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COMMUNICATION

Theoretical Studies Unveil the Unusual Bonding in Oxygenation Reactions Involving Cobalt(II)-Iodylarene Complexes

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DFT calculations reveal that the iodine of cobalt(II)-iodylarene complexes acts as a directing group via halogen bonding interaction to substrates. A transient 3c-4e bond is formed during oxidation reactions to decrease the activation energy by electron delocalization. Dihydrogenation of dihydroanthracene proceeds via a novel concerted hydride transfer/proton transfer mechanism.

Due to the advantages of environmentally benign hypervalent iodine complexes, especially ones containing iodine(III) and iodine(V), they are widely employed in biomimetic oxidation, as well as in organic and drug synthesis.¹⁻² The commonly used iodosylbenzene ((PhIO)_n, Scheme 1a), is a polymer insoluble in most organic solvents. Addition of acids, halogens or metal salts; however, make them soluble in organic solvents, such as acetonitrile, and enable to utilize them in oxidation reactions, by reacting it into stable iodine(III) complexes (examples see Scheme 1a).² Among these iodine(III) complexes, metal-iodosylarenes (M-PhIO) are commonly used as the precursor to generate high-valent metal-oxo oxidants.³ Recently, a debate on the one-oxidant versus the multiple-oxidant mechanism in M-PhIO chemistry was triggered as a hot issue in biomimetic chemistry. In particular, several studies implicated oxidative activity by the M-PhIO intermediate.⁴⁻⁷

Similarly to iodosylbenzene, the iodylbenzene ((PhIO₂)_n, Scheme 1b), is also an insoluble polymer in most solvents and can be used to generate high-valent oxidants.¹ Introducing substituents on the phenyl ring of PhIO₂ enables the formation of an intramolecular halogen bond to make the complexes hold

Scheme 1. Some representative (a) iodine (III) and (b) iodine(V) complexes, and (c) a proposed multiple-oxidant reaction mechanism for oxygenation mediated by metal-iodylarene complexes.

in a pseudocyclic (e.g. ^sPhIO₂) or a cyclic form (e.g. 2-iodylbenzoic acid (IBX)) that increases their solubility.² Introduction of metal complexes can convert them to metal-iodylarene adducts (M-PhIO₂) that are more reactive.⁸⁻⁹ As such, developments into the design of suspected new biomimetic M-PhIO₂ catalysts are actively ongoing.¹⁰⁻¹²

Barret and co-workers reported that by the combination of iodylbenzene and vanadium catalysts, aromatic amines were readily converted into quinone-imines under mild conditions.⁸ It was subsequently found by Zhdankin and co-workers that addition of Fe(III)-phthalocyanine to the IBX system led to the conversion of alcohols to their oxidized products, while a Co(II)-porphyrin complex did not show any significant activity.⁹⁻¹⁰ They attributed this catalyst selectivity to the formation of an iron(IV)-oxo species from the M-PhIO₂ precursors (Scheme 1c).¹⁰ Besides of a rate-limiting formation step of high valent metal-oxo intermediates, there is also a possibility that the metal-iodylarene adducts are directly involved in the oxidation or alter the reaction rates. Subsequently, Leung and co-workers reported the first X-ray structure of a lanthanide Ce(IV)-PhIO₂

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complex which exhibit robust reactivity in organic oxidation.¹¹ Very recently, a cobalt-iodylarene complex, namely $[\text{Co(II)Tp}^{\text{Bu}}(\text{}^5\text{PhIO}_2)]^+$ (Tp = hydrotris(pyrazolyl) borate and $\text{}^5\text{Ph}$ = 2-(tert-butylsulfonyl) phenyl) (**1**), was synthesized and crystallized by Anderson and his co-workers. The complex showed oxidative activity through sulfoxidation of thioanisole and dehydrogenation of 9,10-dihydroanthracene (DHA).¹² Further mechanistic studies supported a mechanism that the Co-PhIO₂ adduct, not the high-valent cobalt-oxo complex (Scheme 1c), is the most likely oxidant in the reactions although no technical details could be determined.¹² In particular, no cobalt(IV)-oxo intermediate could be trapped and characterized and kinetic isotope effects studies were inconclusive whether a potential cobalt(IV)-oxo species was involved in the reaction mechanism.

As little is known on the details of the mechanism and whether either a Co(IV)-oxo or a Co-PhIO₂ species is involved in the substrate activation, we decided to perform a comprehensive computational study of the elusive structure-activity relationship of **1**. Our results are consistent with the experimental observation that **1** is directly involved in reactivity. We also obtain some interesting mechanistic findings, namely that the metal-iodylarene (M-PhIO₂) chemistry is quite different to metal-iodosylarene (M-PhIO). In M-PhIO₂ chemistry, the iodine of metal-iodylarene complexes acts as a directing group via halogen bonding interaction to substrates. A transient three center-four electron bond (3c-4e bond) is formed in the transient T-shaped (metal)-O-I-O-(substrate) moiety of **1** during substrates approach, which decreases the activation energy by electron delocalization. To the best of our knowledge, these two mechanistic properties have not been reported in M-PhIO chemistry.

For **1**, the calculated ground state is the quartet spin state ($S = 3/2$), which is consistent with experimental observation.¹² Since the excited doublet/sextet states are higher in energy than $^4\text{1}$ by 20.9/26.9 kcal mol⁻¹, we will focus in the main text on the quartet spin state data only. For $^4\text{1}$ (Fig. 1a), key distances calculated are: Co-O1 at 1.971 Å, I-O1 of 1.851 Å and I-O2 of 1.788 Å. The I-O(SO₂) distance of the intramolecular halogen bond is 2.544 Å, while the angle of the O1-I-O2 moiety is 106.2°. Overall, the calculated geometry of **1** fits the experimental crystal structure well.¹² Cleavage of the I-O1 bond generates a Co(IV)-oxo complex **2** and a $^5\text{PhIO}$ complex requires more than 40.0 kcal mol⁻¹ in activation energy for **1** (Fig. S2, ESI). Therefore, this conversion is kinetically unfeasible and the active species is the Co-PhIO₂ species **1**, not the high-valent cobalt(IV)-oxo species.

The reactivity of **1** in thioanisole sulfoxidation is presented in Fig. 2. For the reagent complex state (^4RC), there are two halogen bonds (abbreviated to XB): one is the intramolecular I-O(sulfonyl) XB bond retained from $^5\text{PhIO}_2$, with a distance of 2.567 Å (Fig. S4, ESI), while the other is the intermolecular I-S(thioanisole) XB bond, with a distance of 3.114 Å. The iodine of **1** reserves a vacant position for binding of an electron-rich group of the substrate via a halogen bond. Thus, the iodine(V) core acts as a directing group during substrate binding. A reactant complex without such XB interaction (Fig. S8, ESI) lies

Fig. 1 (a) Key energetic and geometric information of **1** on the doublet/quartet/sextet spin state. Hydrogen atoms (except hydrogen of the H-B moiety) are omitted for clarity. Lengths are in Å units, angles are in degree units, and energies are in kcal mol⁻¹ units. (b) Schematic plot of the conversion of **1** to the high-valent Co(IV)-oxo species **2**. The dotted-lines denote halogen bonding.

5.2 kcal mol⁻¹ higher in energy than this RC. Such XB interaction anchors the substrate cis to the oxygen atom of **1**, with a distance of 3.383 Å. The sulfoxidation process proceeds via a direct oxygen-atom transfer mechanism, with an activation

Fig. 2 The energy profile (in kcal mol⁻¹) for sulfoxidation of thioanisole by **1** via a direct oxygen-atom transfer (DOT) mechanism. Energies were calculated at the UB3LYP-D3(BJ)/B2//B1+ZPE/B1 level in solvent. Geometric information of the transition state is presented. Hydrogen atoms (except hydrogen of the H-B moiety) are omitted for clarity. Lengths are in Å units, angles are in degree units, and the imaginary frequency is in cm⁻¹ units. The dotted-lines denote halogen bonding.

energy of 19.3 kcal mol⁻¹. For the transition state (^4TS), there are significant geometric changes in the cobalt-iodylarene moiety (Fig. S4, ESI), i.e., the O1-I-O2 angle increases dramatically from 102.9° for ^4RC to 136.5° for ^4TS , forming an approximate T-shaped O1-I(Ph)-O2 species. This growth of angle extends until the product complex (^4PC) is reached, where the O1-I-O2 angle is ca. 170.9° (Fig. S4 and S5, ESI). Comparison of the three representative Pmentel-Rundle molecular orbitals¹³ (the anti-,

Fig. 3 The representative Pmentel-Rundle MO depiction of 3c-4e bonds (a) in PIDA and (b) in the transition state of thioanisole oxidation by **1**.

Fig. 4 Energy profile (in kcal mol⁻¹) for anthracene formation in DHA oxidation by **1** via a concerted hydride transfer/proton transfer (HT/PT) mechanism. Energies were calculated at the UB3LYP-D3(BJ)/B2//B1+ZPE/B1 level in solvent. Geometric information of the transition states is presented. Hydrogen atoms (except hydrogen of the H-B moiety and hydrogen of the methylene group in DHA) are omitted for clarity. Lengths are in Å units, angles are in degree units, and the imaginary frequency is in cm⁻¹ units. The dotted-lines denote halogen bonding.

non-bonding, bonding ones) of phenyliodine diacetate (PIDA), a well-known molecule having 3c-4e bond (Fig. 3a), with the corresponding MOs of the transition state (Fig. 3b), we can see nearly identical shapes of the MOs. Thus, one 3c-4e bond is gradually formed during oxygen transfer. The delocalization effect of such bonds makes a difference to the reactivity, by reducing the barrier with ca. 18 kcal mol⁻¹ (the non-3c-4e activation barrier is ca. 38.0 kcal mol⁻¹, shown in Fig. S20, ESI). These interactions mimic the charge-donation effect by fluorinated alcohols on epoxidation reactions that were shown to enhance their reactivities.¹⁵

Fig. 5 Energy profiles (in kcal mol⁻¹) for (a) sulfoxidation of thioanisole and (b) hydroxylation of DHA by a ⁵PhIO₂ monomer with key geometric information of the transition states. Energies were calculated at the UB3LYP-D3(BJ)/B2//B1+ZPE/B1 level in solvent. Hydrogen atoms (except hydrogen of the methylene group in DHA) are omitted for clarity. Lengths are in Å units, angles are in degree units, and the imaginary frequencies are in cm⁻¹ units.

Fig. 4 shows energy profiles and key geometric information of transition states of dehydrogenation of DHA by **1**. The activation energy of the first C-H abstraction is 20.7 kcal mol⁻¹, which is much higher than the barrier of DHA oxidation (9.0 kcal mol⁻¹) by a high-valent Mn(V)-oxo complex.¹⁶ After the first C-H abstraction, a concerted second C-H abstraction of the other methylene group occurs and anthracene is formed after such desaturation process. Similar to thioanisole sulfoxidation, the phenyl ring of DHA forms a weak XB interaction with the iodine of the Co-iodylarene adduct **1** (at a distance of 3.373 Å, see Figure S14 in ESI). The O1-I-O2 angle changes dramatically from 102.9° in ⁴RC₁ to 137.9° in ⁴TS₁, forming also an approximate T-shaped O1-I(Ph)-O2 species. Such O1-I-O2 angle variation keeps rising to the product complex (⁴PC₁) state, where the angle is 175.3°. In addition, in the transition states the C-H-O1 angle is 163.1°/164.7°, which is more bent compared to the hydrogen atom abstraction transition states in P450 chemistry.¹⁴ Surprisingly, there is no spin density on H and the DHA-H moiety in ⁴TS₁ (Fig. S17, ESI), the Mulliken charges on the DHA-H group change from a negative value (ca. -0.17) in the reagent complex to a slightly positive one (ca. 0.14) in the ⁴TS₁, which means DHA-H is cationic. Unfortunately, we were not able to obtain the reaction intermediate of the first C-H bond activation as we

had in Cho's Mn-PhIO reaction system.¹⁷ However, in Cho's system, the DHA-H moiety holds similar small positive charge, and the spin is zero in the transition states, similar to the results obtained for Anderson's system. Thus, we can expect that the mechanism of dehydrogenation of DHA by **1** is similar to that in Cho's Mn-PhIO reaction system, namely an ionically concerted hydride transfer¹⁸⁻¹⁹/proton transfer (HT/PT) process.¹⁷ The earliest report we could find of hydride attack from DHA is the work by Buchanan where they found that when DHA was solvated in aprotic SbCl₃/AlCl₃, a novel hydride abstraction process occurred.²⁰ Mizuno reported in 2004 that Ru(OH)x/Al₂O₃ could efficiently catalyze the heterogeneous oxidative dehydrogenation of DHA via a hydride transfer to form a key ruthenium-hydride species.²¹ Hydride transfer has also been extensively found in oxidation of AcrHR (NADH analogues, 10-methyl-9,10-dihydroacridine) with metal-oxo complexes or metal-iodosylarene complexes.²²⁻²⁴ Other C-H oxidations via the hydride transfer mechanism were also proposed (reactions of [Fe^{IV}(O)(TPFP⁺)]⁺ with 1,3,5-cycloheptatriene,²⁵ C-H amination of xanthene with PhINTs,²⁶ methane activation by diatomic 3d transition-metal carbides,²⁷ etc.).

As a comparison, we performed a mechanistic study on sulfoxidation of thioanisole and dehydrogenation of DHA by an iodylarene monomer ^sPhIO₂. The two oxygen atoms in ^sPhIO₂ are inequivalent, i.e., the oxygen without XB interaction is more reactive than the oxygen atom (O2) with XB interaction (Fig. S22 and S25, ESI), thus in text we only present the more reactive O1-related data (Fig. 5). The activation energies of sulfoxidation of thioanisole and hydroxylation of DHA are 18.0 kcal mol⁻¹ and 24.4 kcal mol⁻¹, which is much higher in energy than those using an iodosylarene monomer (e.g., for ^sPhIO, barriers of thioanisole oxidation and DHA oxidation are 17.0 and 20.2 kcal mol⁻¹, respectively. See Fig. S32 and S34, ESI) and the metal-iodylarene adduct **1** as oxidants.^{6,19} In line with the oxidation reactions by **1**, the oxidation by ^sPhIO₂ is an ionic concerted 2e-oxidation, that is, sulfoxidation of thioanisole by ^sPhIO₂ is a direct oxygen-atom transfer process and hydroxylation of DHA is an ionically concerted hydride transfer/hydroxyl rebound process (Fig. S28, ESI).

In summary, we present the first theoretical study on the structure-reactivity relationship of metal-iodylarene (M-PhIO₂) complexes. We show that the system does not need to form a high-valent Co(IV)-oxo species, but instead the M-ArIO₂ species itself acts as the active oxidant in thioanisole sulfoxidation and C-H bond activation of substrates. The computed results presented above demonstrate that the metal-iodylarene (M-PhIO₂) chemistry is quite different to the metal-iodosylarene (M-PhIO). For M-PhIO₂ complexes two distinct functionalities are identified. Firstly, the iodine(V) atom of M-PhIO₂ acts as a directing group during substrate binding, via halogen bonding interaction to an electron-rich group of the substrates. Secondly, a 3c-4e bond is formed during oxidations, which reduces activation energies through a strong electron delocalization effect. During substrate approaching, such delocalized effect makes the O-I(Ph)-O moiety of M-PhIO₂

complexes gradually evolve to a T-shape, which might enhance the selectivity of the M-PhIO₂ complexes.

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Conflicts of interest

There are no conflicts to declare.

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