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ARTICLE

Cobalt(II)-Catalyzed Oxidative Esterification of Aldehydes: A Cooperative Effect between Cobalt and Iodide Ion†

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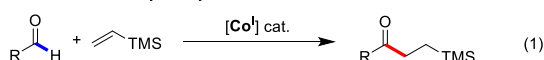
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The efficient cobalt(I) catalyzed oxidative alkoxylation of aldehydes, a method directly leading to the corresponding esters, is presented. Mechanism studies provide extensive insights into the cobalt mediated decomposition of TBHP in the presence of iodide ion. The *in situ* generated hypoiodites ($\text{IO}^-/\text{IO}_2^-$) mainly from conversion of I_3^- to IO_3^- accounts for a cooperative effect with the oxygen centered radical species to make the important hydrogen abstraction of hemiacetal intermediates more selective, thereby offering the high efficiency.

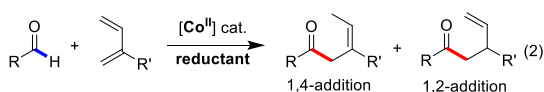
Introduction

Developing cobalt catalysts for the selective functionalization of C-H bonds is a conceptually and economically attractive strategy that overcomes the need for precious metals and enables new transformations.¹ Cross-coupling reaction by low-valent cobalt have emerged as a versatile approach.²⁻⁶ However, the requisite reductive conditions limits the functional group tolerance.⁴⁻⁶ As an alternative strategy, the high-valent-cobalt-catalyzed coupling reactions is attracting increasing attentions and was developed very recently.⁷⁻⁹ For instance, Co(II)-catalyzed C-H bonds activation in the presence of oxidant has been applied in constructing various C-O, C-N and C-C bonds.⁸⁻⁹

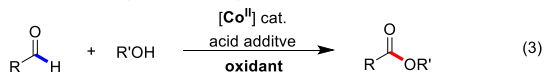
Brookhart's work: hydroacylation of olefin



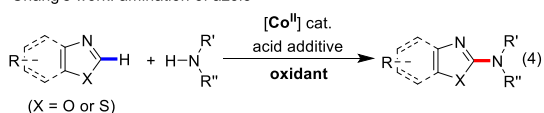
Dong's work: hydroacylation of 1,3-dienes



This work: alkoxylation of aldehyde



Chang's work: amination of azole



Despite these significant progresses, only two examples of

Co(I)-catalyzed functionalization of formyl C-H bond in aldehydes have been reported (eq 1 and eq 2). These include Brookhart's oxidative C-H activation³ and Dong's oxidative cyclization,⁶ respectively. Interestingly, the unusual β -hydride elimination¹ occurred on the cyclic [Co(III)-O-CH] intermediate in the latter case, probably due to the ring tension thereof. Independent to this, the oxidative strategy by using an external oxidant, albeit representing an efficient mode of reactivity towards aldehydes,¹⁰ appears reluctant in the desired cross-coupling with other organic substrates. Therein, the dehydrogenative cross-coupling of aldehydes and alkanols (eq 3) is more challenging because of the fact that alkanols are easily transformed to the corresponding aldehydes (further to acids) or ketones through radical mechanisms.¹¹ Even the intermediate hemiacetal-metal complexes were formed before the undesired decomposition of each substrate, the subsequent β -hydrogen elimination leading to esters might be a limitation in the case of cobalt¹ as compared with palladium or nickel catalysis.¹² Therefore, cobalt-catalyzed direct oxidative esterification of aldehydes with alcohols warrants further study.

Previous studies demonstrated that organic radical species, generated from reactions of some transition-metal complexes or iodides with *tert*-butyl hydroperoxide (TBHP), exhibit high reactivity as oxidizing agents in the oxidative coupling of aldehydes/alcohols.¹³ Chang and his coworkers once reported Co(II)/T-HYDRO catalyzed dehydrogenative C-N cross-coupling in the presence of AcOH (eq 4, T-HYDRO is the trade mark name for 70 wt% *tert*-butyl hydroperoxide solution in water).^{9a} Nucleophilic attack of amine was found more facile by using an acid additive. Noteworthy, subtle differences in the ligands of cobalt complexes were known to result in extreme differences in the catalytic cycles of peroxide decomposition,¹⁴ thereby tuning the efficiency of hydrogen abstraction. Based on these results, we speculated that certain Co(II) species would catalyze the oxidative esterification of aldehydes when they are used in combination with TBHP and proper acids.

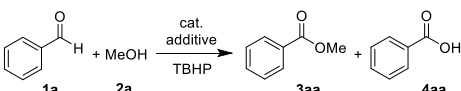
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Herein, we disclose the first CoI_2 -catalyzed direct alkoxylation of aldehyde (eq 3). Interestingly, investigations attribute the high efficiency to a cooperative effect between the iodide chelating ligand and cobalt ion on the catalytic cycle.

Results and discussion

Our study started with developing a $\text{Co(II)}/\text{TBHP}$ system in the oxidative coupling of benzaldehyde (**1a**) and MeOH (**2a**). As expected, the choice of acid additives and their amount employed turned out to be crucial for the selectivity (Table 1, entry 1-9). Brønsted acid AcOH was prone to afford undesired carboxylic acid (entry 1), the origin of which will be discussed later in the paper. In contrast, Lewis acid AlCl_3 was the most effective in the desired product ester formation among various acid co-catalysts screened (entry 2-5), although the mass balance still consisted of a part of carboxylic acid (**4aa**). Moreover, cobalt species other than CoI_2 exhibited reduced catalytic activity (entry 9-13). And the ester yields were not improved by either decreasing or increasing the equivalent of MeOH (entry 8-9) and TBHP (entry 14-15). Under optimized conditions, un-substituted benzaldehyde (**1a**) smoothly reacted with MeOH (**2a**) to provide methyl carboxylate **3aa** in a high yield of 94% (entry 13).

Table 1 Optimization of Cobalt Catalyst System for the Oxidative Esterification of Benzaldehyde (**1a**) with MeOH (**2a**).^a



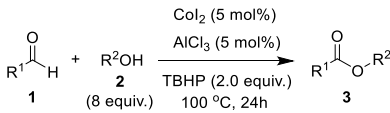
Entry	Cat.	2a (equiv.)	Additive	Conv. (%)	Yield (%) ^b	
					3aa	4aa
1	$\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$	8.0	HOAc	100	15	84
2	$\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$	8.0	InBr_3	95	57	35
3	$\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$	8.0	$\text{BF}_3 \cdot \text{Et}_2\text{O}$	78	41	31
4	$\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$	8.0	In(OTf)_3	62	39	20
5	$\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$	8.0	AlCl_3	98	59	38
6	$\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$	8.0	–	97	37	58
7 ^c	$\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$	8.0	AlCl_3	75	29	40
8	$\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$	4.0	AlCl_3	100	42	53
9	$\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$	16.0	AlCl_3	87	55	30
10	CoCl_2	8.0	AlCl_3	88	64	23
11	Co(acac)_2	8.0	AlCl_3	81	60	15
12	Co(OAc)_2	8.0	AlCl_3	95	62	31
13	CoI_2	8.0	AlCl_3	98	94	3
14 ^d	CoI_2	8.0	AlCl_3	89	83	1
15 ^e	CoI_2	8.0	AlCl_3	100	52	44

^a General conditions: **1a** (1 mmol), cat (5 mol%), additive (5 mol%), TBHP (2 equiv.), 100 °C, 24 h. ^b Yields determined by GC with biphenyl as internal standard. ^c AlCl_3 (10 mol %). ^d TBHP : 1.5 equiv. ^e TBHP : 4.0 equiv.

To explore the substrate scope, we examined a range of aldehydes (**1**) in the coupling with MeOH (**2a**) under the optimized reaction conditions (Table 2, entry 1-16). It was observed that electronic variation of the substituents at *para*- and *meta*-position of benzaldehyde did not significantly affect the reaction efficiency. The corresponding methyl carboxylate

products of benzaldehyde substituted with a methoxy, nitro, methyl group were obtained in satisfactory yields (entry 2-8). Benzaldehyde bearing electron-donating groups such as methoxy at *ortho*-position could also be employed as facile substrates that provided the corresponding ester in a high yield (entry 10). However, the one with electron-withdrawing groups at the same position such as chloride performed poorly in conversion (entry 11). Not only methyl aromatic carboxylates but also methyl aliphatic carboxylates were readily obtained in acceptable yields (entry 12-13). In addition, various heteroaromatic aldehydes were tolerated in such catalytic system and afforded their methyl carboxylates in moderate yields (entry 14-16). We next examined the scope of alcohol reactant in the cobalt-catalyzed oxidative esterification of aldehydes (Table 2, entry 17-20). In the case of benzaldehyde (**1a**), the desired alkoxylation products were obtained in moderate yields when branched alcohols employed instead of linear ones.

Table 2 Scope of CoI_2 -Catalyzed Oxidative Esterification of Aldehydes with Alcohols.^a

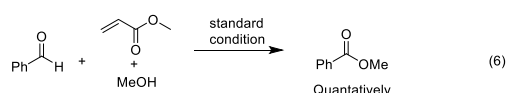
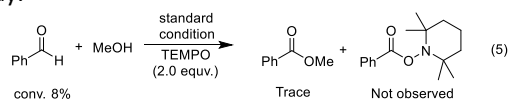


Entry	Substrate 1 (R^1)	Substrate 2 (R^2)	Conv. (%)	Product 3 (yield (%) ^b)
1	1a (Ph)	2a (Me)	97	3aa (94)
2	1b (4- $\text{NO}_2\text{C}_6\text{H}_4$)	2a (Me)	100	3ba (80)
3	1c (4- OMeC_6H_4)	2a (Me)	100	3ca (94)
4	1d (4- MeC_6H_4)	2a (Me)	100	3da (89)
5	1e (4- ClC_6H_4)	2a (Me)	96	3ea (88)
6	1f (3- $\text{NO}_2\text{C}_6\text{H}_4$)	2a (Me)	95	3fa (92)
7 ^c	1g (3- OMeC_6H_4)	2a (Me)	100	3ga (92)
8	1h (3- MeC_6H_4)	2a (Me)	100	3ha (93)
9	1i (3- ClC_6H_4)	2a (Me)	100	3ia (94)
10	1j (2- OMeC_6H_4)	2a (Me)	89	3ja (85)
11	1k (2- ClC_6H_4)	2a (Me)	54	3ka (49)
12	1l (n- C_6H_{13})	2a (Me)	97	3la (65) ^c
13	1m (Ph(CH_2) ₂)	2a (Me)	95	3ma (72)
14	1n (4-pyridine)	2a (Me)	93	3na (75)
15	1o (2-furyl)	2a (Me)	91	3oa (66)
16	1p (2-thiophen)	2a (Me)	97	3pa (69)
17	1a (Ph)	2b (<i>n</i> -Et)	98	3ab (96)
18	1a (Ph)	2c (<i>n</i> -Bu)	94	3ac (94)
19	1a (Ph)	2d (<i>i</i> -Pr)	90	3ad (73)
20	1a (Ph)	2e (<i>t</i> -Bu)	100	3ae (58)

^a General conditions: **1** (1 mmol), **2** (8 mmol), cat (5 mol%), AlCl_3 (5 mol%), TBHP (2.0 mmol), 100 °C, 24 h. ^b Isolated yields. ^c Yields determined by GC-MS.

To begin investigating the mechanism of this Co-catalyzed oxidative coupling of alcohols with aldehydes, the single electron transfer (SET) process was considered. The formation of ester was completely suppressed when two equivalents of TEMPO were introduced into the reaction under standard conditions, but no TEMPO adduct of acyl radical was obtained (eq 5). Importantly, cross-coupling did not occur between aldehyde and the C=C bond in the presence of 16 equiv. of

methyl acrylate (eq 6), thus disfavoring an acyl radical pathway.¹⁵ Moreover, it was also demonstrated that the carboxylic acid (**4aa**) was formed as a side product rather than an intermediate in the oxidative esterification since only traces of the corresponding methyl carboxylate (**3aa**, conversion: 10%, yield: 8%) was obtained under standard conditions by reacting **4aa** with MeOH (8 equiv). Combined with the fact that the reaction is accelerated by strong-Lewis acid, these results indicate that the reaction may proceed *via* a hemiacetal^{13a} pathway.



Notably, some alkali¹⁶ and organic iodides¹⁷ readily react with TBHP. As an alternative to the conventional understanding, a pioneer work reported by Ishihara disclosed the *in situ* generated hypiodites ($\text{IO}^-/\text{IO}_2^-$) are the catalytic active species for the oxidative carbon-oxygen cross-coupling.^{17a} Encouraged by this discovery, many achievements on the new bond formation have been obtained recently by employing iodide/TBHP oxidation system.^{17b} Interestingly, transition-metal catalysis in the presence of iodide either as chelating ligand or additive often shows distinguished reactivity from the others.¹⁸ Although it was ever interpreted as a result of the iodine-assisted effect^{18h-i}, the reaction details were unclear. Indeed, in our study, both *n*-Bu₄NI and KI facilitated this transformation well, albeit providing different yields with respect to specific substituents (Table S1). Thus, an uncertainty of whether Co(II) was involved in the catalytic cycle arised.

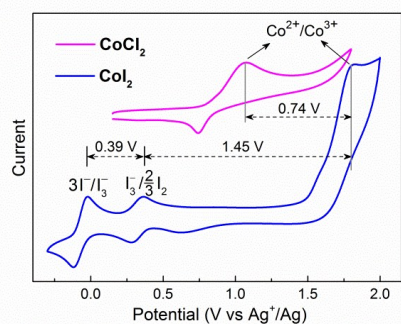


Fig. 1 Cyclic Voltammograms of 1 mM CoI₂ and CoCl₂. Conditions: 0.1 M LiClO₄ in CH₃CN, under Ar, 50 mV/s scan rate.

To address this issue, we performed various control experiments and spectroscopic analysis. A cyclic voltammetry (CV) obtained from an acetonitrile (CH₃CN) solution of CoI₂ (1mM) revealed the presence of two reversible signals at $E_{1/2}$ -0.07 V and $E_{1/2}$ -0.32 V (*vs* Ag⁺/Ag) corresponding to 3I⁻/I₃⁻ and I₃⁻/3/2I₂, respectively, and a broad irreversible Co²⁺/Co³⁺ wave at a relative higher positive $E_{\text{ox}} \sim 1.80$ V (*vs* Ag⁺/Ag) (Fig. 1). These iodides oxidative features are nearly the same as those observed with a solution containing non-transitional-metal iodides (NaI and *n*-Bu₄NI, Fig. S2), however, the oxidative potential of Co²⁺/Co³⁺ couple is much higher compared with

that detected for the chlorine-ligated analogue (CoCl₂). These CV data indicated the iodide chelating ligand is relatively more sensitive to oxidants other than the Co(II) ion, on the other hand, Co(III)I₂ is capable of oxidizing I⁻ and I₃⁻ ions if formed.

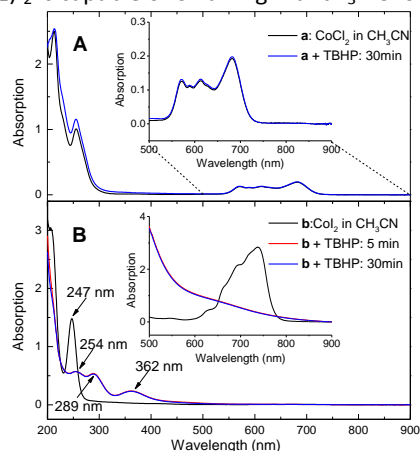


Fig. 2 UV-visible spectra acquired from monitoring the reaction time courses of the oxidation of CoI₂ and CoCl₂ by TBHP. (A: 0.05mM CoCl₂, CoCl₂: TBHP = 1: 26, react at 100 °C; B: 0.05mM CoI₂, CoI₂: TBHP = 1: 26, react at 60 °C; insert: CoI₂: 4.0 mM, CoI₂: TBHP = 1: 7, react at 25 °C.)

The lack of reactivity between halogen-ligated Co(II) and TBHP was subsequently demonstrated by UV-visible spectroscopic study, indicating oxidation did not occur in the reaction with CoCl₂ at 100 °C for 30 min (Fig. 2, A). But it readily proceeded in the case of CoI₂ even under lower temperature. Representative spectral were obtained during oxidation of CoI₂ in CH₃CN at 60 °C (Fig. 2, B). The absorption band of I⁻ ion at 247 nm decreased with time. Instead, the transient iodide species referenced at 289 nm and 362 nm¹⁹ emerged and reached their potential concentration limit within 5 min. Importantly, the absorption band at a range from 600 nm to 800 nm typically assigned to tetrahedral complexes of halogenated Co(II)²⁰ decreased sharply, coinciding with a broad signal at around 650 nm appeared. Moreover, the obtained spectrum was also different from Co(II)I₂ plus I₂ (Fig. S5). The charge variation on cobalt ion was, therefore, most likely involved.

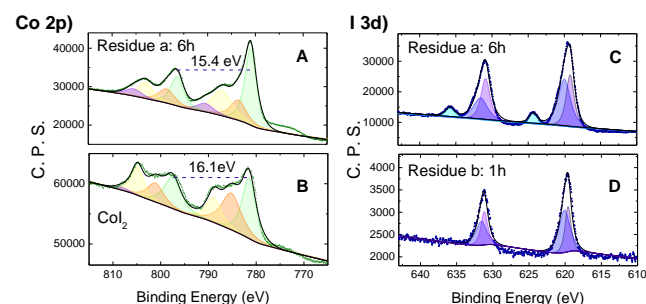


Fig. 3 The Co2p (left) and the I3d (right) XPS spectrum of the catalyst residue and raw CoI₂ along with deconvolution of the photopeaks and corresponding best fitting lines. (reaction condition for residue a: 0.1 M CoI₂, 2.0 M TBHP, CH₃CN as solvent, 6h at 60°C; reaction condition for residue a: 2.6 × 10⁻³ M; CoI₂: TBHP = 1:20, CH₃CN as solvent, 1h at 60°C).

Co2p XPS (X-ray photoelectron spectroscopy) spectra were then acquired for the reaction residue of I₃ and TBHP (20

equiv.) to elucidate the electronic state variation of the cobalt ion during the catalytic cycle. Upon reaction at 60 °C for 6h, the sample showed a Co2p spectrum of main peak at 781.0 eV, integrating about 49% of the overall signal area, and minor satellites at 783.5, 787.0 and 790.5 eV, with ΔE_{SO} (spin-orbital splitting) contributions of 15.4 eV (Fig. 3, A). The XPS Co2p spectral features of CoI_2 (Fig. 3, B), on the other hand, showed a higher ΔE_{SO} (16.0 eV), with high intensity satellites, as expected for 3d ions with unquenched orbital momentum.²¹ This difference in ΔE_{SO} of Co2p spectrum suggested the presence of ls-Co(III) (ls = low spin) in the oxidized sample.²² In addition, the corresponding I3d XPS spectra study of the residue (Fig. 3, C and D) showed two separated bands at both I 3d_{5/2} and 3d_{3/2} levels. The narrow and asymmetric band at the relative lower level was deconvoluted into two peaks of intensity ratio ca. 1.4:1 with different binding energies, containing values assigned to I_2 at 620.0 eV²³ and I^- at 619.2 eV. Note that the I_3^- ion is a resonating system consisting of I^- ion and I_2 molecule and the 3d core-level spectra for some I_3^- show a band composed of a 2:1 double-component peaks. This detected iodine species was, therefore, attributed to a mixture of I_3^- and unconverted I^- ions. Independent to this, the higher energy iodate, IO_3^- , was directly formed (Fig. 3, C) as illustrated by the I 3d_{5/2} band typically locating at 624.3 eV.²³ In comparison, this band for IO_3^- was not detected in the residue of $n\text{-Bu}_4\text{NI}$ with TBHP under identical conditions (Fig. S6). These observations can be interpreted as a result of an oxidative conversion from I^- to IO_3^- via I_3^- , leading to a mixture with different ratio depending on conditions. It's understandable that no iodate emerged in the residue (Fig. 3, D) after react the substrates of reduced concentration (CoI_2 : 2.6×10^{-3} M; CoI_2 : TBHP = 1:20) for a shorter time (1h). Noteworthy, the rapid generation and subsequent disproportionation of the transient hypoiodites ($\text{IO}^-/\text{IO}_2^-$) accounts for the transformation either from I^- to I_3^- or the subsequent from I_3^- to IO_3^- .^{17a,19} Thus, albeit undetected, hypoiodites were poised to be in the catalytic cycle.

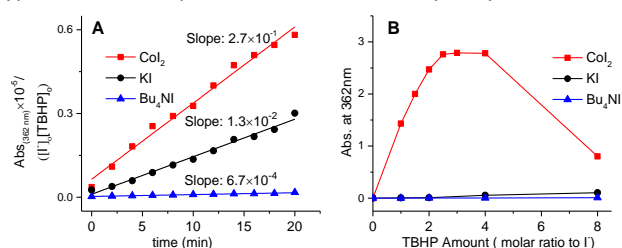
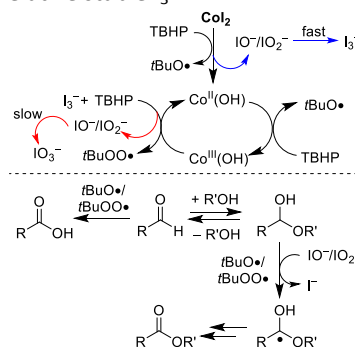


Fig. 4 A: Plot of initial slope acquired from monitoring the reaction time course of the oxidation of iodides by TBHP at 25 °C. **B:** Plot of the potential amount limit of IO^-/I_3^- produced by reaction of iodides ($[\text{I}^-]$: 0.4 mM) with variant concentrations of TBHP at 60 °C.

Kinetic evidence that CoI_2 is quite different from KI and $n\text{-Bu}_4\text{NI}$ as the catalyst in the decomposition of TBHP was obtained by comparing their specific rate on iodide oxidation. Indicated by the literature and our cross experiments (Fig. 3, Fig. S3 and Fig. S4), the oxidative conversion from I^- to I_3^- was supposed to occur in each case at the initial stage, especially with employing dilute substrates. These oxidations were

monitored at 362 nm by UV-visible spectrum which was assigned to the *in situ* generated transient hypoiodites (IO^- and IO_2^-) and relative stable I_3^- .



Scheme 1 Proposed mechanism for CoI_2 catalyzed oxidative esterification of aldehydes.

It was found the cobalt mediated iodide oxidation proceeds much faster than the other two non-transitional metal cases from the initial slope of the plots (Fig. 4, A). Additionally, the saturated capacity of transient iodides at equilibrium in the case of either KI or $n\text{-Bu}_4\text{NI}$ was not significantly affected (Fig. 4, B). In contrast, the oxidized species of iodide was quickly predominant in the solution of CoI_2 at a lower equivalent of TBHP and reached the potential limit with around only two equivalents to $[\text{I}^-]$, a 20-fold lower presenting in the catalytic reaction. Specifically, with increased concentration of TBHP to eight equivalents, the absorption at 362 nm decreased sharply (Fig. 4, B). It's attributable to the second oxidative conversion from I_3^- to IO_3^- . Thus, the iodide chelating ligand in CoI_2 was prone to be quickly converted to an inert I_3^- ion and the hypoiodites thereof formed was no kinetically competent to serve as the active site unless the subsequent generation occurs during the deep oxidation to IO_3^- .

Table 3 Mechanistic study

Entry	Cat.	Additive (mol%)	Yield(%) ^b
1	CoI_2	—	94
2 ^c	Co(OH)_2	—	70
3 ^c	Co(OH)_2	I_2 (5)	68
4 ^c	Co(OH)_2	AgIO_3 (10)	66
5	Co(OH)_2	$n\text{-Bu}_4\text{NI}_3$ (10)	90
6	Co(OH)_2	$n\text{-Bu}_4\text{NI}$ (10)	89

^a General conditions: **1a** (1mmol), ^b Yields determined by GC with biphenyl as internal standard. ^c Yield of **4aa**: 2: 29%; 3: 31%; 4: 30%.

Collectively, the reaction of CoI_2 with TBHP was poised to start with oxidative transformation of the iodide chelating ligand to the active intermediate, while the charge variation on cobalt remained at this stage (Scheme 1). It seems likely that the active Co(II)OH species were thereof formed and initiated another pathway to decompose TBHP. In this emerged hydroxyl system, the cobalt is cycling between oxidation states +II and +III. And as soon as the Co(III) species were formed, they reacted as one-electron oxidant to accelerate the transformation speed of I^- to I_3^- and thus making the second oxidative conversion to IO_3^- possible.

The subsequent control experiment by using $\text{Co}(\text{OH})_2$ instead of CoI_2 as the catalyst proceeded in a reduced efficiency leading to **3aa** in a yield of 70% (Table 3, entry 2). We, therefore, could not completely rule out a catalytic role of the iodide. And the *in situ* generated hypoiodites accounts for the catalytic active species making the important hydrogen abstraction from hemiacetals more selective (Scheme 1), however, they are probably mainly from the second oxidative conversion from I_3^- to IO_3^- under $\text{Co}(\text{II})$ mediation. In consistence with this assumption, the reaction by using a combination of $\text{Co}(\text{OH})_2$ with either *n*- Bu_4NI or *n*- Bu_4NI_3 as the catalyst provided a comparable yield as CoI_2 (entry 5 and 6). But the performance was not improved upon direct addition of either molecular iodine or iodate additive (entry 3 and 4). In these cases without efficient iodide additives, carboxylic acid **4aa** was formed as the main side product (entry 2, 3 and 4).

Conclusions

The present study reports practical CoI_2 catalyzed system for the oxidative C-O cross-coupling of various aldehydes and alcohols. It is the first homogeneous inexpensive cobalt catalyst system for oxidative esterification of aldehydes. The methods are compatible with substrates bearing a variety of functional groups, including electron-poor or rich aromatic aldehydes, as well as aliphatic and heterocyclic aldehydes. And, the methods exhibit highly favorable practical characteristics: solvent free system, rather low alcohol/aldehyde ratio and the catalyst components are inexpensive and commercially available reagents. More importantly, this study has provided extensive insights into the cobalt mediated decomposition of TBHP in the presence of iodide ion. The *in situ* generated hypoiodites mainly from I_3^- to IO_3^- accounts for a cooperative effect with oxygen centered radical species to offer the high efficient conversion.

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