**In silico** investigation of ligand-regulated palladium-catalysed formic acid dehydrative decomposition under acidic conditions

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**Introduction**

Carbonylation reactions constitute a potent tool to manufacture carboxylic acids and their derivatives both in industry and academic organic synthesis. In general, the proceeding of carbonylation requires the use of toxic carbon monoxide, which thus usually demands certified high pressure reaction vessels. Therefore, developing non-gaseous CO surrogate for conducting safe and facile-operation carbonylation with stoichiometric amount of CO in common Pyrex glass vessels (e.g., the two-chamber reactor and sealed glass tube) is an important and ongoing research topic in the realm of homogenous catalysis. Among these established CO surrogates, formic acid and its derivatives is one kind of versatile atom-economic C1 source. Different to the decomposition of formic ester or N-formyl imides releasing CO in the basic conditions for the carbonylation of aryl or alkyl halides, the dehydrative decomposition of HCOOH to CO generally depends on the Morgan reaction using excess strong mineral acid (e.g., excess high-concentration sulfuric acid), which is incompatible to the conditions for most of transition-metal catalysed carbonylation reactions. Moreover, undesired dehydrogenation of HCOOH to CO\, and \, H_2, which is more thermodynamically favoured, can facilely occur in the presence of various homogenous transition-metal complex catalysts or heterogeneous catalysts and lead to the reduction of unsaturated bonds. Thus, to avoid this side reaction, acetic anhydride has to be added as the activator for in-situ generating the more active CO source mixed anhydride. In 2018, Beller and co-workers achieved the selective CO generation directly from HCOOH under acidic condition by a palladium-catalysed system with bidentate tertiary phosphine ligand bearing pyridyl substituents (py/bpx), which was derived from 1,2-bis(di-tert-butylphosphino)methylbenzene (d'pbx) (Figure 1). The utility of this catalytic system in the autoclave-free hydrocarbonylation of all kinds of alkenes was also demonstrated.
The ligand-regulated palladium-catalysed selective decomposition of HCOOH to CO.

PTSA = para-toluenesulfonic acid.\(^2\) Molar percentage of gaseous products and in parentheses are total pressure (unit: bar) after reaction.\(^3\) Without adding PTSA.

The experimental investigation by Beller et al. disclosed that the activity and selectivity of Pd catalyst to the HCOOH dehydration was regulated by both the ligand and the acid promoter (Figure 1). The ligand py\(\text{t}bpx\) resulted from replacing two tetra-butyl substituents in d\(\text{t}bpx\) with 2-pyridyl groups exhibited significantly higher CO selectivity than the original d\(\text{t}bpx\) ligand (67\% vs. 26\%). Adding catalytic amount of para-toluenesulfonic acid (PTSA) can improved the CO selectivity (88\% and 87\%, respectively). Meanwhile, the activity towards dehydration using Pd-py\(\text{t}bpx\) complex is considerably increased (5.5 bar vs. 2.2 bar) and higher than that of Pd-d\(\text{t}bpx\) complex (more detailed results see Figure 1 of ref. 25). These results indicated the importance of “built-in base” (i.e., 2-pyridyl group) in enhancing the activity and selectivity of palladium catalyst.\(^2\) Since the plausibility of in-situ generated methyl formate acting as CO-releasing agent has been experimentally ruled out\(^2\) (details see Scheme 4 and S1 of ref. 25), we intended to elucidate the role of acid promoter and basic 2-pyridyl group of the ligand in palladium-catalysed formic acid dehydration decomposition. By density functional theory-based computation, the difference between the Pd-py\(\text{t}bpx\) and Pd-d\(\text{t}bpx\) catalysts on the mechanism of formic acid dehydration to CO was revealed.

**Computational method**

All DFT calculations were performed using Gaussian 16 program.\(^2\) Considering the applicability of meta-generalized gradient approximation (meta-GGA) functional M06\(^2\) on homogeneous organometallic thermochemistry,\(^2\) the M06 functional in conjugation with the def2-SVP basis set\(^3\) was used for structure optimization. Corresponding frequency calculation using the same method was done to characterize the nature of the optimized structures; i.e., energy minimums without imaginary frequencies or transition states with only one imaginary frequency. Intrinsic reaction coordinate (IRC) was used to check the imaginary model that connects the initial and the final states. In addition, we used M06 in conjugation with the def2-TZVP basis set to conduct the self-consistent reaction field (SCRF) single-point calculations based on the M06/def2SVP-optimized geometries by using the SMD solvation model\(^3\) and methanol as solvent to Gibbs free energies (M06-SCRF/def2-TZVP//M06/def2-SVP). The thermal corrections to Gibbs free energy at 373 K calculated by the Shermo program\(^3\) were added to the total electronic energies from the SMD single-point energy calculations. The corrected Gibbs free energy (\(\Delta G\)) at 373 K were therefore used in the following discussion and comparison.

**Results and discussion**

HCOOH dehydration by Pd-py\(\text{t}bpx\) or Pd-d\(\text{t}bpx\) (paths A-D)

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**Figure 1.** The ligand-regulated palladium-catalysed selective decomposition of HCOOH to CO. PTSA = para-toluenesulfonic acid.\(^2\) Molar percentage of gaseous products and in parentheses are total pressure (unit: bar) after reaction.\(^3\) Without adding PTSA.
Experimental results have demonstrated that the presence of PTSA is critical to the activity and selectivity of Pd-catalysed dehydration of HCOOH.\textsuperscript{25} Thus, two sets of mechanism with or without the aid of PTSA promoter were therefore considered for this process. A previous study has revealed that the nitrogen atom of the pyridyl ring has a higher proton affinity than the palladium atom in the acidic conditions;\textsuperscript{26} similar trend is also found in this study. Therefore, the cationic Pd\textsuperscript{d}-py/bpx complex 1-py\textsuperscript{bpx} bearing protonated pyridyl group is regarded as the active species for py/bpx ligand, while the zero-valent palladium complex is chosen as the active species for d’bpx ligand.

Fig. 2 illustrated the two plausible paths for HCOOH dehydration to CO catalysed by the palladium catalyst of py/bpx (path A and B). Path A starts from the C-H activation of HCOOH by 1-py\textsuperscript{bpx} (HCOOH + 1-py\textsuperscript{bpx} \rightarrow 2-py\textsuperscript{bpx} via TS1-py\textsuperscript{bpx}) followed by the intramolecular dehydration facilitated by the pyridinium group (2-py\textsuperscript{bpx} \rightarrow 3-py\textsuperscript{bpx} + H\textsubscript{2}O via TS2-py\textsuperscript{bpx}). The first step is endergonic by 10.3 kcal/mol, with a barrier of 12.3 kcal/mol. The generated 2-py\textsuperscript{bpx} has an intramolecular hydrogen-bonding between the OH of COOH group and the proton attaching to the nitrogen atom of pyridyl group. The combination of OH and (N-)H and subsequent delivering one H\textsubscript{2}O molecule has low barrier of 11.6 kcal/mol and is highly exergonic by 17.6 kcal/mol. Afterwards, the carbonyl palladium hydride complex 3-py\textsuperscript{bpx} can directly release CO with the formation of palladium hydride complex 4b-py\textsuperscript{bpx} followed by the direct hydrogen migration of 4b-py\textsuperscript{bpx} to regenerate 1-py\textsuperscript{bpx} via TS3b-py\textsuperscript{bpx}. As shown in Fig. 2, the decarbonylation process is highly endergonic by 29.7 kcal/mol, but the hydrogen migration is almost barrierless. Considering the co-existence of PTSA, HCOOH and CH\textsubscript{3}OH in the catalytic system, PTSA-, HCOOH- or CH\textsubscript{3}OH-assisted hydrogen migration processes are investigated. It is found that although the ligand exchange with these three species is all endergonic, the three intermediates 4-py\textsuperscript{bpx}, 4a-py\textsuperscript{bpx} and 4c-py\textsuperscript{bpx} are all thermodynamically more stable than the 4b-py\textsuperscript{bpx} (1.5, 4.1, 4.6 vs. 22.4 kcal/mol). And the apparent Gibbs free energies of TS3-py\textsuperscript{bpx} and TS3a-py\textsuperscript{bpx} are lower than that of TS3b-py\textsuperscript{bpx} (15.5, 16.1 vs. 20.3 kcal/mol), while the Gibbs free energy of TS3c-py\textsuperscript{bpx} is much higher than that of TS3b-py\textsuperscript{bpx} (34.3 vs. 20.3 kcal/mol). Therefore, we can deduce that PTSA- and HCOOH-assisted hydrogen migration processes are both possible. Since the following three reasons: i) the intermediate 4-py\textsuperscript{bpx} is more stable than 4a-py\textsuperscript{bpx} by 2.6 kcal/mol; ii) the Gibbs free energy of TS3-py\textsuperscript{bpx} is 0.6 kcal/mol lower than that of TS3a-py\textsuperscript{bpx}; iii) the N-protonation of ligand’s pyridyl group in 3-py\textsuperscript{bpx} by PTSA is exothermic, while the corresponding protonation by less-acidic HCOOH is endothermic (more details see Fig. S1 in ESI), the PTSA-aid regeneration of 1-py\textsuperscript{bpx} is more facile than the corresponding process with HCOOH.

Path B also starts from the C-H activation of HCOOH by 1-py\textsuperscript{bpx} (HCOOH + 1-py\textsuperscript{bpx} \rightarrow 2a-py\textsuperscript{bpx} via TS1a-py\textsuperscript{bpx}). Differently, the intramolecular hydrogen-bonding in TS1a-py\textsuperscript{bpx} and 2a-py\textsuperscript{bpx} lies between the oxygen atom of carbonyl group and the H-N moiety of pyridinium group. When 2a-py\textsuperscript{bpx} undergoes the intramolecular dehydration to 3a-py\textsuperscript{bpx} facilitated by PTSA or HCOOH as the proton shuttle respectively via TS2a-py\textsuperscript{bpx} and TS2b-py\textsuperscript{bpx} both containing eight-membered proton transfer ring or TS2d-py\textsuperscript{bpx} and TS2e-py\textsuperscript{bpx} both containing six-membered proton transfer ring, the corresponding energy barriers are high as 46.1, 39.0, 49.5 and 48.3 kcal/mol. The afforded H\textsubscript{2}O comes from the combination of OH group of COOH and the proton of acid, while the hydrogen atom binding to Pd centre is transferred to the oxygen terminal of acid. In the absence of both PTSA and HCOOH, the subsequent intramolecular
dehydration of 2a-py'bp(2x) squeezing out one H2O molecule via TS2c-py'bp also needs to surmount the energy barrier of high as 39.9 kcal/mol. And the formed H2O comes from the combination between the OH group of COOH and the H atom connecting to Pd. Finally, 1-py'bp is regenerated from the decarbonylation of 3a-py'bp, which is strongly endothermic by 19.8 kcal/mol. Whether the acid promoter attends or not, the high free energy for the transition state of dehydration is obviously disadvantageous to the reaction proceeding along path B.

The obtained free-energy results about path A and B revealed the dehydration step (2-py'bp → TS2-py'bp and 2a-py'bp → TS2a-py'bp) is the rate-degerming step in both paths. However, the free energy of TS2-py'bp is evidently much lower than that of TS2a-py'bp (21.9 vs. 48.7 kcal/mol). Suggesting that the protonated pyridyl group, which is known as “built-in base” group, can drastically reduce the apparent activation energy of HCOOH dehydration to CO by contributing its own proton. Furthermore, PTSA can considerably promote the regeneration of active species 1-py'bp. Such outcomes indicate that adding PTSA can effectively relieve the hindrance to the regeneration of active species 1-py'bp during the dehydration.
Fig. 3 displays the two plausible paths (path C and D) for HCOOH dehydration catalysed by the palladium catalyst of d'bpx (1-d'bpx). Similar to the dehydration by Pd-py'bpx, both path C and D are also initiated from the C-H activation of HCOOH with 1-py'bpx (HCOOH + 1-d'bpx → 2-d'bpx via TS1-d'bpx). The process is endergonic by 12.1 kcal/mol, with a barrier of 14.9 kcal/mol. The further transformation of 2-d'bpx has two alternatives: i) the acid-facilitated intermolecular dehydration to the carbonyl palladium hydride intermediate 3-d'bpx (path C); ii) the acid-promoted intermolecular dehydration or acid-absent intramolecular dehydration to the carbonyl palladium intermediate 3a-d'bpx (path D).

For path C, the PTSA-mediated intermolecular dehydration via TS2-d'bpx exhibited significantly lower energy barrier than the HCOOH-mediated process via TS2a-d'bpx (11.7 vs. 17.6 kcal/mol). The former process to 3-d'bpx is much more exothermic than the latter one (-30.6 vs. -14.8 kcal/mol). Thus, the transformation from 2-d'bpx to 3-d'bpx via TS2-d'bpx is both kinetically and thermodynamically more favoured. For the PTSA- and HCOOH-attended intermolecular dehydration of 2-d'bpx, we also obtained the transition states TS2e-d'bpx and TS2f-d'bpx bearing six-membered ring structure for transferring proton from the acid onto the OH group. But both have much higher free energy than TS2-d'bpx and TS2a-d'bpx, respectively (details see Fig. S2 in ESI). Intermediate 4-d'bpx generated from the ligand exchange between carbonyl of 3-d'bpx and free para-toluenesulfonate anion is also more stable than 4a-d'bpx afforded from the ligand exchange between carbonyl ligand of 3-d'bpx and free formate anion. In the final step for regenerating 1-dtbpx, the location of TS3-d'bpx on the free energy surface is 2.8 kcal/mol lower than that of TS3a-d'bpx. In path D, the intermolecular dehydration to 3a-d'bpx with the mediation of PTSA or HCOOH as proton shuttle via TS2b-d'bpx and TS2c-d'bpx both bearing eight-membered proton transfer chain requires to overcome the energy barrier of 13.8 or 18.7 kcal/mol. In comparison, the acid-absent intramolecular dehydration of 2-d'bpx to 3a-d'bpx via TS2d-d'bpx requires to overcome the energy barrier of high as 37.8 kcal/mol. Moreover, the decarboxylation of 3a-d'bpx to regenerate 1-d'bpx and produce CO gas is endoergic by 15.3 kcal/mol. Although, the acid-mediated intermolecular dehydration in path D has moderate energy barrier, the lower free energy of TS2-d'bpx than TS2b-d'bpx by 2.1 kcal/mol suggests that PTSA-mediated path C is more advantageous than path D that also requiring the mediation of PTSA.

In Scheme 1, the solvated free-energy changes of path A for py'bpx ligand and path C for d'bpx ligand are compared. The lower free energy of TS2-py'bpx than TS2-d'bpx by 1.9 kcal/mol clearly manifests that the intramolecular dehydration by the protonated “built-in base” in py'bpx ligand validly improves the catalytic efficiency of palladium catalyst in the dehydration of HCOOH to CO. Moreover, the lower free energy of TS1-py'bpx than TS1-d'bpx by 2.6 kcal/mol discloses that the presence of hydrogen-bonding interaction between HCOOH and the protonated py'bpx ligand significantly mitigates the energy barrier for the C-H bond cleavage of HCOOH and stabilizes the intermediate 2-py'bpx.
Scheme 1 The solvated free-energy changes of path A and C at 373 K.

HCOOH dehydrogenation by Pd-py'bpX or Pd-d'bpX (path E and F)

As the side reaction during the dehydration of HCOOH, the HCOOH dehydrogenation to H₂ and CO₂ by Pd-py'bpX (path E) or Pd-d'bpX (path F) demonstrated in Fig. 4 undergoes a two-step process starting from the C-H activation of HCOOH by 1-py'bpX or 1-d'bpX followed by the dehydrogenative decomposition of 2a-py'bpX and 2-d'bpX yielding H₂ and CO₂. Similar to the scenario in the dehydration, the dehydrogenation of 2a-py'bpX and 2-d'bpX also have three different channels: PTSA- or HCOOH-mediated intermolecular dehydrogenation correspondingly via TS4a and TS4b, as well as the direct intramolecular dehydrogenation via TS4. Different circumstance was exhibited on the catalysts of Pd-d'bpX and Pd-py'bpX. For Pd-d'bpX, the free energy of TS4b-py'bpX is about 2.2 kcal/mol lower than TS4-py'bpX and TS4a-py'bpX. The HCOOH-mediated dehydrogenation is more favoured. Meanwhile, for Pd-py'bpX, the free energy of TS4a-d'bpX is much lower than TS4-d'bpX and TS4b-d'bpX. The PTSA-mediated dehydrogenation is preferred. In path E and F, the intramolecular dehydrogenation of 2a-py'bpX and 2-d'bpX respectively via TS4b-py'bpX and TS4a-d'bpX is the rate-determining step with the energy barrier of 24.7 and 19.2 kcal/mol. The apparent activation energy for path E and F are high as 34.4 and 31.3 kcal/mol.
Comparing the energy profiles of four paths (path A, C, E and F) together in Scheme 2, we can see that although the reaction process of dehydrogenation has fewer elementary steps than dehydration, the PTSA-mediated dehydration of HCOOH catalysed by Pd-py/bpx is obviously more favourable than the corresponding dehydrogenation, owing to the much lower apparent activation energy of path A than E. Such advantage is unaffected under the PTSA-free reaction conditions, since the dehydrogenation of 2a-py/bpx should be accomplished by HCOOH instead of PTSA (via TS4b-py/bpx instead of TS4a-py/bpx), which rationalizes the stable chemoselectivity to CO by Pd-py/bpx under the PTSA-absent conditions. In sharp contrast to the observed remarkable stability of Pd-py/bpx catalyst,25,33,34 the catalyst of Pd-d/bpx is always prone to decompose in either the absence or the presence of PTSA under heating conditions, which leads to the formation of Pd nanoparticles (i.e., Pd black).34,35 Such distinction on stability is more obvious under the water-contained acidic conditions.34,35 Since the dehydrogenation of HCOOH catalysed by palladium nanoparticle under low temperature is rather facile,36-39 we infer that the dehydrogenation during the dehydration of HCOOH catalysed by Pd-d/bpx is probably contributed by the palladium nanoparticle resulted from the degradation of Pd-d/bpx catalyst. The palladium nanoparticles were also reported to exhibit somewhat both size- and morphology-dependent
dehydration activity.\textsuperscript{40-42} Thus, the catalyst of Pd-d'bpx fails to possess the stable chemoselectivity that comparable to Pd-py'bpx.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{scheme2.png}
\caption{The solvated free-energy changes of path A, C, E and F at 373 K.}
\end{figure}

**Conclusions**

In summary, the DFT-based computational survey unveils the role of “built-in base” and strong para-toluenesulphonic acid promoter in the dehydrative decomposition of HCOOH to CO catalysed by Pd-py'bpx. The basic pyridyl group installed in the ligand of py'bpx changes the mode of intermolecular dehydration aid by the acid promoter to the mode of intramolecular dehydration facilitated by the pyridinium group, which turns down the apparent activation energy of reaction. The participation of para-toluenesulphonic acid in the process of regenerating active Pd-py'bpx catalyst promotes the proceeding of reaction.

**Author Contributions**

C. S.: writing original draft, investigation, formal analysis, methodology, visualization; X. T.: review & editing conceptualization, methodology, project administration; Z. W.: review & editing; K. D.: conceptualization, funding acquisition. All the authors discussed the results and contributed to the writing of the manuscript.

**Conflicts of interest**

There are no conflicts to declare.

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