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Oxidation Catalysis via an Aerobically Generated Dess-Martin Periodinane Analogue

Asim Maity, Sung-Min Hyun, Alan K. Wortman, and David C. Powers*

Abstract: Hypervalent iodine(V) reagents, such as Dess-Martin periodinane (DMP) and 2-iodoxybenzoic acid (IBX), are broadly useful oxidants in chemical synthesis. Development of strategies to access these reagents from O_2 would immediately enable use of O_2 as a terminal oxidant in a broad array of substrate oxidation reactions. Recently we disclosed the aerobic synthesis of I(III) reagents by intercepting reactive oxidants generated during aldehyde autoxidation. Here, we couple aerobic oxidation of iodobenzenes with disproportionation of the initially generated I(III) compounds to generate I(V) reagents. The aerobically generated I(V) reagents oxidation chemistry analogous to that of DMP. Further, the developed aerobic generation of I(V) has enabled the first application of I(V) intermediates in aerobic oxidation catalysis.

O₂ is a conceptually ideal oxidant for synthesis ¹ but challenges, such as 1) the proclivity of O₂ to participate in unselective single-electron transfer chemistry, 2) the kinetic barriers associated with reaction of the triplet ground state of O2 with singlet organic molecules,² and 3) the difficulty in choreographing four-electron O₂ reduction with two-electron substrate oxidation, often prevent application of O₂ as a selective reagent in organic synthesis.³ In some cases, redox mediators - small molecules that participate in predictable oxidation chemistry with O2 - have enabled O2 reduction to be coupled to substrate oxidation chemistry. For example, the hydroquinone-quinone redox couple has been exploited to couple O2 reduction with a variety of Pd-catalyzed processes.⁴ In the absence of general strategies to utilize O₂ directly, an array of synthetic two-electron oxidants (i.e. hypervalent iodine reagents), which are not directly derived from O₂, have been developed. Generally, use of these reagents results in the formation of stoichiometric quantities of chemical waste. The need for more sustainable methods for oxidation chemistry demands the development of new strategies and methods for O₂ utilization.

We recently reported the aerobic oxidation of aryl iiodobenzenes (1) to iodosylbenzenes (2) using strong oxidants generated during aldehyde autoxidation and applied the aerobically generated I(III) reagents to olefin functionalization, carbonyl α -oxidation, and N–H arylation (Scheme 1).⁵ Contemporaneously, Miyamoto and Uchiyama *et al.* reported iodoarene-catalyzed aerobic glycol cleavage

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Scheme 1. Here, we show that rapid disproportionation of aerobically generated iodosylbenzenes can enable aerobic oxidation via iodylbenzene intermediates.

and Hofmann rearrangements under similar aldehydepromoted aerobic oxidation conditions.⁶ We reasoned that the scope of aerobic oxidation chemistry that can be achieved via hypervalent iodine intermediates would be substantially expanded if the aerobic oxidation of iodobenzenes could be extended to the synthesis of I(V) reagents (iodylbenzenes, 3).7 I(V) reagents,8 such as Dess-Martin periodinane (DMP)⁹ and 2-iodoxybenzoic acid (IBX),¹⁰ display complementary substrate oxidation chemistry as compared with iodosylbenzenes (2), and have been applied to the oxidation of primary and secondary alcohols,^{9,11} 1,2-¹² and 1,4-diols, ¹³ and amines, ¹⁴ as well as the dehydrogenation of carbonyl compounds to generate α , β unsaturated carbonyls,¹⁵ and benzylic C–H bond oxidation.¹ Currently, iodylbenzenes are prepared by the action of strong chemical oxidants, such as periodate, hypochlorite, dimethyldioxirane, or oxone, in stongly acidic conditions, 8f,17 by the metal-catalyzed ¹⁸ or high-temperature ¹⁹ or disproportionation of iodosylbenzenes. The harsh reaction conditions and strong oxidants typically employed in the synthesis of I(V) reagents limit the utility of I(V) intermediates in catalysis.²⁰ Here we demonstrate that aerobic oxidation of I(I) to generate I(III) compounds can be coupled with facile disproportionation of I(III) to enable oxidation catalysis via iodylbenzene intermediates.

During our initial investigation of the aerobic oxidation of iodobenzenes (1) to iodosylbenzenes (2), we noted that oxidation of 2-(tert-butylsulfonyl)iodobenzene (1a) afforded iodylbenzene 3a, not the corresponding I(III) derivative 2a.5,21 Chelating substitutents in the 2-position are frequently employed in hypervalent iodine chemistry to enhance solubility by breaking up I–O–I–O polymers that are common for iodosylbenzenes.²² With interest in developing aerobic synthesis of soluble I(V) reagents, we have investigated the aerobic oxidation of a family of iodobenzenes bearing potentially chelating substituents in the 2-position (Scheme 2). In order to achieve reproducible aerobic oxidation chemistry, these investigations were carried out in the presence of CoCl₂ (1 mol%), which serves as an initiator of aldehyde autoxidation^{5,23} (see Figures S1 and S2). Oxidation of 2-tertbutylsulfonyl-, 2-nitro-, and 2-(2'-pyridyl)iodobenzene (1a-1c)

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Scheme 2. Aldehyde-promoted aerobic oxidation can provide access to a variety of iodylbenzene derivatives.

with O_2 in the presence of acetaldehyde afforded iodylbenzenes **3a–3c** in good yield. Attempts to generate IBX by aerobic oxidation of 2-iodobenzoic acid (**1d**) have not been productive; I(III) derivative **2d** is the exclusive product of aerobic oxidation. We have also examined the aerobic oxidation of iodobenzene derivatives bearing substituents at the 3- or 4-positions. While iodosylbenzenes **2e–2i** are obtained by aldehyde-promoted aerobic oxidation of iodobenzenes **1e–1i** in AcOH,⁵ at long reaction times in dichloroethane (DCE) or nitromethane, iodylbenzenes **3e–3i** are obtained.

With a family of aerobically generated iodylbenzenes in hand, we turned our attention to characterizing the reactivity profile of these reagents towards substrate oxidations typical of IBX and DMP (Scheme 3). Treatment of cyclohexanol with iodylbenzene 3a in CH₃NO₂ at 70 °C affords cyclohexanone in 95% yield (Scheme 3a; see Table S1 for optimization details). In comparison, iodylbenzenes 3b and 3e were found to be less efficient reagents for cyclohexanol oxidation (0% and 66% yield of cyclohexanone, respectively). While 3a efficiently oxidizes secondary alcohols, it does not effect the dehydrogenation of the resulting carbonyl compounds to generate α,β -unsaturated carbonyls: addition of excess **3a** to the oxidation of cyclohexanol or treatment of cyclohexanone with 3a did not result in dehydrogenation to afford 2cyclohexenone, even in the presence of additives, such as DMSO or N-oxides, which have previously been used to promote I(V)-mediated desaturation chemistry.^{15b} Treatment of primary alcohols, such as benzyl alcohol (6a) and geraniol (6b) resulted in the corresponding aldehydes 7a and 7b in 99% and 81% yield, respectively (Scheme 3b). Compound 3a effects oxidative cleavage of 1,2-diols - oxidation of hydroxybenzoin (8) with 3a results in oxidative C-C cleavage to generate benzaldehyde in 86% yield (Scheme 3c) which is characteristic of the chemistry of DMP.¹² In contrast, IBX typically provides access to dicarbonyls.²⁴ 3a effects the oxidation of 1,4-diol 10 to lactone 11 in 60% yield, based on recovered starting materials. Compound 3a does not

a. Oxidation of Secondary Alcohols



Scheme 3. Aerobically generated iodylbenzene reagent **3a** a. oxidizes secondary alcohols to ketones, b. primary alcohols to aldehydes, c. mediates glycol cleavage to aldehydes, oxidizes 1,4-diols to lactols, and d. accomplishes dehydrogenative amine oxidation. ⁱyield based on recovered starting material.

promote benzylic C–H oxidation (*i.e.* oxidation of ethylbenzene), which has been observed for some I(V) derivatives, but **3a** can be applied to the oxidative dehydrogenation of amines to generate imines (**13a** and **13b**), oximes (**13c**), and *N*-heterocycles (**13d**) (Scheme 3d).

lodylbenzene-mediated oxidation reactions typically rely on stoichiometric amounts of I(V) reagents.²⁰ Based on the dual hypotheses that the strong oxidants (*i.e.* oxone) typically needed to generate I(V) derivatives limit application of I(V) derivatives in catalysis, and that facile disproportionation of **2a** provides ready access to I(V) derivative **3a**, we turned our attention to the application of iodylbenzene intermediates (*i.e.* **3a**) in aerobic oxidation catalysis (Scheme 4). In order to accomplish *in situ* aerobic oxidation at the elevated temperatures required for substrate oxidation (70 °C), acetaldehyde (b.p. = 20 °C) was replaced with *n*-butyraldehyde (b.p. = 75 °C). Examination of catalyst loading led us to pursue the following experiments with 15 mol% **1a** as catalyst. With 15 mol% **1a**, cyclohexanol

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b. Oxidation of Primary Alcohols



Scheme 4 Aerobic oxidation secondary alcohols catalyzed by 3a provides access to a wide variety of ketones. Application of 3a-catalysis to the oxidation of primary alcohols and 1,2-diols results in the formation of carboxylic acids and oxidation of oxidation of 1,4-diols affords lactones. The overoxidation in the catalytic reaction arises from autoxidation of the initially formed products under the aerobic conditions. PrCHO = *n*-butryaldehyde.

oxidation proceeds in 86% yield (see Table S1 for optimization experiments). Alcohol oxidation catalysis can be achieved using air in place of pure O_2 ; using air, cyclohexanol oxidation is accomplished in 66% yield. In the absence of **1a**, 15% yield of cyclohexanone was obtained, which arises from background Co(II)-catalyzed alcohol oxidation²⁵ (see Table S2 for background reactions for all substrates reported).

Using 3a as catalyst, we have investigated the oxidation chemistry of a series of secondary alcohols (Scheme 4a). Substituted aryl and heteroaryl ethanols participate in alcohol oxidation to afford the corresponding acetophenone derivatives (5b-5l). Of particular note, electron deficient (i.e. 5e and 5g) and electron-rich (i.e. 5d, 5j, and 5l) derivatives are tolerated, as well as heteroaryl substituents (5i). Oxidation of methoxy-substituted alcohol 4f affords acetophenone derivative 5f in low yield, which may be due to background reaction of weak C-H bonds with reactive oxidants in aldehyde autoxidation. Oxidation of aliphatic alcohols also generates ketones: cyclopentanone (5m), cyclohexanone (5a), cycloheptanone (5n), and 2hexanone (50) are all accessed by oxidation of the corresponding alcohol. α, α -Disubstituted acetophenone **5k** was accessed in 64% yield, but the presence of larger α substituents results in dimished oxidation efficiency (*i.e.* α, α diphenyl ketone 5p is generated in 33% yield). Oxidation of benzoin (4q), an α -hydroxycarbonyl, affords dicarbonyl 5q in 60% yield. Olefinic substrates are tolerated in the aerobic oxidation catalysis. As examples, 2-cyclohexenone (5r) is generated from the oxidation of 2-cyclohexenol (4r) and cholesterol (4s) participates in aerobic oxidation to afford 5s in 57% yield.

Application of the optimized reaction conditions to iodoarene-catalyzed oxidation of primary alcohols results in the formation of carboxylic acids (Scheme 4b). Benzyl alcohols 6a and 6c, heteroaromatic benzyl alcohol 6d, as well as long-chain aliphatic alcohols 6e and 6f participate in aerobic oxidation to afford the corresponding carboxylic acids in good yield. The observation of carboxylic acids in catalytic reactions, but aldehydes in stoichiometric reactions, is likely due to the initial oxidation of primary alcohol to the aldehyde, followed by corresponding subsequent autoxidation to the carboxylic acid under the reaction conditions used to generate iodylbenzenes. The reactive intermediates of autoxidation also likely interfere with application of the developed aerobic oxidation catalysis to geraniol (6b); exposure of 6b to the developed catalytic conditions results in a mixture of products. lodylbenzene catalyzed aerobic oxidation of 1,2-diol 8 affords benzoic acid in 79% yield and oxidation of 1,4-diol 10 generates lactone 11 in 73% yield (Schemes 4c and 4d).

We propose that substrate oxidation proceeds via the catalytic cycles pictured in Scheme 5a. Initial oxidation of aryliodide **1a** generates iodosylbenzene **2a**. Facile disproportionation of **2a** generates equimolar quantities of **1a** and **3a**. Substrate oxidation by **3a** generates **2a**, which, following disproportionation, affords **1a** that is poised to participate in subsequent aldehyde-promoted aerobic oxidation. The critical role of I(V) intermediates in substrate oxidation chemistry is evidenced by comparison of the chemistry of iodosylbenzenes that participate in facile disproportionation with those that do not rapidly disproportionate. Iodosylbenzene **2a** participates in facile disproportionation: *in situ* monitoring of the oxidation of **1a** by

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Scheme 5. a. Proposed catalytic cycle for iodylbenzene-catalyzed aerobic oxidation. b. Disproportionation of both 2a and 2e are thermodynamically preferred. Experimentally, 2a is observed to participate in rapid disproportionation whereas 2e is indefinitely stable.

¹H NMR revealed the consumption of aryliodide 1a and evolution of iodylbenzene 3a without the intermediacy of observable iodosylbenzene 2a (Figure S3). In addition, subjecting a solution of independently prepared 2a to AcOH, which is generated during autoxidation, results in the immediate disproportionation to **1a** and **3a** (Figure 5b; for ¹H NMR spectrum, see Figure S4). Density Functional Theory (DFT) calculations — carried out with the M06-2X functional²⁶ (basis sets: LANL2DZ²⁷ for I, 6-31G(d,p)²⁸ for other atoms) and the SMD solvation model 29 - indicate that disproportionation of 2a to generate 1a and 3a is thermodynamically favored ($\Delta G = -8.8$ kcal/mol; see Supporting Information for computational details). In contrast to 2a, iodosylbenzene 2e does not participate in facile disproportionation: in situ monitoring of the oxidation of 1e by ¹H NMR spectroscopy indicates that initial oxidation affords I(III)-derivative 2e, which subsequently converts to I(V) derivative **3e** slowly (Figure S5). Despite beina thermodynamically favorable (calculated $\Delta G = -18.1$ kcal/mol), treatment of independently synthesized 2e with AcOH resulted in no observed disproportionation (Figure 5b). While independently prepared 3e effects oxidation of cyclohexanol in 66% yield, 1e (which generates 2e, an iodosylbenzene derivative that does not rapidly disproportionate) is an ineffective oxidation catalyst (24% yield for oxidation, for comparison, Co-catalyzed background provides 15% yield). These data indicate that when facile disproportionation of I(III) is not available, the efficiency of aerobic oxidation catalysis is significantly compromised.

In conclusion, here we have reported the first aerobically generated I(V) reagents that participate in substrate oxidation chemistry. By coupling aerobic oxidation

of I(I) to I(III) with facile disproportionation of the initially formed I(III) reagents, efficient access to I(V) is accomplished. The I(V) reagent generated in this protocol is functionally analogous to DMP, and provides a platform to couple O2 reduction with oxidation of alcohols, diols, and amines. In situ generation of iodylbenzene intermediates supports aerobic oxidation catalysis and we have demonstrated that efficient catalysis requires access to the I(V) oxidation state. These studies add to the growing field of aerobically generated oxidants that underpin development of sustainable oxidation chemistry. We anticipate that development of new strategies to couple O₂ reduction to iodobenzene oxidation without the intermediacy of reactive aldehyde autoxidation intermediates will engender broadly applicable hypervalent-iodinecatalyzed aerobic oxidation chemistry.

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Keywords: aerobic oxidation • hypervalent iodine • sustainable • autoxidation

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