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Methyl formate as a carbonylating agent for the catalytic conversion of phenol to methyl phenyl carbonate†

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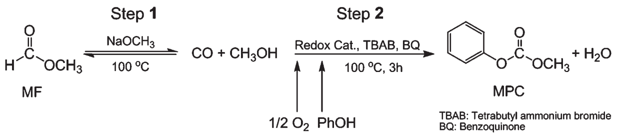
Methyl formate was used as a green and efficient carbonylating agent in the synthesis of methyl phenyl carbonate from phenol. Methyl formate showed better performance compared to toxic CO gas and the ability to produce other useful carbonylated products, *e.g.*, dimethyl carbonate and dimethyl oxalate.

The oxidative carbonylation of phenol to diphenylcarbonate (DPC) has been studied extensively during recent decades.[1] The method is one of the most promising alternatives to replace the current industrial process of DPC production.[1a] DPC is a key component for the manufacture of polycarbonates. However, this process needs to be improved due to hazard problems related to the handling of toxic CO gas.[2] Thus, a process involving a safer and more sustainable carbonylating agent is preferred for industrial applications.

Methyl formate (MF) has been widely utilized as a C_1 building block in organic synthesis.[3] This key intermediate can be produced by hydrogenation of CO_2 in the presence of methanol,[4] enabling the effective recycling of carbon into chemical products.[5] Using an appropriate catalyst, MF can be activated to take part in carbonylation reactions.[6a] Transition metals like Ru and Ir are able to activate MF *via* carbonyl–hydrogen bond dissociation, which leads to direct methoxycarbonylation.[6b] This reaction usually requires temperatures higher than 180 °C. Activation of MF by strong bases (*e.g.*, $NaOCH_3$) results in partial decarbonylation to CO and CH_3OH at low temperatures (40–80 °C).[7] Given the weak acidity of MF,[8] the hydrogen bound to the carbonyl group acts as a proton source against strongly basic methoxide. Using $PdCl_2(PPh_3)_2$ as a catalyst under such basic conditions, the oxidative carbonylation of alkenes was reported.[9] The key steps in this reaction are (i) decarbonylation of MF by $NaOCH_3$, (ii) formation of a methoxycarbonyl–Pd complex, (iii) insertion of alkene and (iv) β-hydride elimination giving the olefinic ester.



(1)

In this study, MF was utilized as a carbonylating agent for phenol to obtain methyl phenyl carbonate (MPC) as the target product. MPC can be converted subsequently to DPC by transesterification with phenol.[10] To the best of our knowledge, there is no report on the application of MF in the carbonylation of phenol. As phenol is much more acidic than MF, it reacts faster with methoxide. Therefore, the activation of MF (Step 1) was separated from the carbonylation of phenol (Step 2), as summarized in eqn (1) (see Experimental details in S1, ESI†).

Step 1: Activation of MF was catalysed here by alkali metal methoxides $MOCH_3$ (M = Na or K), which resulted in increasing pressure in the reactor. This pressure was generated by the partial decarbonylation of MF and formation of CO (*vide infra*).

Step 2: For the carbonylation of phenol by MF, various well-known Pd(II) catalysts were screened together with $Mn(acac)_3$ as the co-catalyst. The pressure at the beginning of this step reached 67–69 bar. As the results in Table 1 show, a high selectivity to MPC along with a low conversion for phenol was obtained. Another phenolic product was phenyl acetate (PAC). Among these Pd catalysts, $PdBr_2$, $Pd(OAc)_2$ and Pd(salen) showed selectivities to MPC higher than 90% (entries 1, 4 and 5). Exchange of CH_2Cl_2 by non-halogenated polar-aprotic solvents, such as dimethyl formamide and tetrahydrofuran, provided similar results (entries 2 and 3). Also other redox couples, such as $PdBr_2$–$CuCl_2$, showed excellent selectivities to MPC (97%, entry 9). Homogeneous systems using $Pd(OAc)_2$–

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Table 1 Carbonylation of phenol by MF using different redox catalysts[a]

No.	Catalyst	Co-catalyst	Conv.[b] (%)	Select.[c] (%)
1	$PdBr_2$	$Mn(acac)_3$	1.6	94.5
2[d]	$PdBr_2$	$Mn(acac)_3$	1.4	93.6
3[e]	$PdBr_2$	$Mn(acac)_3$	1.1	94.4
4	$Pd(OAc)_2$	$Mn(acac)_3$	1.7	95.2
5	Pd(salen)[f]	$Mn(acac)_3$	1.7	91.3
6	Pd(10%)/C	$Mn(acac)_3$	1.1	83.7
7	Pd(5%)/C	$Mn(acac)_3$	1.7	75.4
8	$Pd(OAc)_2$	$Ce(OAc)_2$	1.8	85.0
9	$PdBr_2$	$CuCl_2$	1.3	97.0
10	$Pd(OAc)_2$	$Cu(OAc)_2$	3.6	57.9
11	$PdCl_2(CH_3CN)_2$	$Cu(OAc)_2$	2.3	59.7

[a] For experimental details, see Table S1, ESI. [b] Conversion of phenol. [c] Selectivity to MPC. [d] Solvent: dimethyl formamide. [e] Solvent: tetrahydrofuran. [f] Salen: *N*,*N*′-bis(salicylidenyl)-ethylenediamine.

$Cu(OAc)_2$ or $PdCl_2(CH_3CN)_2$–$Cu(OAc)_2$ as the catalyst (entries 10 and 11) provided higher conversions of phenol (3.6% and 2.3%, respectively), while the selectivities to MPC were lower (57–59%).

As mentioned above, the pressure at the beginning of Step 2 representing the equilibrium CO pressure was generated by the decarbonylation of MF with $NaOCH_3$ (Step 1). In other words, this pressure was the initial CO pressure (P_{CO}) for the carbonylation reaction. The effect of P_{CO} on the carbonylation of phenol by MF was studied by adjusting the amount of $NaOCH_3$ in the range of 4.68–9.36 mmol, thereby controlling the rate of the decarbonylation of MF. In consequence, P_{CO} was controlled within the range of 10–67 bar. As shown in Fig. 1, by reducing P_{CO} from 67 to 10 bar, the conversion of phenol increased, while the selectivity to MPC decreased. Reducing the $NaOCH_3$ amount to lower than 4.68 mmol, resulting in a P_{CO} of less than 10 bar (*ca.* 8 bar), led to an even higher conversion of phenol (up to 6%), while the high selectivity to MPC (60%) was maintained. At amounts lower than 4.68 mmol resulting in P_{CO} less than 7 bar, phenol conversion decreased drastically and the selectivity to MPC dropped to less than 5%. In this case, most of the phenol was converted to PAC.

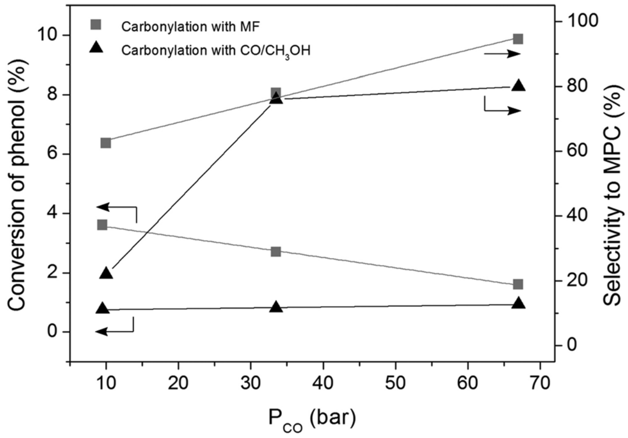


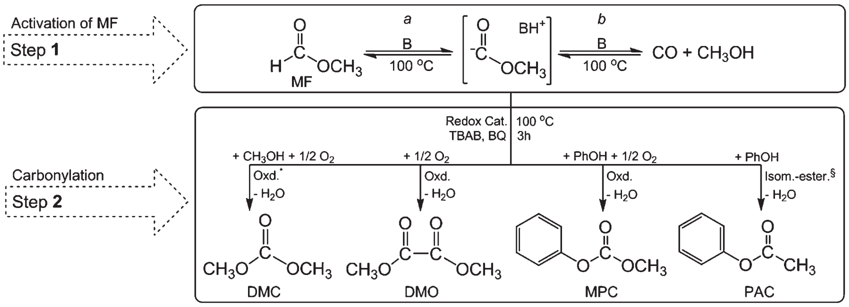
Fig. 1 Conversion of phenol and selectivity to MPC in the carbonylation of phenol by MF or CO/CH_3OH varying the initial CO pressure (P_{CO}). Reaction conditions: phenol (9.09 mmol), $PdBr_2$ (0.11 mmol), $Mn(acac)_3$ (0.688 mmol), TBAB (1.7 mmol), BQ (0.25 mmol), CH_2Cl_2 (10 mL), O_2 (7% of P_{CO}), 100 °C; ■ carbonylation with MF: MF (45 mL), $NaOCH_3$ (4.68–9.36 mmol); ▲ carbonylation with CO/CH_3OH: CH_3OH (45 mL), $NaOCH_3$ (4.68 mmol), CO (10–70 bar).

The efficiency of MF in the carbonylation of phenol was evaluated by performing comparative tests, whereby CO/CH_3OH was used instead of MF under the same reaction conditions (see S2, ESI†). Phenol conversion was independent of P_{CO} (Fig. 1), while most importantly phenol conversion in all cases was lower with CO/CH_3OH compared to MF. The selectivity to MPC decreased with decreasing P_{CO}. At low P_{CO} (10 bar), MPC production was more than 14 times higher, when MF was used (0.202 mmol) compared to CO/CH_3OH (0.014 mmol). At high P_{CO} (67 bar) this effect was less pronounced; the use of MF still resulted in a 2 times higher MPC production (0.137 mmol) compared to CO/CH_3OH (0.065 mmol). These results suggest that under our reaction conditions, MF is a better carbonylation agent compared to the conventional CO/CH_3OH system. Further, it allowed us to propose a mechanistic model for the carbonylation of phenol by MF (*vide infra*).

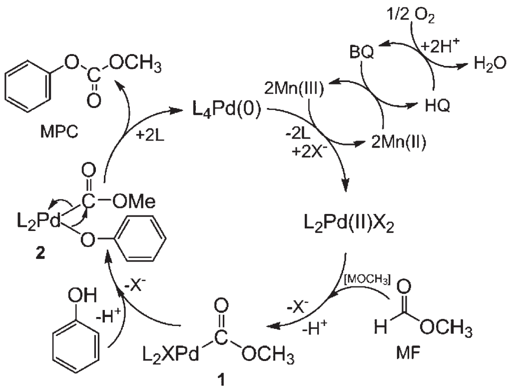
The decarbonylation of MF was also performed using $KOCH_3$, which is a stronger base than $NaOCH_3$.[11] Lower amounts of $KOCH_3$ were required to achieve similar P_{CO}. By varying the amount of $KOCH_3$ within the range of 2.5–6 mmol, P_{CO} was adjusted in the range of 13–67 bar. As for the reactions with $NaOCH_3$, an increase (from below 1% to more than 3%) in phenol conversion and a decrease (from 75% to 60%) in MPC selectivity were observed upon reducing P_{CO} from 67 to 13 bar (see Fig. S1, ESI†). The reaction did not proceed using $LiOCH_3$, most likely, as it is a weaker base than $NaOCH_3$,[11] and was not able to activate/decarbonylate MF at 100 °C.

Other than MPC and PAC, dimethyloxalate (DMO) and dimethylcarbonate (DMC) were identified as side-products by GC-MS. An overview of the reaction network involving the pathways to each product is shown in Scheme 1. DMO is the result of oxidative self-carbonylation of MF, while DMC is the result of the carbonylation of methanol (formed by decarbonylation of MF). Thus, the Pd catalyst enables four parallel catalytic reactions. The overall turnover number (TON) with respect to Pd was as high as 70 (P_{CO} 67 bar) comparable to related studies.[1b,12] Note that DMO and DMC can be converted to DPC *via* transesterification with phenol.[1a] Nonetheless, DPC was not detected in the final reaction mixture (*vide infra*).

Concerning the MPC production and its side products, a mechanism is proposed as shown in Scheme 2. MF is activated by $MOCH_3$ *via* carbonyl–hydrogen bond dissociation, which in the presence of Pd(II) leads to the formation of methoxycarbonyl–palladium intermediate **1**.[13] This complex is very stable and depending on the type of ligand can be formed even at room temperature.[14] The corresponding phenoxycarbonyl–palladium complex proposed as an intermediate in the formation of DPC is apparently not formed.[15] Note that we have not observed DPC in the reaction mixture. The activation of MF by $MOCH_3$ can be represented by the equilibrium equation in Scheme 1 (Step 1). A methoxycarbonyl ion is formed as an



Scheme 1 Reaction pathways during the oxidative carbonylation of phenol by methyl formate; B: base (methoxide); *oxidation; §isomerization–esterification.



Scheme 2 Mechanism of the carbonylation of phenol by MF to MPC using Pd(II) catalysts (L: neutral ligand; X: ionic ligand like Br⁻, OAc⁻) and Mn(acac)$_3$ as the co-catalyst.

intermediate by dissociation of the carbonyl–hydrogen bond.[16] When low amounts of $MOCH_3$ are used (*e.g.*, 4.68 mmol $NaOCH_3$ corresponding to a P_{CO} of *ca.* 10 bar), a relatively long lifetime of the methoxycarbonyl species is expected. In consequence, the kinetics of MF activation (Scheme 1, Step 1*a*) dominates and the methoxycarbonyl ion is the main agent for the formation of **1**. When larger amounts of $NaOCH_3$ are employed, the formation of CO and CH_3OH (Step 1*b*) is faster and **1** is also formed by a consecutive methoxylation–carbonylation. Since MPC production by the comparative reaction using CO/CH_3OH was less efficient, it is concluded that **1** is formed mostly *via* the methoxycarbonyl ion, which readily explains the higher MPC productivity of MF compared to CO/CH_3OH. In the next step, **1** reacts with phenol to form the intermediate **2**. Finally, MPC is formed by reductive elimination of the methoxycarbonyl and the phenolate group. Simultaneously, Pd(II) is reduced to Pd(0), which is then re-oxidized by Mn(III) to complete the cycle. The general aspects of this mechanism are similar to the mechanism proposed for the oxidative carbonylation of phenol by CO and O_2.[17] It also resembles a Wacker-type catalytic reaction.[18]

The formation of the particular side-products identified in the reaction mixture is readily explained by the postulated reaction intermediates.

- MF can undergo isomerization to acetic acid,[19] which in the presence of phenol leads to PAC through esterification. At low P_{CO}, the isomerization of MF to acetic acid is more plausible, leading to formation of higher amounts of PAC.
- DMO is produced by the coordination of a second methoxycarbonyl group to Pd(II), followed by coupling of the two methoxycarbonyl groups *via* reductive elimination (see Scheme S1, ESI†).[20] At P_{CO} lower than 33 bar, the formation of DMO is drastically reduced (see Fig. S2, ESI†). Probably, a relatively high P_{CO} is required for generating the $[L_2Pd(COOCH_3)_2]$ intermediate.
- DMC is formed by reaction of a methoxide ion with **1**. Subsequent reductive elimination of the methoxycarbonyl and the methoxide group results in the DMC formation.

In summary, a new protocol for the formation of MPC by oxidative carbonylation of phenol with MF was developed, which does not require the use of toxic CO gas. The rate of the decarbonylation of MF is controlled by the concentration of $NaOCH_3$. At low concentrations of $NaOCH_3$ (low P_{CO}), the activation of MF to a methoxycarbonyl ion dominates and higher phenol conversions and MPC productivities are obtained. In comparison, MF is a much more efficient carbonylation agent compared to the conventional CO/CH_3OH system. Most noteworthy, the carbonylation of phenol by MF proceeds *via* an activated MF intermediate (most likely, a methoxycarbonyl ion) and not *via* molecular CO. Two further oxidative carbonylation reactions occur in parallel, resulting in the formation of DMO and DMC, two other useful starting materials for DPC production. Thus, MF emerges as a safe and promising substitute for gaseous CO in carbonylation reactions.

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