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Thibault Cantat

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## Catalytic Carbonylation of Acrylic Acid to Succinic Anhydride\*\*

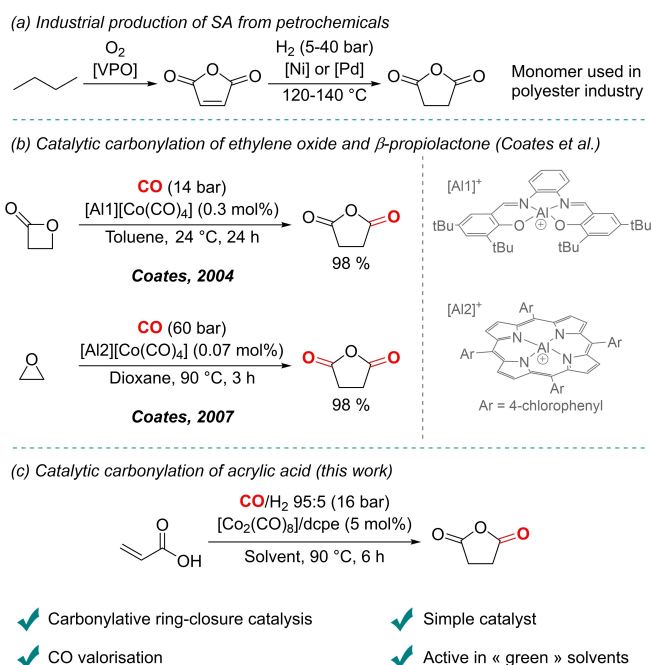
Marie-Hélène Pietraru,<sup>[a]</sup> Nicolas Lentz,<sup>[a]</sup> Louise Ponsard,<sup>[a]</sup> Emmanuel Nicolas,<sup>\*,[a]</sup> and Thibault Cantat<sup>\*,[a]</sup>

Alternative sources for polymeric materials have been sought in the past few years to reduce our dependence on fossil feedstock. We report the catalytic carbonylation of acrylic acid, a platform chemical that can be bio-sourced, as a new pathway toward the formation of a useful monomer to polyesters, namely succinic anhydride. The novel system reported herein tackles the difficult carbonylation of unsaturated carboxylic acids through the utilization of an Earth-abundant metal

catalyst,  $[\text{Co}_2(\text{CO})_8]$ , in presence of a bidentate ligand, 1,2-bis(dicyclohexylphosphino)ethane (dcpe), and  $\text{H}_2$ . We investigated the influence of the reaction conditions through the variations of metal, ligand, temperature, pressure, and gas composition. The carbonylative ring-closure of acrylic acid was successfully obtained in high yield and selectivity toward the formation of succinic anhydride using mild conditions (90 °C and 16 bar of  $\text{CO}/\text{H}_2$  95:5).

## Introduction

The rising cost, environmental impact, and recyclability issues of petro-sourced polymers have led to direct research efforts to use alternative resources to produce plastics, either *via* the use of bio-sourced monomers<sup>[1]</sup> or the integration of waste molecules like  $\text{CO}_2$  in the polymeric chain.<sup>[2]</sup> Polyesters are desirable targets for applications such as packaging, textile fibers, or performance materials, and can be obtained from the copolymerization of epoxides and cyclic anhydrides, such as succinic anhydride (SA).<sup>[3]</sup> The current industrial synthesis of SA relies on the oxidation of *n*-butane to maleic anhydride (Scheme 1a),<sup>[4]</sup> followed by its hydrogenation. Alternative pathways to form SA from  $\beta$ -propiolactone or ethylene oxide relying on carbonylation reactions have also been uncovered (Scheme 1b).<sup>[5]</sup> In the context of the rising interest in the sourcing of SA from biomass,<sup>[6]</sup> we propose herein an alternative pathway starting from acrylic acid (AA), a widespread platform chemical, whose production from the dehydration of lactic acid or glycerol is under study.<sup>[7]</sup> Through catalyst design, we report the



**Scheme 1.** (a) Industrial production of SA; [VPO] = vanadium phosphorus oxide catalyst; (b) previous work on the synthesis of SA from the carbonylation of unsaturated molecules; (c) this work.

first example of the catalytic carbonylative ring-closure of AA to SA (Scheme 1c).

The carbonylation of AA is a longstanding challenge, and interest in such a reaction emerged in the 1960s (Scheme 2). Falbe reported the carbonylation of acrylamide to succinimide in the presence of cobalt carbonyl,<sup>[8]</sup> but a few years later he noted that attempts to apply such a reaction to AA failed due to polymerization of the substrate under the applied reaction conditions (200 °C,  $P_{\text{CO}} = 300$  bar).<sup>[9]</sup> In 1969, Tsuji observed AA as a side-product of the catalytic carbonylation of  $\beta$ -propiolac-

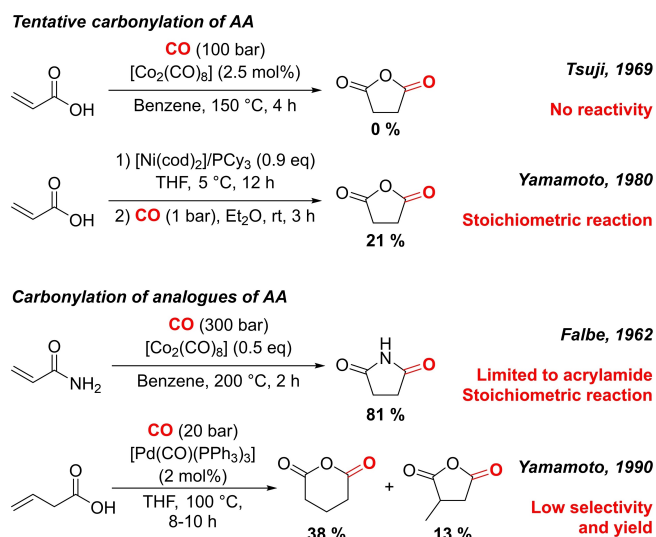
[a] M.-H. Pietraru, Dr. N. Lentz, Dr. L. Ponsard, Dr. E. Nicolas, Dr. T. Cantat  
Université Paris-Saclay, CEA, CNRS, NIMBE  
91191 Gif-sur-Yvette (France)  
E-mail: emmanuel.nicolas@cea.fr  
thibault.cantat@cea.fr

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Scheme 2. Carbonylative ring-closures of bifunctional alkenes

tone to SA, however using AA as the starting material led to no observation of SA, and the authors ruled out the possibility to carbonylate AA in their conditions.<sup>[10]</sup> It is only in 1980 that the carbonylation of AA to SA was unlocked by Yamamoto, yet with a stoichiometric amount of metal substrate *via* a two-step process: the formation of a nickel metallacycle from  $[\text{Ni}(\text{cod})_2]$ ,  $\text{PCy}_3$  and AA, and its subsequent carbonylation, yielding 21% of SA.<sup>[11]</sup> The palladium-catalyzed carbonylative ring-closure of 3-butenic acid was later achieved by the same group, producing glutaric anhydride and methylsuccinic anhydride in moderate yields (respectively 38% and 13%). The authors reported however that methacrylic acid polymerized under these conditions.<sup>[12]</sup>

Remarkably, hydroformylation, although developed and studied since the first half of the 20<sup>th</sup> century,<sup>[13]</sup> has been scarcely applied to unsaturated acids.<sup>[14]</sup> To the best of our knowledge, the only two examples of hydroformylation of  $\alpha,\beta$ -unsaturated acids described in the literature required strategies of protection of the carboxylic acid function, either through hydrogen bonding to the ligand coordinated to the active metallic site,<sup>[15]</sup> or *via* its fixation on a polymeric support.<sup>[16]</sup> Other examples of carbonylation of unsaturated acids are limited to the formation of diacids or diesters.<sup>[17]</sup> As highlighted by Elsevier and de Bruin in the case of hydrogenation reactions,<sup>[18]</sup> carboxylic acids are challenging substrates because of their ability to coordinate to metal centers, often leading to the deactivation of the organometallic catalyst.

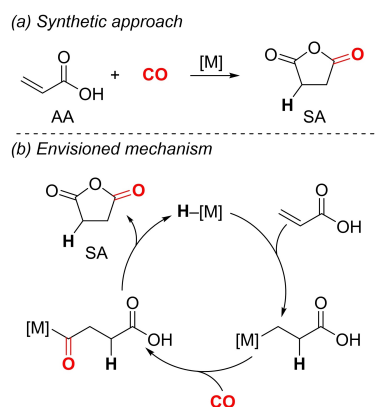
The selective, catalytic carbonylation of AA to SA thus constitutes a challenge in terms of reactivity: how to achieve the carbonylation of acrylic acid without polymerization of the starting material, and without relying on a protection strategy of the carboxylic acid function. In this work, we report that the combination of a phosphine-modified cobalt carbonyl catalyst and moderate temperature and pressure enabled for the first time the catalytic carbonylation of AA to SA.

## Results and Discussion

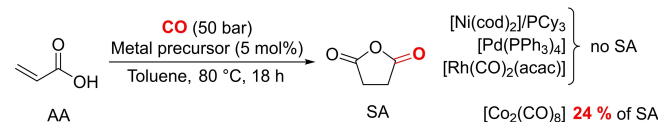
Based on a simple retrosynthetic analysis of SA production from AA, and inspired by the mechanism of hydroformylation, we envisioned a catalytic cycle (Scheme 3), where AA inserts into the  $[\text{M}]-\text{H}$  bond of a reactive metal-hydride complex, to afford an intermediate acyl complex after CO insertion. A final step, where the reactive carboxylic acid group ring-closes by nucleophilic addition onto the carbonyl group, would close the catalytic cycle by forming the C–O bond.

The carbonylation of AA was first attempted using metal catalysts previously described as active in the carbonylation of unsaturated substrates.<sup>[11–12,16]</sup> SA was not observed in the presence of catalytic amounts of  $[\text{Ni}(\text{cod})_2]/\text{PCy}_3$ ,  $[\text{Pd}(\text{PPh}_3)_4]$ , or  $[\text{Rh}(\text{CO})_2(\text{acac})]$ , whereas 24% of SA was obtained using  $[\text{Co}_2(\text{CO})_8]$  (Scheme 4). Toluene was selected as a solvent after a first screening, due to its high boiling point and its absence of interaction with cobalt carbonyl complexes (see S.I. for details, Section 1.1).

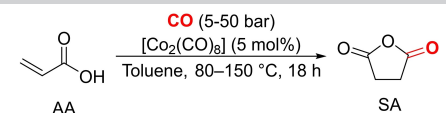
The study of CO pressures ranging from 5 to 50 bar, and temperatures ranging from 80 to 150 °C could not afford a yield higher than 24% (Table 1). Overall, it was detrimental either to increase the temperature to 150 °C (1, 3 and 6% yield of SA at respectively 5, 15 and 50 bar), or to decrease the pressure to 5 bar (9, 2 and 1% yield of SA at respectively 80, 110 and 150 °C). These trends are in line with the observations of Tsuji, who reported no catalytic activity at high pressure and temperature (Scheme 2, 100 bar, 150 °C). Three sets of pressure/temperature afforded similar yields, namely 15 bar/80 °C (23%),



Scheme 3. (a) Synthetic approach for the carbonylation of AA to SA; (b) envisioned mechanism for the carbonylation of AA to SA.

Scheme 4. Screening of metal catalysts. Conditions: AA (1 mol L<sup>-1</sup>) and mesitylene (internal standard, 10 mol %) with catalyst (5 mol %) in toluene (2 mL), heated for 18 h under CO pressure. SA yields measured by GC-MS analysis.

**Table 1.** Temperature and pressure optimization.<sup>[a]</sup>

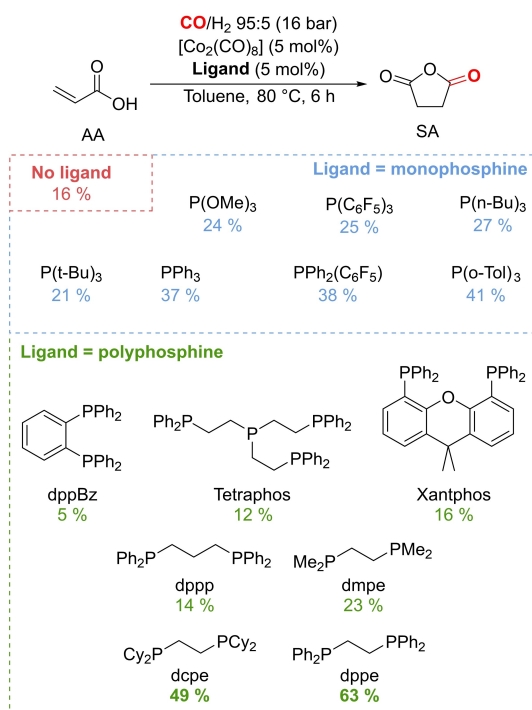


T	80 °C	110 °C	150 °C	
P	5 bar	8% (6 h), 9%	2%	1%
	15 bar	18% (6 h), 23%	5% (6 h), 8%	3%
	50 bar	24%	22%	6%

[a] Conditions: AA (1 mol·L<sup>-1</sup>) and mesitylene (internal standard, 10 mol%) with [Co<sub>2</sub>(CO)<sub>8</sub>] (5 mol%) in toluene (2 mL), heated for 18 h under CO pressure. SA yields measured by GC-MS analysis.

50 bar/80 °C (24%), and 50 bar/110 °C (22%), and the mildest conditions were chosen for the rest of the study.

Interestingly, at 80 °C and under 15 bar of CO, the yield of SA was already of 18% after 6 h of reaction (vs. 23% after 18 h), suggesting a deactivation of the catalytic system. To circumvent this issue while improving the activity of the catalytic system, two additional parameters were explored (Scheme 5). First, we reasoned that the introduction of a small amount of H<sub>2</sub> in the gas phase would facilitate the formation of cobalt hydride species (See Scheme 3).<sup>[19]</sup> When a gas mixture of CO/H<sub>2</sub> 95:5 (16 bar) was applied, neither the stability of the catalytic system, nor the activity was improved, since 16% and 17% of SA were recovered after respectively 6 and 18 h of reaction. Second,



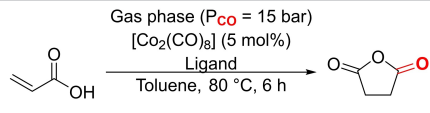
**Scheme 5.** Screening of phosphine ligands. Conditions: AA (1 mol·L<sup>-1</sup>) and mesitylene (internal standard, 10 mol%) with catalyst (5 mol%) and ligand (5 mol%) in toluene (2 mL), heated at 80 °C for 6 h under a CO/H<sub>2</sub> (95:5) pressure of 16 bar. SA yields measured by GC-MS analysis.

phosphine ligands, which are known to tune the reactivity of cobalt carbonyl complexes,<sup>[20]</sup> were selected among mono and polyphosphines, with aryl or alkyl substituents, showcasing different electronic and steric properties. Compared to the ligand-free system, monophosphines improved the catalytic system: specifically PPh<sub>3</sub>, PPh<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>), and P(o-Tol)<sub>3</sub> yielded 37 to 41% of SA. Various behaviors were observed among polyphosphines depending on their nature: while dppBz or Tetraphos reduced the activity of the catalyst, dcpe and dppe afforded SA in respectively 49 and 63% yield.

With these encouraging results in hand, we wanted to understand whether the good performances of the diphosphine dppe compared to the monophosphine PPh<sub>3</sub> could simply arise from the difference in cobalt-to-phosphorus ratios (Co/P = 1 or 2). Under a 95:5 CO/H<sub>2</sub> pressure, at Co/P = 2, dppe and PPh<sub>3</sub> yielded respectively 55 and 37% (Table 2, entries 1 and 2), whereas at Co/P = 1, they yielded respectively 63 and 13% (Table 2, entries 4 and 5). dppe outperformed PPh<sub>3</sub> at both ratios, indicating a positive impact of the bidentate character of the ligand on the activity of the cobalt catalyst. Furthermore, both phosphines follow opposite trends: upon decreasing Co/P from 2 to 1, while the yield of SA increased from 55 to 63% with dppe, it decreased from 37 to 13% with PPh<sub>3</sub>. This difference in activity of PPh<sub>3</sub> and dppe was also observed with the addition of H<sub>2</sub> in the gas phase: whereas H<sub>2</sub> did not affect the yield of SA with PPh<sub>3</sub>, it had a significant positive influence with dppe, affording 55 instead of 28% of SA for Co/P = 2 (Table 2, entry 2) and 63 instead of 7% of SA for Co/P = 1 (Table 2, entry 5). The diphosphine dcpe presented the same trend as dppe (Table 2, entries 3 and 6).

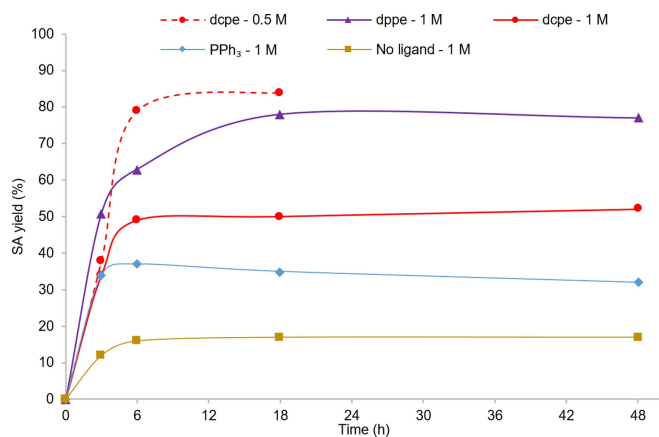
The influence of the ligands PPh<sub>3</sub>, dcpe and dppe was studied over time (0–48 h, Figure 1). In absence of any ligand, the yield of SA was limited (17%) and did not evolve after 6 h. In the presence of ligands, the activity was overall improved and higher yields of SA, up to 52 and 77%, were obtained for dcpe and dppe, respectively; but deactivation of the catalyst still occurred. We hypothesized that the observed deactivation could be caused by the carboxylic acid substrate.<sup>[18]</sup> To reduce this side-reaction, the concentration of AA was lowered from 1 mol·L<sup>-1</sup> to 0.5 and 0.25 mol·L<sup>-1</sup>. For all ligands, lowering the concentration of AA to 0.25 mol·L<sup>-1</sup> was detrimental, since

**Table 2.** Study on the ratio of Co/P with PPh<sub>3</sub>, dcpe and dppe.<sup>[a]</sup>



Entry	Co/P	Ligand (mol%)	CO	CO/H <sub>2</sub> 95:5
1	2	PPh <sub>3</sub> (5)	39%	37%
2	2	dppe (2.5)	28%	55%
3	2	dcpe (2.5)	36%	42%
4	1	PPh <sub>3</sub> (10)	12%	13%
5	1	dppe (5)	7%	63%
6	1	dcpe (5)	23%	49%

[a] Conditions: AA (1 mol·L<sup>-1</sup>) and mesitylene (internal standard, 10 mol%) with [Co<sub>2</sub>(CO)<sub>8</sub>] (5 mol%) in toluene (2 mL), heated for 18 h under CO (partial pressure of 15 bar). SA yields measured by GC-MS analysis.



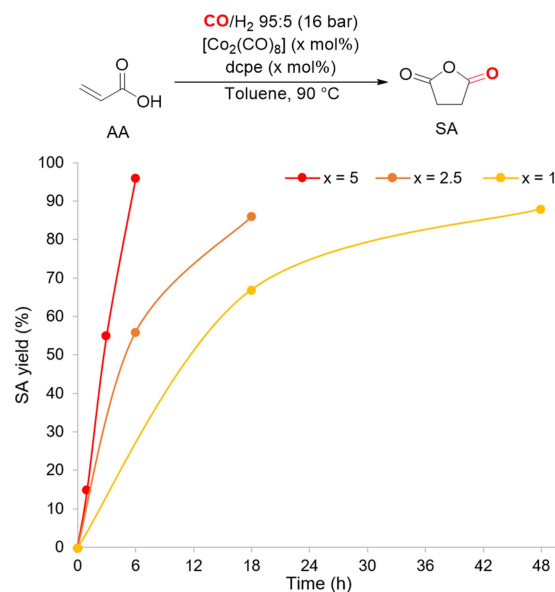
**Figure 1.** SA yield obtained over time from the carbonylation of AA. Conditions: AA (0.5 or 1 mol·L<sup>-1</sup>) and mesitylene (internal standard, 10 mol%) with [Co<sub>2</sub>(CO)<sub>8</sub>] (5 mol%) and ligand (5 mol%) in toluene, heated at 80 °C for the indicated duration under a CO/H<sub>2</sub> (95:5) pressure of 16 bar. SA yields measured by GC-MS analysis. N.B.: each point of the graph is a distinct experiment.

respectively 20, 16, and 26% of SA were obtained in presence of PPh<sub>3</sub>, dcpe, and dppe (Table 3, entry 1). Surprisingly, whereas lowering [AA] to 0.5 mol·L<sup>-1</sup> had no effect with PPh<sub>3</sub> and dppe, it led to a remarkable increase of the yield of SA with dcpe, affording 79% after 6 h (Table 3, entry 2 and Figure 1). This effect may be due to the acidity of the reaction mixture, and to probe this hypothesis, propionic acid (PA, 1 eq) was added in the reaction mixture. At [AA]=[PA]=0.25 mol·L<sup>-1</sup>, this addition contributed to an increase in yield from 16 to 52%, whereas at [AA]=[PA]=0.5 mol·L<sup>-1</sup>, it led to a slight reduction of activity (from 79 to 69%). These results match the trends observed respectively at [AA]=0.5 and 1 mol·L<sup>-1</sup>, and suggest that the acidity of the reaction mixture is a key parameter in controlling the outcome of the reaction.

Using these conditions with a slight increase in temperature to 90 °C led to the formation of SA in a quantitative yield of 96%. We tested whether the catalyst loading could be decreased: the optimized reaction was tested at 1, 2.5, and 5 mol% loading (Figure 2). The catalytic activity was fully

Table 3. Influence of AA concentration. <sup>[a]</sup>				
Entry	AA [AA] (mol·L <sup>-1</sup> )	Ligand PPh <sub>3</sub>	SA	
			dcpe	dppe
1	0.25	20%	16%	26%
2	0.5	37%	79%	64%
3	1	37%	49%	63%

[a] Conditions: AA and mesitylene (internal standard, 10 mol%) with [Co<sub>2</sub>(CO)<sub>8</sub>] (5 mol%) and ligand (5 mol%) in toluene (1 or 2 mL), heated for 6 h under CO/H<sub>2</sub> 95:5 pressure (16 bar). SA yields measured by GC-MS analysis.

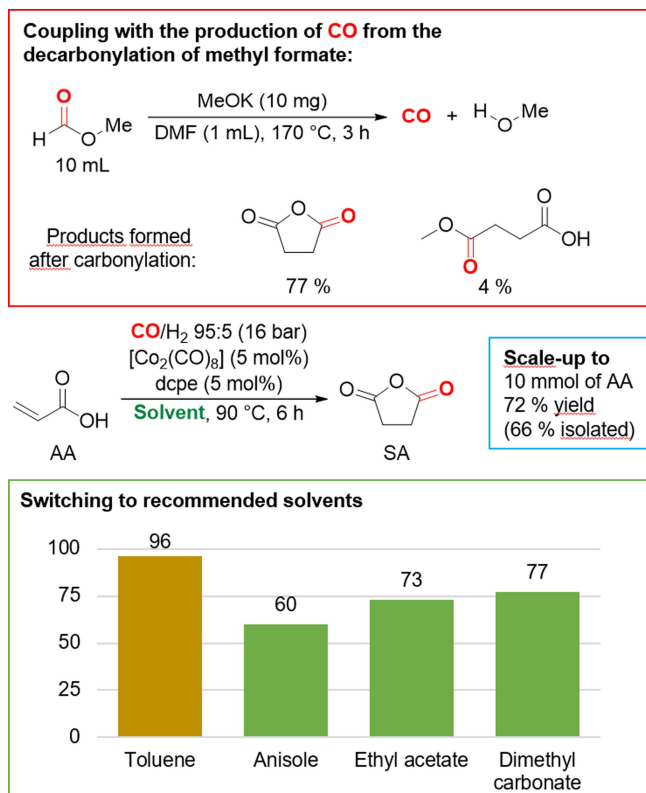


**Figure 2.** SA yield obtained over time from the carbonylation of AA, at different catalyst loadings. Conditions: AA and mesitylene (internal standard, 10 mol%) with [Co<sub>2</sub>(CO)<sub>8</sub>] (x mol%) and dcpe (x mol%) in toluene (2 mL), heated at 90 °C under CO/H<sub>2</sub> 95:5 pressure (16 bar). SA yields measured by GC-MS analysis.

retained, even though the reaction proceeded more slowly: with 2.5 mol% of catalyst, 18 h were required to yield 86% of SA, when at 1 mol% loading, 48 h were required to form 88% of SA. For practical reasons, we kept the catalytic loading at 5 mol% for the remainder of the study.

We probed the applicability of the optimized system in various settings: scaling-up, using less toxic solvents, or different sourcing of CO. First, the reaction was successfully scaled-up to 5 or 10 mmol of AA, and afforded SA in 82 and 72% GC-MS yield respectively (Figure 3, middle). The latter experiment gave, after isolation, 665 mg (66 % yield) of analytically pure SA.<sup>[21]</sup> Second, three “recommended solvents”, anisole, ethyl acetate, and dimethyl carbonate, were selected based on the classification in terms of health, environment, and toxicity proposed by the group of Prat.<sup>[22]</sup> The reaction proceeded with good yields when using such alternative solvents, leading to the formation of SA in 60%, 73%, and 77% yield respectively (Figure 3, bottom). Finally, the use of an alternative source of CO was tested. The decarbonylation of formic acid, a C<sub>1</sub> chemical which can derive from biomass or CO<sub>2</sub> electroreduction,<sup>[23]</sup> was performed, using methyl formate as a recyclable intermediate (Figure 3, top).<sup>[24]</sup> The reaction was setup using the standard conditions, then the atmosphere of the autoclave was purged with H<sub>2</sub>, and finally 16 bar of CO, previously synthesized *via* the methoxide-catalyzed decarbonylation of methyl formate, were introduced. After 6 h at 90 °C, SA was formed in 77% yield, together with 4% of monomethyl hydrogen succinate. The latter side-product is likely formed from the reaction of SA with methanol or through alkoxycarbonylation of AA,<sup>[25]</sup> presumably present as a vapor impurity in the stream of CO.





**Figure 3.** Application of the optimized conditions including scale-up, greener solvents and coupling with CO generated from a liquid source.

## Conclusions

In summary, we have reported the first catalytic carbonylative ring-closure of acrylic acid to succinic anhydride, using cobalt carbonyl, in the presence of a bidentate phosphine ligand and hydrogen. The formation of succinic anhydride was achieved in quantitative yield after 6 h at 90 °C at a low pressure of CO/H<sub>2</sub> (95:5; 16 bar). The catalytic system is efficient in alternative solvents, scaled-up to gram-scale, and alternative sources of CO have been used. To get further insights into the mechanism of the reaction, and understand the exact role of the ligands and hydrogen, our research is currently ongoing on the speciation of the different cobalt complexes at play in the reaction and their implication in the catalytic cycle.

## Experimental Section

### Representative procedure for the carbonylation of acrylic acid

**Preparation of the autoclave** Before each experiment, the autoclave was thoroughly washed with ethanol (bottom and top part), while the glass tube and the magnetic stirrer were washed with ethanol, acetone, and diluted nitric acid to eliminate any residues of metallic compounds. The bottom part of the autoclave, the glass tube, and the magnetic stirrer were dried in an oven at 120 °C for at least 30 minutes. The top part was dried as much as possible under a

flow of compressed air. The bottom part of the autoclave, a glass tube, and a magnetic stirrer were cooled at room temperature, then the autoclave was locked thanks to a 42 mm wrench. In order to remove any residual trace of washing solvents, the autoclave was put under vacuum for at least 20 minutes. Finally, the tightness of the autoclave was checked by putting it under pressure for at least 10 minutes and checking if the pressure decreased, and the autoclave was flushed three times with 10 bar of the gas mixture used for the reaction.

**Preparation of the mixture** –Inside the dry box, in a vial, [Co<sub>2</sub>(CO)<sub>8</sub>] (17.1 mg, 0.05 mmol, 5 mol%) and 1,2-bis(dicyclohexyl)phosphinoethane (21.1 mg, 0.05 mmol, 5 mol%) were weighed and mixed in toluene (2 mL). Bubbling (of carbon monoxide) was observed. When the bubbling stopped, mesitylene (internal standard, 14 μL, 0.1 mmol, 0.1 eq) was added in the vial, followed by acrylic acid (68 μL, 1 mmol). The mixture was homogenized, then taken into a syringe. The needle of the syringe was stuck in the septum of a sealed vial to keep the mixture under inert atmosphere during the transfer outside the dry box.

**Injection in the autoclave and start of the reaction** –The mixture prepared in the dry box and collected in the syringe was injected quickly in the purged autoclave thanks to the use of a long metallic needle. The autoclave was purged one more time with 10 bar of the gas mixture used for the reaction, *i.e.* CO/H<sub>2</sub> 95:5. The autoclave was then pressurized at 16 bar with the gas mixture, and put in a heating block for 6 h at 90 °C.

**End of the reaction and analysis of the raw mixture** – The reaction was stopped by cooling the autoclave in an ice bath. After depressurization and unlocking of the autoclave, ethyl acetate, a solvent that solubilizes well succinic anhydride, was added in the glass tube (3 mL of solvent per mmol of acrylic acid initially injected). According to Yang *et al.*, this volume is twice the minimal amount required to dissolve 1 mmol of SA at 288 K.<sup>[26]</sup> Acetone can also be used to dissolve SA in a similar manner.

The mixture was then filtered on a Celite pad, and a sample was collected for GC-MS analysis.

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** carbonylation · acrylic acid · succinic anhydride · cobalt · catalysis

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