^{IV}(XO_3) and porphyrin-Ru^{IV}(XO_3)$_2$ (X = Cl and Br), which afforded manganese(IV)-oxo porphyrins, manganese(V)-oxo corroles and *trans*-dioxoruthenium(VI) porphyrins, respectively. For comparison under identical conditions, we found that photochemical cleavages of the nitrite complexes were considerably more efficient than cleavages of chlorate or bromate complexes to generate the corrole-manganese(V)-oxo species. In addition, manganese(IV) nitrites are much safer to handle as manganese(IV) bromates or chlorates are potentially explosive. Photolysis of porphyrin-manganese(III) nitrate complexes was reported to give manganese(IV)-oxo species by homolytic cleavage of an O—N bond [27]. However, we found that photolyses of corrole-manganese(IV) nitrate complexes did not afford the manganese(V)-oxo complexes **4** even with more intensive light and prolonged time.

Photochemical generation of corrole-manganese(V)-oxo species **4** permits direct kinetic studies of their oxidations. Of note, **4a** appeared to react with excess nitrite ions in solution, which gave a second-order rate constant of 55.6 ± 10 M^{-1} s^{-1} (2σ) (see Fig. S4), a larger rate constant than those with most organic substrates [15]. In self-decay reaction or in reactions with excess amounts of organic reductants such as thioanisole, the less electron-deficient species **4a** or **4b** regenerated a Mn^{IV} species, which was characterized by its known Soret band of λ_{max} at 430 nm (Fig. 2A and Fig. S5 in the Supplementary material). Consistent with previously reported studies [15,19], conversion from Mn^V(TPC)O (**4a**) to Mn-^{IV}(TPC) (**3a**) was shown not to be due to direct reaction of **4a** with organic substrate. In contrast, the electron-deficient **4c** returned to that of manganese(III) corrole **1c** with a characteristic Soret band of λ_{max} at

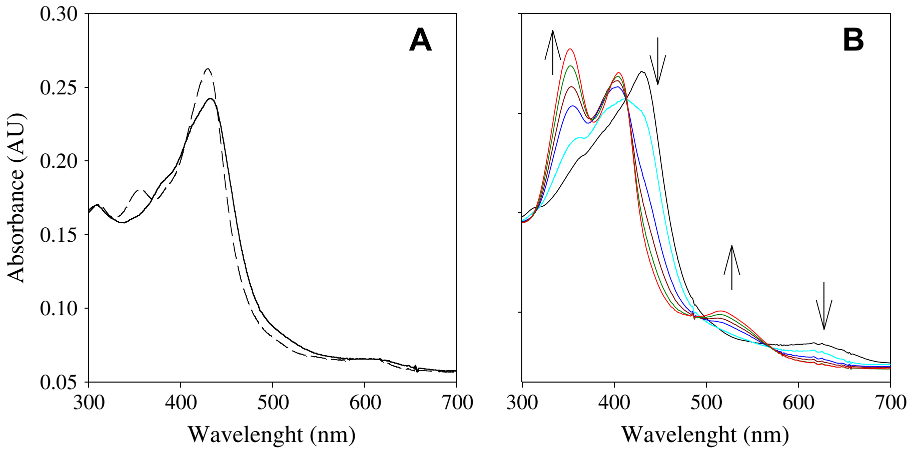

Fig. 1. (A) UV–vis spectra of Mn^{IV}(TPC)Cl (**2a**, dashed line) and Mn^{IV}(TPC)NO_2 (**3a**, solid line) in CH_3CN; (B) Time-resolved formation spectra of **4a** (red line) following irradiation of **3a** (ca. 3.0 × 10^{-6} M) with visible light in anaerobic CH_3CN solution over 8 s at 23 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)