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An *in situ* acidic carbon dioxide/glycol system for aerobic oxidative iodination of electron-rich aromatics catalyzed by $Fe(NO_3)_3·9H_2O$†

Ran Ma, Cheng-Bin Huang, An-Hua Liu, Xue-Dong Li and Liang-Nian He*

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An environmentally benign CO_2/glycol reversible acidic system was developed for the iron(III)-catalyzed aerobic oxidative iodination of electron-rich aromatics without the need for any conventional acid additive or organic solvent. Notably, moderate to high isolated yields (up to 97%) of the aryl iodides were attained with comparable regioselectivity when ferric nitrate nonahydrate was used as the catalyst with molecular iodine under 1 MPa of CO_2.

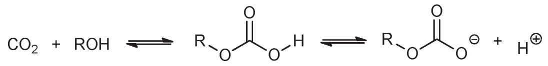
Introduction

Aryl iodides are important synthetic intermediates and precursors in organic transformation which could undergo oxidative addition, and thus are subject to a variety of carbon–carbon and carbon–heteroatom bond formation reactions, such as Negishi,[1] Suzuki,[2] Stille,[3] and Buchwald–Hartwig coupling.[4] Meanwhile, iodoarenes are prevalent building blocks of biologically active molecules, including drugs, pesticides and fungicides,[5] as well as radiocontrast agents for medical X-ray examinations.[6] Due to the significant and versatile properties of iodinated aromatics, great efforts have been devoted to optimize their preparation methods across the field of scientific research and industrial manufacture.[7] The well-established Sandmeyer reaction is among the most efficient methodologies for the construction of aryl iodides,[8] while electrophilic substitution of aromatics with molecular iodine or iodide anions is confronted with the problem of low reactivity. Although iodination protocols using the pre-synthesized iodonium species, such as NIS,[9] ICl,[10] *N*-iodosaccharin,[11] IPy_2BF_4 (ref. 12) and HIO_4,[13] could be possible solutions to this circumstance, its restriction to highly activated arenes remains a challenge.

Oxidative iodination, which requires the combination of molecular iodine/metal iodide with an appropriate oxidant and, in many cases, a catalyst, emerges to be a promising approach that can overcome the limitation caused by the employment of iodonium reagent.[14] Although it offers advantages in terms of high efficiency, good selectivity and wide substrate scope, oxidative iodination is often promoted by Brønsted acids as solvents or additives, such as H_2SO_4,[14b,c,i,j] AcOH[14f,g] and TFA,[14l] which are generally corrosive and require post-reaction neutralization and salt waste disposal.

The reversible reaction of CO_2 and alcohols could yield alkylcarbonic acids, temporarily generated proton-donating species which could serve as acid catalysts and be inherently neutralized by readily removing CO_2, thus resulting in simple neutralization without the need for waste disposal (Scheme 1). Notably, CO_2 is considered as an abundant, non-toxic and easily available C1 resource[15] as well as an ideal reaction environment for aerobic oxidation[16] which could render such self-neutralizing *in situ* acid catalysts sustainable, renewable and safe. The self-neutralizing acid catalysis derived from CO_2 has been applied to many approaches, with profound advantages for both green chemistry and improved economics.[17]

We have exploited two *in situ* acidic systems, *i.e.* $scCO_2$/ethanol and $scCO_2/H_2O$, as reversible acidic media for copper-catalyzed aerobic oxybromination of aromatic ethers and sulfides, respectively.[18] Moreover, based on the understanding of reversible acidic catalysis as well as the advances in catalytic oxidative iodination, we believe that *in situ* alkylcarbonic acids derived from CO_2 and ROH could also promote the iodination reaction as both a proton donor and a reaction accelerant, thus offering an alternative chemical methodology for the synthesis of aryl iodides. In this article, we would like to present ferric nitrate nonahydrate-catalyzed aerobic oxidative iodination of electron-rich aromatics in a CO_2/glycol system with molecular iodine, as shown in



Scheme 1 *In situ* formation of alkylcarbonic acids.

State Key Laboratory and Institute of Elemento-Organic Chemistry, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin, 300071, PR China. E-mail: heln@nankai.edu.cn

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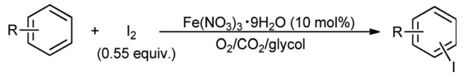


Scheme 2 Aerobic oxidative iodination of electron-rich aromatics.

Scheme 2. Comparable yields and regioselectivities along with facilitated post-processing of reaction were achieved by the introduction of CO_2 and glycol, providing a meaningful example of the beneficial utilization of the greenhouse gas in the production of fine chemicals. Furthermore, such an approach becomes especially attractive because iron was employed as the catalyst with profound environmental and economic advantages.[19]

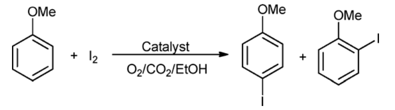
Results and discussion

As an extension of our interest in the utilization of reversible alkylcarbonic acids as alternative and benign surrogates for Brønsted acids, we initially set out to explore the aerobic oxidative iodination of anisole (**1a**), which holds two possible reaction sites, in the CO_2/EtOH system. Accordingly, treatment of anisole with $Fe(NO_3)_3·9H_2O$ (10 mol%) gave a monoiodinated product in 74% yield under the tentative reaction conditions (1 MPa of O_2, 0.1 mL of EtOH, 0.55 equiv. of I_2) with the aid of 1 MPa of CO_2 (entry 1, Table 1). Notably, the molar ratio of the *p*-isomer to the *o*-isomer reached as high as 95 : 5. The absence of CO_2 obviously led to a lower oxidative iodination yield (entry 2). Subsequently, further investigation was carried out to study the catalytic activity for iodination of anisole. As summarized in Table 1, several iron catalysts with different anions were screened and none exhibited a superior reactivity to that of $Fe(NO_3)_3·9H_2O$ (entries 3–6). Two copper salts that had been demonstrated to have excellent reactivity toward oxybromination were also examined, but were less active than their iron counterparts (entries 7–8). The use of the oxidative properties of sodium tungstate and phosphotungstate failed to deliver comparable yields of iodoanisole (entries 9–10). As a consequence, $Fe(NO_3)_3·9H_2O$ was selected as the most efficient catalyst with the best regioselectivity among the metal salts examined and was employed for further optimization.

In the second stage, various reaction parameters were systematically optimized to further enhance the reactivity of iodination, and the results are depicted in Table 2. Firstly, 2 atm of oxygen was found to be adequate to obtain an acceptable yield of *p*-iodoanisole (entry 2 *vs.* 1), and a moderate yield could be obtained in the case of air as the terminal oxidant (entry 3). Meanwhile, as the formation of alkylcarbonic acids had been proven to be vital for the high efficient oxidative iodination (entry 1 *vs.* entry 2, Table 1), the influence of CO_2 pressure was then studied. As expected, without the participation of CO_2, the reaction was restrained (entry 4). Elevating the pressure of CO_2 from 1 MPa also depressed the reactivity of iodination (entries 5–6), in contrast to the previous reports that the acidity of *in situ* acids derived from CO_2 is enhanced by increasing the pressure of CO_2.[18,20] Such phenomena might be explained by the dilution effect of 2 atm of O_2 on dense CO_2.

Beyond the influence of CO_2, the actual proton donor, *i.e.* the alcohols, could also play a crucial role in the formation of *in situ* acids. It was found that slightly increasing or decreasing the amount of ethanol just led to a decrease in yield (entries 7–8). Consequently, the structure of ROH was optimized to evaluate its activity toward the generation of alkylcarbonic acids. While methanol, *n*-propanol and even water did not promote the reaction better than ethanol (entries 9–11), ethylene glycol fulfilled our mission by improving the total yield of iodoanisole to above 95% (entry 12). The introduction of glycerol as a proton donor failed to further enhance the reactivity, probably due to its high

Table 1 Oxidative iodination of anisole in the CO_2/O_2/EtOH system[a]



Entry	Catalyst	CO_2 (MPa)	Yield[b] (%)	
			p-Isomer[c]	*o*-Isomer[d]
1	$Fe(NO_3)_3·9H_2O$	1	70	4
2	$Fe(NO_3)_3·9H_2O$	0	48	3
3	$FeCl_3·6H_2O$	1	59	4
4	$FeCl_2·4H_2O$	1	49	4
5	$Fe(acac)_3$	1	3	Trace
6	Fe_3O_4	1	18	Trace
7	$CuCl_2·2H_2O$	1	22	2
8	$Cu(NO_3)_2·3H_2O$	1	30	2
9	$Na_2WO_4·2H_2O$	1	13	Trace
10	$Na_2PO_4·WO_3$	1	10	Trace

[a] Reaction conditions: catalyst (10 mol%), I_2 (0.55 equiv.), EtOH (0.1 mL), O_2 (1 MPa), 100 °C, 10 h. [b] Determined by GC with biphenyl as the internal standard. [c] Yield of *p*-iodoanisole. [d] Yield of *o*-iodoanisole.

Table 2 Optimization of various reaction parameters[a]

Entry	CO_2 (MPa)	O_2 (MPa)	ROH	Yield[b] (%)	
				p-Isomer[c]	*o*-Isomer[d]
1	1	1	EtOH	70	4
2	1	0.2	EtOH	62	3
3[e]	1	—	EtOH	39	2
4	0	0.2	EtOH	45	2
5	2	0.2	EtOH	57	3
6	4	0.2	EtOH	53	3
7[f]	1	0.2	EtOH	61	2
8[g]	1	0.2	EtOH	46	2
9	1	0.2	H_2O	53	4
10	1	0.2	MeOH	39	2
11	1	0.2	*n*-PrOH	58	3
12	1	0.2	Glycol	91	6
13	1	0.2	Glycerol	49	2
14[h]	1	0.2	Glycol	81	5

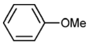
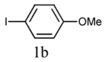
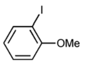
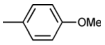
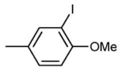
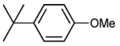
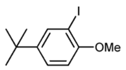
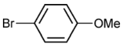
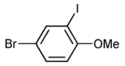
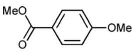
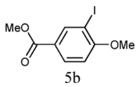
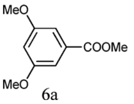
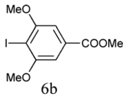
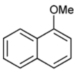
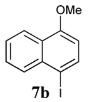
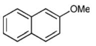
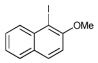
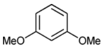
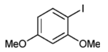
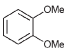
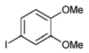
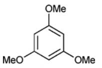
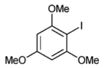
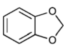
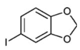
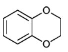
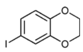
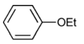
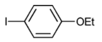
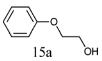
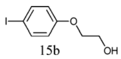
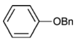
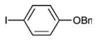
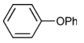
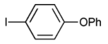
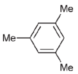
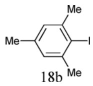
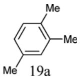
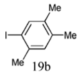
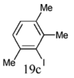
[a] Reaction conditions: $Fe(NO_3)_3·9H_2O$ (10 mol%), I_2 (0.55 equiv.), ROH (0.1 mL), 100 °C, 10 h. [b] Determined by GC with biphenyl as the internal standard. [c] Yield of *p*-iodoanisole. [d] Yield of *o*-iodoanisole. [e] Air as the oxidant. [f] EtOH, 0.075 mL. [g] EtOH, 0.125 mL. [h] $Fe(NO_3)_3·9H_2O$ (5 mol%).

viscosity and low solubility (entry 13). As the attempt to reduce the catalyst loading turned out to be ineffective (entry 14), the reaction conditions were eventually settled as $Fe(NO_3)_3{\cdot}9H_2O$ 10 mol%, I_2 0.55 equiv., ethylene glycol 0.1 mL, O_2 0.2 MPa, CO_2 1 MPa, 100 °C, 10 h.

With the optimal reaction conditions in hand, the generality and feasibility of the present protocol were demonstrated by performing oxidative iodination with a broad range of electron-rich aromatics (Table 3). The *para* substituent group on anisole caused the reaction to occur at the *ortho* position (entries 2–5), and the electron-withdrawing group suppressed the iodination reactivity (entries 4–5). By attaching an additional methoxy group to the electron-deficient aromatic ring, the reaction proceeded a bit more readily (entry 6 *vs.* 5). Naphthalene methyl ethers are popular substrates in the present system as well (entries 7–8). Mono-, di- and trimethoxy-substituted benzenes underwent oxidative iodination smoothly with moderate to good yields, but disubstitution occurred in all cases (entries 9–11). Benzodioxole (**12a**) was found to decompose under the standard reaction conditions (entry 12) and, as a result, the yield of its iodide was far less than that of the analogous benzodioxane (**13a**) (entry 13). Other aromatic ethers also proved to be competent in the promotion of alkylcarbonic acid formation, as ethyl-, 2-hydroxyethyl-, phenyl-, benzyl-derived phenyl ethers reacted smoothly, resulting in good yields of *para*-iodinated products (entries 14–17). To our delight, alkylbenzenes were successfully used as substrates for iodination, indicating the versatility of the present approach. Mesitylene (**17a**) could be transformed into a monoiodinated product in 84% isolated yield (entry 18), but 1,2,4-trimethylbenzene (**18a**) gave an inseparable mixture of two regioisomers (entry 19).

A plausible reaction pathway was proposed for the iron-catalyzed oxidative iodination of electron-rich aromatics on the basis of the experimental results of this study and previous reports. The proposed mechanism is depicted in Scheme 3. Dissociation of the *in situ* alkylcarbonic acid produced from CO_2 and ethylene glycol could release protons, which would be crucial for the reaction [eqn (1)]. I_2 is oxidized by NO_3^- in the presence of H^+ [eqn (2)]. Then, the tentative intermediate NO is reoxidized to NO^+ in the presence of oxygen as presented by eqn (3), which then oxidizes another I_2 to I^+ [eqn (4)]. However, I^+, as a kinetically independent species in a strongly acidic media, is difficult to rationalize in this proposed mechanism. In addition, the effect of ferric iron needs further exploration and study.

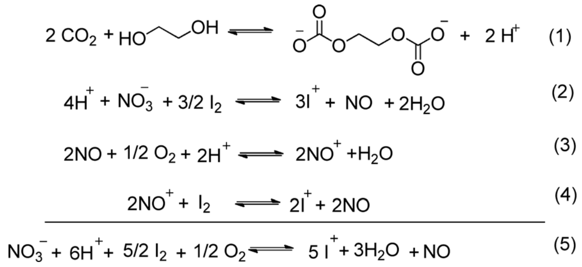
Table 3 Substrate scope[a]

Entry	Substrate	Product	Yield[b] (%)
1[c]	 1a	 1b  1c	97
2	 2a	 2b	78
3	 3a	 3b	89
4[d]	 4a	 4b	72
5[e]	 5a	 5b	47
6[f]	 6a	 6b	40
7	 7a	 7b	77
8	 8a	 8b	82
9	 9a	 9b	83
10	 10a	 10b	81
11	 11a	 11b	62
12	 12a	 12b	17
13	 13a	 13b	86
14	 14a	 14b	85
15	 15a	 15b	81
16[f]	 16a	 16b	80
17[g]	 17a	 17b	73
18[h]	 18a	 18b	84
19[i]	 19a	 19b  19c	64

[a] Reaction conditions: substrate (1 mmol), $Fe(NO_3)_3{\cdot}9H_2O$ (10 mol%), I_2 (0.55 equiv.), ethylene glycol (0.1 mL), CO_2 (1 MPa), O_2 (0.2 MPa), 100 °C, 10 h. [b] Isolated yield. [c] A mixture of two regioisomers (**1b** : **1c** = 91 : 6). [d] $Fe(NO_3)_3{\cdot}9H_2O$ (50 mol%), 15 h. [e] $Fe(NO_3)_3{\cdot}9H_2O$ (50 mol%). [f] $Fe(NO_3)_3{\cdot}9H_2O$ (20 mol%). [g] $Fe(NO_3)_3{\cdot}9H_2O$ (30 mol%). [h] I_2 (0.75 equiv.). [i] $Fe(NO_3)_3{\cdot}9H_2O$ (30 mol%), a mixture of two regioisomers (**19b** : **19c** = 92 : 8).

Conclusions

In summary, we have performed efficient iron-catalyzed oxidative iodination of electron-rich aromatics under aerobic conditions with the aid of an *in situ* acidic CO_2/glycol system. This methodology affords monoiodinated aromatics in up to 97% isolated yields without any corrosive acid additive or organic solvent. The present protocol represents an attractive



Scheme 3 The proposed mechanism for oxidative iodination.

green approach which offers high iodine atom economy, simple post-reaction neutralization with no salt waste disposal and safe operation for aerobic reaction. The reaction showed a remarkably broad substrate scope including mesitylene.

Experimental

Materials and methods

The aromatic ethers were purchased from Alfa Aesar China Co., Ltd and Aladdin Reagent Inc. The other reagents were obtained commercially from the Tianjin Guangfu Fine Chemical Research Institute and used without further purification except for the alcohols, which were distilled according to a documented method prior to use. ^{1}H NMR spectra were recorded using a Bruker 400 spectrometer in $CDCl_3$; $CDCl_3$ (7.26 ppm) was used as the internal reference. ^{13}C NMR spectra were recorded at 100.6 MHz in $CDCl_3$; $CDCl_3$ (77.0 ppm) was used as the internal reference. GC-MS data were collected on a Finnigan HP G1800 A. GC analyses were performed with a Shimadzu GC-2014 equipped with a capillary column (RTX-17, 30 m × 0.25 μm) using a flame ionization detector.

Safety warning

Experiments with large amounts of compressed gases, especially molecular oxygen and CO_2, are potentially hazardous and must only be carried out by using the appropriate equipment and under rigorous safety precautions.

General procedure for oxidative iodination of aromatics

A mixture of the substrate (1 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (40.4 mg, 10 mol%), I_2 (139.6 mg, 0.55 equiv.), and 0.1 mL of ethylene glycol was placed in a 50 mL stainless steel autoclave equipped with an inner glass tube at room temperature. CO_2 (0.5 MPa) and O_2 (0.2 MPa) were subsequently introduced to the autoclave and the system was heated under the predetermined reaction temperature for 15 min to reach equilibrium. Then the final pressure was adjusted to the desired pressure by introducing the appropriate amount of CO_2. The mixture was stirred continuously for the desired reaction time. After cooling, the mixture was diluted with dichloromethane and analyzed by GC. Then, the mixture was concentrated by removing the solvent under vacuum. The residue was purified by column chromatography on silica gel (200–300 mesh, eluting with *n*-hexane/ethyl acetate from pure *n*-hexane to 50 : 1) to afford the desired product. The isolated products were further identified by their NMR and GC-MS spectra, which are consistent with those reported in the literature.

Characterization data for the representative products

1-Iodo-4-methoxybenzene (1b)[21]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 3 H), 6.61–6.74 (m, 2 H), 7.48–7.65 (m, 2 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 55.3, 82.7, 116.3, 138.2, 159.4. GC-MS: *m*/*z* (%): 233.95 (100) $[M]^+$.

2-Iodo-1-methoxy-4-methylbenzene (2b)[22]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 3 H), 3.85 (s, 3 H), 6.72 (d, *J* = 8.3 Hz, 1 H), 7.10 (dd, *J* = 8.3, 1.5 Hz, 1 H), 7.60 (d, *J* = 1.7 Hz, 1 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 19.9, 56.4, 85.7, 110.8, 129.9, 132.0, 139.8, 156.1. GC-MS: *m*/*z* (%): 248.00 (100) $[M]^+$.

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