

EXPANDING THE HORIZONS OF Pd-CATALYSED OSCILLATORY CARBONYLATION REACTIONS: SOLVENT, SUBSTRATE, CATALYST

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ABSTRACT

On our way to producing all-polymeric self-oscillatory systems, we have expanded the horizons of oscillatory palladium-catalysed oxidative carbonylation reactions by searching for alternative substrates, solvents and even catalysts. In this paper, we demonstrate that pH oscillations of a similar pattern occur both in methanol and ethanol solutions, when using mono- and dialkyne-functionalised benzenes (phenylacetylene and diethynylbenzene, respectively) and when a non-leaching polyacrylate-palladium catalyst is used. The resulting oscillations are highly regular and can be sustained for a long time, suggesting that carbonylation reactions have strong potential for the discovery and development of new oscillatory chemical systems.

INTRODUCTION

Aiming to produce fully self-oscillatory materials [1], materials that act life-like and are able to carry and dispense their content in a predefined rhythm, we have focused on the oscillatory palladium-catalysed oxidative carbonylation reaction (PCOC) as a driving force. PCOC readily proceeds under mild temperatures (0-40 °C) and atmospheric pressure in batch and can sustain oscillations in pH, redox properties and turbidity over a prolonged period of time (monitored up to a month)[2–6]. We have made a number of advancements in the area of polymeric oscillators within the framework of PCOC. Firstly, we demonstrated polymeric alkyne-terminated polyethylene glycol (PEG) as a viable substrate [7]. Secondly, we studied polymer-bound catalytic species, successfully yielding oscillations under a range of conditions using polymeric dicyclohexylphenylphosphine palladium diacetate [8]. Aiming to aid the ongoing efforts of producing an all-polymer oscillating system, we report here studies employing a new substrate, catalyst and solvents, and showcase their ability to yield sustained oscillatory behavior.

EXPERIMENTAL

Reactions were performed at approximately 20 °C in a flat-bottom Erlenmeyer flask (100 mL) at constant stirring, while the HEL micronote (or Labview by Jon Howse) system logged pH and temperature within the bulk of the reaction mixture. Prior to the reaction, the pH probe was calibrated at room temperature against NIST-traceable buffer solutions of pH 2, 7 and 10. KI (4.150 g) and palladium diacetate ($\text{Pd}(\text{OAc})_2$) (30 mg) were charged into the flask in their solid state and suspended in 100 mL of solvent (methanol (MeOH), ethanol (EtOH), isopropanol (IPA) or PEG400-OH) by stirring. When polymeric catalyst is used in place of $\text{Pd}(\text{OAc})_2$, 200 mg of catalyst is added. In the experimental study employing diethynylbenzene (DEB) as the substrate, 90 mL of methanol is initially added.

The pH and temperature monitoring started while the KI and catalyst were dissolving and continued throughout the experiment. Stabilisation of pH indicated that the dissolution of KI was complete. Following this, the CO and air purging (15 mL min⁻¹ each) through the solution commenced. Once the pH value had stabilised following an initial pH drop, substrate was added. Either phenylacetylene (PhAc) (1.38 mL, 12.57 mmol) or diethynylbenzene (DEB) (1.585 g (12.57 mmol) in 10 mL of acetone) was used. A sample of the reaction mixture was taken at the end of the reaction and analysed using GC-MS to determine substrate conversion as well as product content. A Varian Saturn 2200 GC-MS fitted with a VF-5ms column (30 m) was used. The method was as follows: injector temperature 150 °C; helium flow rate 1 mL min⁻¹; oven temperature 100-195 °C over 35 min in 5 steps. Prior to analysis, samples were filtered over silica and then diluted 1:1 with 0.02 M solution of naphthalene in methanol. Naphthalene was used as an internal standard.

RESULTS AND DISCUSSION

Firstly, we explored four different solvents: MeOH, EtOH, IPA and PEG₄₀₀-OH, while phenylacetylene was used as a substrate and $\text{Pd}(\text{OAc})_2$ was used as a catalyst. This selection of solvents, which in carbonylation reactions also serve as reactants yielding the formation of esters, covered a range of densities and solubilities of carbon monoxide [9]. As can be noted from Figure 1a), following the initial pH drop oscillations in pH occurred only in the methanol and ethanol reaction systems. The drop of pH during CO purging was associated with the discoloration of the reaction solution, indicating the incorporation of CO into the structure of $\text{Pd}(\text{OAc})_2$ catalyst. The oscillations in MeOH and EtOH had similar amplitudes (0.40-0.50 for MeOH and 0.45-0.65 for EtOH) and periods (35-45 min for MeOH; and 40-45 min for EtOH),

although the induction period in EtOH was longer than in MeOH (275 min against 79 min). These similarities speak for the comparable affinity of both solvents towards the substrate and CO [7]. End sample GC-MS analysis showed that after 4000 min in both MeOH and EtOH, conversion of substrate was approximately the same (6.6% and 6.7%, respectively), with a similar distribution of products [8] (Figure 2, compounds **1-3** and **4-6**, respectively; Table 1). Only three products were generated as a result of the reaction: Z- and E-isomers of the diester product and a phenylfuranone compound.

At the same time, neither IPA, nor PEG400-OH demonstrated any significant pH changes upon purging with CO. No colour change associated with the incorporation of CO into the structure of the catalyst was observed [8]. While solubility of CO in PEG₄₀₀-OH is anticipated to be low, this should not be the case with IPA [9]. Yet, no substrate conversion was observed by GC-MS, indicating that in these two solvents in the absence of CO insertion into the Pd(OAc)₂ structure, the carbonylation did not occur.

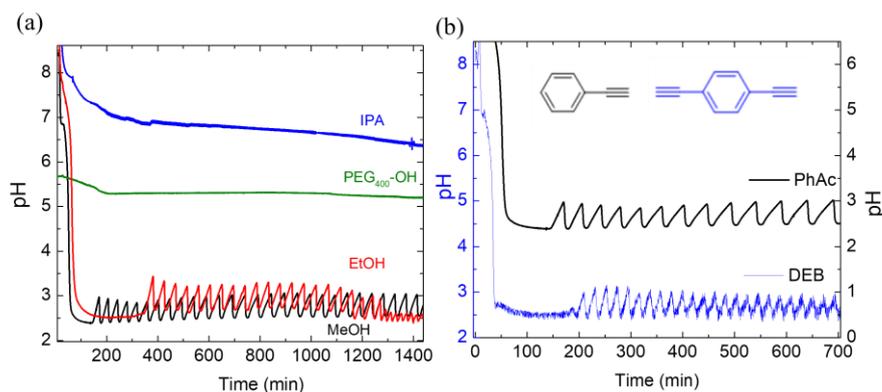


Figure 1. (a) pH recorded in the PCOC of phenylacetylene in methanol (black), ethanol (red), isopropanol (blue) and PEG₄₀₀-OH (green line). (b) pH recorded in the PdOAc-catalysed PCOC of phenylacetylene (PhAc, black line) and diethynylbenzene (DEB, blue line).

When phenylacetylene (PhAc) as a mono-functionalised substrate was substituted for diethynylbenzene (DEB) under the same conditions (MeOH as solvent and Pd(OAc)₂ as a catalyst), the pH oscillations, as well as induction period, were similar to those observed in the PhAc substrate system (Figure 1b). The period was shorter for DEB, 19-21 min against 35-45 min for PhAc with the same amplitude of 0.60-0.65 pH units. Importantly, as indicated by GC-MS analysis, in the DEB system, the second alkyne group did not participate in the reaction (Figure 2, compounds **7-9**; Table 1). This might be associated with the electronic effects of the substituents on the

benzene ring affecting the reactivity of the second alkyne group, and thus preventing it from participation in the carbonylation. This example of dialkyne-functionalised molecule and prospective studies where both alkyne groups should remain active in the PCOC reaction, suggests the importance of a spacer between these two functionalities.

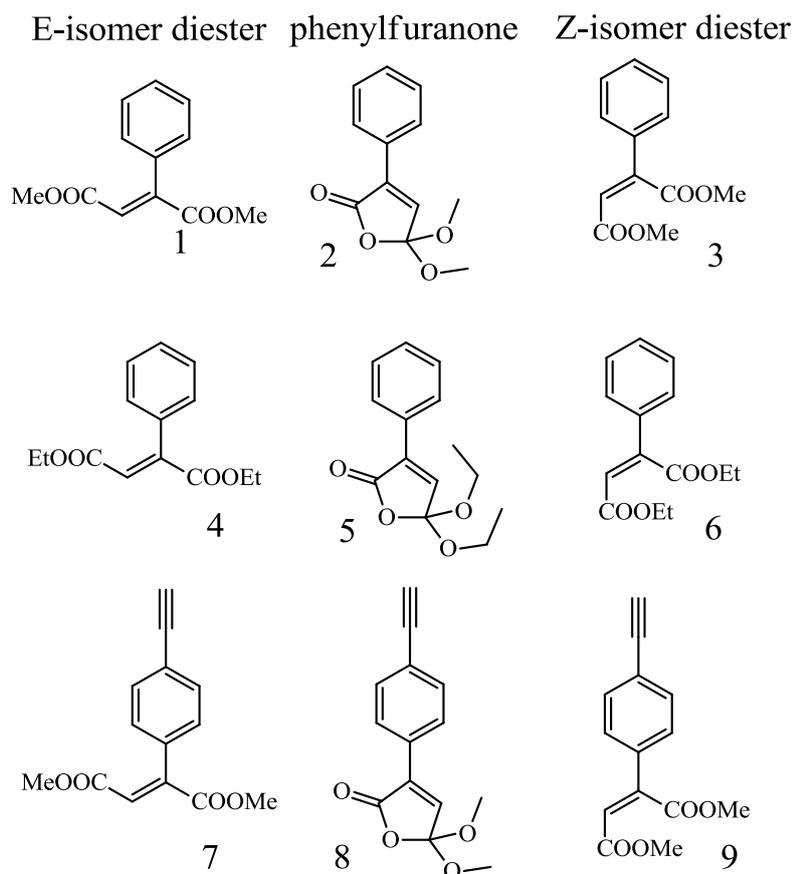


Figure 2. Products of the PCOC reaction: **1** dimethyl (2E)- 2- phenyl- 2- butenedioate; **2** 5,5- dimethoxy- 3- phenyl- 2(5H)- furanone; **3** dimethyl (2Z)- 2- phenyl- 2- butenedioate; **4** diethyl (2E)- 2- phenyl- 2- butenedioate; **5** 5,5- diethoxy- 3- phenyl- 2(5H)- furanone; **6** diethyl (2Z)- 2- phenyl- 2- butenedioate; **7** dimethyl (2E)- 2- (4-ethynyl)phenyl- 2- butenedioate; **8** 5,5- dimethoxy- 3- (4-ethynyl)phenyl- 2(5H)- furanone; **9** dimethyl (2Z)- 2- (4-ethynyl)phenyl- 2- butenedioate.

Table 1. Product distributions and starting material conversions for various PCOC conditions after 4000 min of the reaction.

	E-isomer, mmol (1, 4, 7)*	Z-isomer, mmol (3, 6, 9)*	phenyl furanone, mmol (2, 5, 7)*	Conversion [%]
PhAc/PdAc/MeOH	-	0.53	0.30	6.60
PhAc/PdAc/EtOH	0.036	0.50	0.30	6.70
PhAc/PdAc/IPA	-	-	-	-
PhAc/PdAc/PEG₄₀₀-OH	-	-	-	-
DEB /PdAc/MeOH	0.036	0.51	0.56	8.84
PhAc/ polyacrylate-Pd /MeOH	0.040	0.40	0.47	6.95
* the calculations were based on the assumption of the same detector response for E-isomer diester compounds 1,4,7; phenylfuranone compounds 2,5,8; and Z-isomer diester compounds 3,6,9.				

Finally, we substituted the small catalyst molecule Pd(OAc)₂, with a polymeric polyacrylate-Pd [11] in the same experiments (phenylacetylene (PhAc) as a substrate and MeOH as a solvent) (Figure 3). In polymeric polyacrylate-Pd the molecules of palladium serve as crosslinkers between the polymer chains, and polyacrylate as a counter ion, rather than as a ligand to support palladium [8]. This construct allowed a high loading of palladium to be achieved (16.26% as determined by inductively-coupled plasma optical emission spectrometry, ICP-OES) and zero leaching of palladium from the catalyst (as determined by ICP-OES, after the reaction).

In the polyacrylate-Pd-catalysed system, the pH behaved in a similar way to when small molecule Pd(OAc)₂ was used. An initial pH drop was recorded while the KI/catalyst mixture was purged with CO. A further pH drop was observed after addition of the PhAc substrate. This pH drop then recovered from 5.05 to 5.59 when the pH oscillations started, 206 min after addition of PhAc. The oscillations occurring at this high pH are rarely observed [4,12]. It is worth noting that in the case of polyacrylate-Pd, the recorded oscillations had a period of 18-24 min and a small amplitude of 0.1-0.15 pH units.

After 4000 min, the conversion was 6.95%, very similar to conversion in the Pd(OAc)₂ systems in MeOH and EtOH (Table 1). However, product distribution was different, with almost equal concentrations of compounds **2** and **3**.

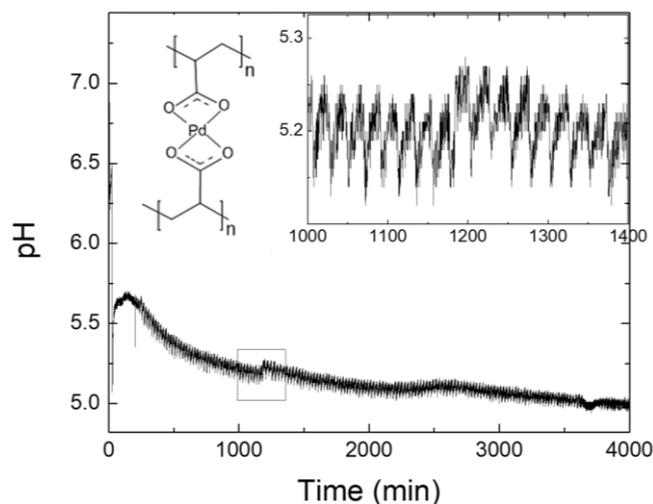


Figure 3. pH recorded in PCOC of phenylacetylene (PhAc) in methanol using polyacrylate-Pd catalyst. The structure of the catalyst is shown as an inset.

CONCLUSION

We have demonstrated the versatility of the PCOC reaction by obtaining oscillations in pH in Pd(OAc)₂-catalysed carbonylation of phenylacetylene in both ethanol and methanol, solvents with a similar carbon monoxide solubility, whereas no oscillations were observed in isopropanol or PEG400-OH. Furthermore, oscillations had a very similar pattern, period and amplitude. The same oscillatory patterns were demonstrated when dialkyne-functionalised substrate was employed, with only one alkyne group participating in the reaction (as determined by GC-MS). Finally, oscillations were demonstrated, using polymeric polyacrylate-Pd catalyst with zero leaching rates, a promising candidate for future exploration in all-polymeric self-oscillating systems.

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