Ethylene carbonate as a unique solvent for palladium-catalyzed Wacker oxidation using oxygen as the sole oxidant†

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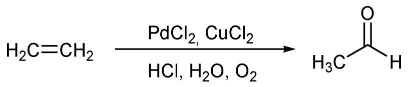
Ethylene carbonate (EC) as a unique solvent for the Wacker oxidation of higher alkenes and aryl alkenes has been successfully developed using molecular oxygen as the sole oxidant, in which colloidal Pd nanoparticles stabilized in EC are considered to facilitate its reoxidation under cocatalyst-free conditions.

The Wacker process, typically a $PdCl_2$-catalyzed $CuCl_2$-mediated oxidation of ethylene to acetaldehyde in acidic aqueous media under an oxygen atmosphere (eqn (1)),[1] has evolved into one of the most versatile families of reactions. Moreover, its discovery has been considered as a burgeoning interest in organometallic chemistry and homogeneous catalysis.[2]



(1)

The past five decades have witnessed the widespread research advances and practical application of Wacker oxidations,[3] due in large part to conveniently constructing carbonyl compounds from corresponding terminal alkenes through the Wacker process. Up to now, there have been numerous advancements in Wacker oxidations documented, with notable aspects including developing direct oxygen-coupled reactions,[3c] searching for appropriate co-catalysts[4] and/or solvents,[5] and supporting the catalyst ingredients onto polymers.[6] It is not an exaggeration to declare that using molecular oxygen as the sole oxidant would be a significant breakthrough in Wacker oxidation in terms of cost-effectiveness, atom efficiency, product separation, as well as selectivity improvement.[3c,7] Based on mechanistic considerations, the achievements on direct O_2-coupled Wacker process are probably attributable to the coordinating ability of the basic solvent (DMF, DMA, NMP),[8] and/or nitrogen-based ligands (phenanthroline, (–)-sparteine).[9,10]

Nowadays, one of the pivotal areas in green chemistry is to search for environmentally benign reaction media to replace the commonly-used organic solvents in chemical processes.[11] Organic carbonates, in particular organic cyclic carbonates, have offered distinct benefits as eco-friendly solvents,[12] mainly owing to their biodegradability, high solvency, high boiling and flash points, low odor levels, and low toxicities. On the other hand, organic carbonates have not yet received much attention to be a solvent in catalysis, and the number of examples seems to be small in the literature.[13] To continue our research on organic carbonates,[14] we herein want to describe the potential of ethylene carbonate (EC) as an environmentally benign slovent for Wacker oxidation using oxygen as the sole oxidant. There would be certain merits using EC as an alternative solvent for catalysis: (1) as one of the cyclic organic carbonates, EC has several outstanding properties as a solvent for catalysis (*vide supra*); (2) the metal catalyst *e.g.* Pd nanoparticles could be stabilized by EC,[13e] and thus could retard aggregation of Pd(0) as well as facilitate its reoxidation directly by oxygen; (3) the product could readily be separated by extraction; (4) higher alkenes and aryl alkenes, which were considered as notoriously difficult substrates, would be compatible with the catalytic system.

As demonstrated in the Pd(II)-catalyzed aerobic alcohol oxidation in EC reported by Blackburn *et al.* in 1977,[15] we assumed that the direct O_2-coupled Wacker process could also operate under similar reaction conditions. The Wacker oxidation of 1-dodecene, catalyzed by a binary catalyst system comprising $PdCl_2$/NaOAc, was chosen as a bench reaction in EC using oxygen as a sole oxidant.‡ In the preliminary study, we screened the reaction conditions, such as reaction temperature, reaction time, partial pressure of oxygen, and additive/ligand (Table S1–5 and Table S1, ESI).† As anticipated, the reaction proceeded smoothly in EC (3 mL)/H_2O (0.01 mL) under the reaction conditions to afford dodecan-2-one in good yield as well as high selectivity (Table 1, entry 1).

As described in the Pd(II)-catalyzed direct-O_2 coupled reactions,[7,16] it has been known that either a solvent or ligand plays significant role in stabilizing the catalyst, and accelerating the reaction. In this context, the efficacy of different kinds of organic carbonates, including cyclic carbonates and linear carbonates such as propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), was investigated in detail. It is found that the reaction strongly depended on the structure of carbonates used (Table 1, entries 1–4). Linear carbonates, *i.e.* DMC, DEC, were inactive for the Wacker reaction, and just a trace amount of the isomerization product of 1-dodecene was detected. The commonly-used solvents, like DMF, DMA and NMP, showed only poor performance under otherwise identical reaction conditions (entries 5–7) compared with EC. The presence of a proper amount of water would enhance the reaction, as shown in Figure S4, ESI.† This is understandable, as a solvent effect in the metal-catalyzed reaction would rely on the physicochemical nature of the solvents (polarity, donor

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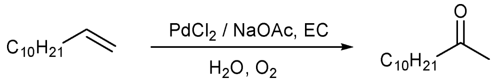
† Electronic supplementary information (ESI) available: Copies of the NMR spectra and experimental data for products, and results on optimizing reactions. See DOI: 10.1039/b913779n

Table 1 The effects of solvent and ligand on the direct O_2-coupled Wacker oxidation of 1-dodecene[a]



Entry	Solvent	Conv. (%)	Yield (%)[b]	$E_T{}^N$ [c]
1	EC	78	74	0.552
2	PC	35	7	0.472
3	DMC	9	0	0.256
4	DEC	10	0	0.185
5	DMF[d]	5	3	0.386
6	DMA[e]	20	15	0.377
7	NMP[f]	26	22	0.355

[a] Reaction conditions: dodecene (0.5 mmol, 0.11 mL), $PdCl_2$ (0.01 mmol, 1.77 mg), NaOAc (0.05 mmol, 4.1 mg), ligand (10 mol% with respect to the initial amount of substrate), solvent (3 mL), O_2 (10 atm), water (0.01 mL), 6 h, 60 °C. [b] Determined by GC. [c] Solvent polarities ($E_T{}^N$) from the literature.[18] [d] Dimethyl formamide. [e] Dimethyl acetamide. [f] *N*-Methylpyrrolidone.

number, and acceptor number).[17] The solvent polarity ($E_T{}^N$) may play a crucial role in the direct O_2-coupled Wacker oxidation. Addition of water ($E_T{}^N = 1.0$) could increase solvent polarity, thus improving the reaction. On the other hand, the solubility of alkenes and/or catalyst and cocatalyst could also influence the effectiveness of the Wacker oxidation.

Subsequently, the influence of various ligands was evaluated. As easily seen in Table S1 (ESI),† the nitrogenous ligands including pyridine, 1,10-phenanthroline and triethylamine, as well as the oxygenous ligands *e.g.* acetylacetone, showed a drastically negative effect on the reaction. Accordingly, the eco-friendly solvent, *i.e.* EC, could play a crucial role in the present Wacker oxidation without any co-catalyst/ligand.

In an attempt to further boost the reaction, the dependence of the Wacker oxidation on additives was also measured in EC.

Table 2 The dependence of the additive on the direct O_2-coupled Wacker oxidation in EC[a]

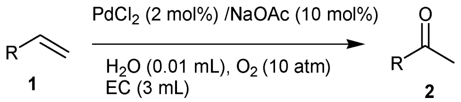
Entry	Additive (%)	Yield[b] (%)	Entry	Additive (%)	Yield[b] (%)
1	—	0	8	NH_4OAc (10)	0
2	NaOAc (5)	22	9	$Mg(OAc)_2$ (10)	0
3	NaOAc(10)	74	10[c]	KOAc (10)	50
4	NaOAc (20)	60	11[d]	KOAc (10)	72
5	NaOAc (40)	45	12	K_2CO_3 (10)	0
6	LiOAc (10)	13	13	*n*-Bu_4NBr (10)	0
7	KOAc (10)	2	14	*n*-Bu_4NCl (10)	0

[a] Reaction conditions: dodecene (0.5 mmol, 0.11 mL), $PdCl_2$ (0.01 mmol, 1.77 mg), EC (3 mL), O_2 (10 atm), 60 °C, 6 h, [b] Determined by GC, [c] 80 °C, [d] 100 °C.

As tabulated in Table 2, The experimental results showed that the amount of NaOAc had a great influence on the reaction. The reaction did not take place at all without adding NaOAc (entry 1), and its suitable quantity was screened to be 10 mol% relative to the initial amount of 1-dodecene (entries 2–5). Due to the indispensable role of NaOAc, the effects of similar types of additives was also explored. The results strongly suggested that the acetates with different countercations are responsible for the catalytic reactivity (entries 3, 6–9). It turned out to be that Na^+ was the best countercation among the tested cations (Li^+, Na^+, K^+, $NH_4{}^+$, Mg^{2+}) under the identical conditions, and KOAc could be an alternative to NaOAc when the reaction was run at an elevated temperature (entries 10, 11). Other tested additives such as K_2CO_3, *n*-Bu_4NBr, *n*-Bu_4NCl gave rise to an adverse influence on the reactivity (entries 12–14).

To evaluate the scope of substrates for the present direct O_2-coupled Wacker oxidation in EC, two kinds of notoriously difficult substrates, higher alkenes and aryl alkenes, were subjected to the established protocol, as presented in Table 3. This methodology is easily found to be applicable to both kinds of

Table 3 The direct O_2-coupled Wacker oxidation of higher alkenes and aryl alkenes in EC[a]



Entry	1	R	2	Temp./°C	Time/h	Conv. (%)	Yield (%)[b]
1	**1a**	*n*-C_6H_{13}	**2a**	80	12	65	62
2	**1b**	*n*-C_8H_{17}	**2b**	80	12	85	80
3	**1c**	*n*-$C_{10}H_{21}$	**2c**	80	12	93	92
4	**1d**	*n*-$C_{14}H_{29}$	**2d**	80	12	75	73
5[c]	**1c**	*n*-$C_{10}H_{21}$	**2c**	80	12	30	28
6	**1e**	C_6H_5	**2e**	80	12	64	61
7				100	24	78	74
8	**1f**	*p*-$CH_3C_6H_4$	**2f**	80	12	62	58
9				100	24	83	82
10	**1g**	*p*-$CH_3OC_6H_4$	**2g**	80	12	57	51
11				100	24	91	86
12	**1h**	*m*-$CH_3C_6H_4$	**2h**	80	12	60	58
13				100	24	85	83
14	**1i**	*o*-$CH_3C_6H_4$	**2i**	80	12	56	52
15				100	24	76	53
16	**1j**	*p*-ClC_6H_4	**2j**	80	12	33	29
17				100	24	70	56

[a] Reaction conditions: substrate (0.5 mmol), $PdCl_2$ (0.01 mmol, 1.77 mg), EC (3 mL), NaOAc (10 mol%, 4.1 mg), O_2 (10 atm). [b] Isolated yield. [c] The second run of the catalyst.

terminal alkenes, producing the corresponding methylketones in good to excellent yield. Gratifyingly, higher alkenes were oxidized to the corresponding methylketones without detectable olefin isomerization, which is considered to be a common side reaction in Wacker oxidation. It is worth mentioning that the aryl alkenes with an electron-donating substituent at the phenyl ring gave higher reactivity towards the Wacker product (entries 8, 10, 12, 14 *vs.* 6), whereas an electron-withdrawing group led to decreasing in the yield of the methyl ketone (entry 16). As a consequence, an electronic effect of substituents on the phenyl ring had great influence on the reactivity of the double bond. It is important to note that the aryl chloride was not activated under these conditions (entry 16).

Furthermore, good to excellent yields and selectivity were attained by just increasing the reaction temperature to 100 °C and elongating the reaction time to 24 h (entries 7, 9, 11, 13, 15, 17, Table 3). Accordingly, to the best of our knowledge, this work presented herein is the first example of the aryl alkenes subjected to the cocatalyst-free and/or ligand-free Wacker oxidation system.

Another benefit of employing EC as the alternative solvent is the facile separation of the product. After reaction, the product is very easy to extract with *n*-hexane (for higher alkenes) or ethyl ether (for aryl alkenes), and the catalyst is allocated exclusively in the solid EC phase under the cooling conditions.

Among the reported Wacker oxidations using oxygen as the sole oxidant, Fujimoto and Kunugi[19] reported that the addition of a material with high surface area, such as active charcoal, could increase the reaction rate substantially by dispersing the Pd(0) and facilitating its reoxidation. It is also worth mentioning that PC could be used to stabilize the colloidal Pd nanoparticle for the ligand-free Heck type reaction.[13e] To further gain insight into the effect of EC on the present Wacker process, we set out to verify the involvement of palladium nanoparticles in our catalyst system. Indeed, transmission electron microscopy (TEM) examination of a mixture of $PdCl_2$/NaOAc in EC stirred for 30 min at 50 °C, revealed the presence of highly dispersed colloidal Pd nanoparticles (Fig. 1, *left*). After reaction, the nanoparticles began to cluster, resulting in formed agglomerates with less surface area, which presumably accounts for the lower catalytic activity (Fig. 1, *right*), being consistent with the experimental result of the second run of the catalyst system using 1-dodecene as a model substrate under the identical reaction conditions giving 28% yield of dodeca-2-one (entry 5, Table 3). With the observation of Pd nanoparticles in Wacker oxidation, we reasoned that the success of the cocatalyst-free process could probably be attributed to facilitating reoxidation of the colloidal Pd nanoparticles, which was stabilized by EC.

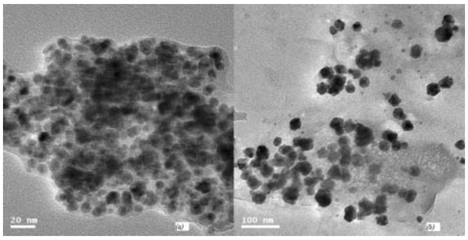


Fig. 1 TEM images of colloidal Pd nanoparticle: (a) before reaction, (b) after reaction.

In conclusion, we showed that EC as an alternative green solvent is of considerable potential in Wacker oxidations using oxygen as the sole oxidant. Besides its environmentally benign characters, the advantages of using EC as the reaction medium in the present study appear particularly interesting in widened substrate scope, facile separation of the product, and stabilizing effect on the colloidal Pd nanoparticle. Further investigation of organic carbonates as ecofriendly reaction media for catalysis and organic transformation is currently under investigation in our laboratory.

Acknowledgements

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Notes and references

‡ General experimental procedure for the palladium-catalyzed direct O_2-coupled Wacker oxiation of 1-dodecene in EC: CAUTION: The procedure described below is conducted in closed reaction apparatus that is under pressure. It must only be carried out by using the appropriate equipment and under rigorous safety precautions. The reaction was carried out in a 50 mL stainless-steel autoclave with an inner glass and a magnetic stirrer. A mixture of $PdCl_2$ (1.77 mg, 0.01 mmol), NaOAc (4.1 mg, 0.05 mmol), and 3 mL EC was placed in the inner glass and stirred at 50 °C for 30 min. Then, the substrate (0.5 mmol) and H_2O (0.01 mL), 1 MPa of O_2 were successively introduced. The mixture was stirred for 12 h at 60 °C. After the reaction, the reactor was quickly cooled to 0 °C in ice water. The excess of O_2 was depressurized slowly. The resultant mixture was then extracted with an appropriate solvent (*n*-hexane was used for higher alkenes, and ethyl ether for aryl alkenes) (5 mL × 3), dried over $MgSO_4$. The solvent was removed, and the residue was subjected to column chromatography with ethyl acetate/petroleum (1 : 20 to 1 : 10) as eluent to obtain the desired product.

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