## **Reaction Kinetics**



# A Convenient Method for the Direct Acquisition of Kinetic Rate Data for Catalytic Organic Reactions by Gas Uptake Measurements

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**Abstract:** Kinetics studies play an indispensable role in determining the mechanism of many catalytic organic reactions. In this context, real-time rate data, rather than concentration data, have proved particularly valuable for mechanistic analysis. However, methods that can directly yield rate data of sufficiently high quality are still limited. In this paper, a convenient method for the direct measurement of rate profiles of homogeneous catalytic organic reactions that involve a gaseous reactant is described. By integrating a highprecision pressure controller and an accurate mass flow

## Introduction

Kinetics measurements are an indispensable part of mechanistic studies of catalytic reactions in both academia and industry. For homogeneous organic reactions especially, kinetics studies provide a wealth of mechanistic information by revealing the order of the reaction components, the performance of the catalyst, and the complete reaction progress profile, which contributes greatly to reaction optimization and rational catalyst design.<sup>[1]</sup>

For a given reaction, a kinetics study usually corresponds to an analysis of the factors that affects the reaction rate (i.e. concentrations of reaction components, temperature, and so forth), and rate data (differential data) are mostly preferred. To date, only a small number of experimental methods are available to acquire rate data directly, such as isothermal calorimetry,<sup>[2]</sup> but their use is limited in many reaction systems of interest. As a result, most kinetics studies are performed by acquiring concentration data (integral data). A variety of methods, both offline and operando, have been used to measure the

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This manuscript is part of a special issue dedicated to Early Career Researchers in China. Click here to see the Table of Contents of the special issue. meter, real-time rate profiles of catalytic reactions on a research laboratory scale at isobaric conditions could be acquired. The method is precise, easy to implement for most organic chemists, and can produce kinetic data of comparable or even superior quality to established kinetic methods, such as ReactIR. The potential of this method in kinetics studies was demonstrated by the study of the initial rate and reaction progress kinetic analysis of several aerobic oxidation reactions.

concentration as a function of time, including gas chromatography,<sup>[3]</sup> HPLC,<sup>[4]</sup> NMR spectroscopy,<sup>[5]</sup> IR spectroscopy,<sup>[6]</sup> and UV/vis spectroscopy.<sup>[7]</sup> The experimental concentration data provided by these methods are then differentiated to obtain rate data for kinetics analysis. These methods are suitable for the traditional initial rate method, but are limited in producing high-quality rate data over the full reaction course, which is increasingly important in modern kinetics studies.

In this and the last decade, modern methods for kinetics analysis, such as reaction progress kinetic analysis (RPKA)<sup>[8]</sup> and variable time normalization analysis (VTNA),<sup>[9]</sup> have been developed. These are able to extract an abundance of mechanistic information from a limited number of experiments by taking the advantage of full-course kinetic data. However, to obtain suitable rate profile for use in RPKA, smoothing and fitting procedures usually have to be applied to the experimental concentration data, which can bias the results and introduce artifacts into the inherent reaction kinetics.<sup>[9,10]</sup> Therefore, new methods that allow for direct acquisition of high-quality rate data over the full course of a reaction would circumvent these drawbacks and benefit kinetics studies significantly.

Notably, a variety of homogeneous catalytic organic reactions involve a gaseous reactant, such as hydrogenation (H<sub>2</sub>), hydroformylation (H<sub>2</sub> and CO), carbonylation (CO), and aerobic oxidation (O<sub>2</sub>). These reactions have attracted significant interest in terms of mechanistics, and gas consumption could serve as a good measure of reaction kinetics in corresponding mechanistic studies. Although great efforts have been devoted to this topic, most of the reported kinetics studies rely on the measurement of integral data, that is, the change of pressure in a sealed system,<sup>[11]</sup> or the total volume of gas consumption

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as a function of time,<sup>[12]</sup> and direct acquisition of kinetic rate data by gas uptake for such reactions is unprecedented. We envisioned that, if the rate of gas absorption could be measured for such reactions, differential data, rather than integral data, over the full course of the reaction could be acquired directly, and this would facilitate the analysis of the reaction kinetics significantly.

Herein, we report a convenient method that enables direct acquisition of rate data for determining gas uptake kinetics. By integrating a precise pressure controller and a high accuracy mass flow meter, the real-time rate of gas consumption in a reaction could be measured and recorded under isobaric conditions. This setup allows for determining the initial rate of homogeneous catalytic reactions and full-course rate data acquisition on a research scale (millimole), and is superior to the methods currently used for studying the kinetics of gas uptake. This method provides a convenient, precise, and inexpensive way to measure the kinetics of gas-participating organic reactions, which might facilitate related mechanistic studies.

## **Materials and Methods**

#### **General Considerations**

For a homogeneous catalytic reaction involving a gaseous reactant, to measure the rate of gas consumption under constant pressure in real time, the reaction should be performed in a system that maintains the volume, pressure, temperature, and the nature of the gaseous phase unchanged during the full course of the reaction. Thus, the gas consumed in the reaction needs to be compensated from an external source, and the gas mass flow for the compensation process directly reflects the real-time rate of the reaction. Although the concept is simple, no precedent has been reported in previous mechanistic studies on research-scale reactions, and to realize this concept requires careful design and planning. In this context, we designed a measurement system comprised of three parts: 1) a pressure controller that could provide the gas at a given pressure and maintain that pressure during the reaction; 2) a mass flow meter that could measure the real-time mass flow of the gaseous reactant accurately; 3) a reaction vessel to host the reaction of interest, providing agitation and temperature control.

#### Instrument Setup

According to the design described above, the setup of the measurement system is depicted in Figure 1.

#### **Pressure Controller**

The gas supplied by a cylinder equipped with a regulator is introduced into a digital dual-valve pressure controller. This type of pressure controller is able to deliver the working gas at a precise pressure ( $\pm$  0.1 kPa), which is adjustable from 0 to 600 kPa (absolute pressure). This feature is important for studying the reaction under a low gas pressure (<1 atm) and for evaluating the catalytic efficiency as a function of gas pressure. A stop valve (valve 1, Figure 1) is installed after the pressure controller. 2195351, 2018, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/ajoc.201700406 by CochraneChina, Wiley Online Library on [26/10/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/doi/10.1002/ajoc.201700406 by CochraneChina, Wiley Online Library on [26/10/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/doi/10.1002/ajoc.201700406 by CochraneChina, Wiley Online Library on [26/10/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/doi/10.1002/ajoc.201700406 by CochraneChina, Wiley Online Library on [26/10/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/doi/10.1002/ajoc.201700406 by CochraneChina, Wiley Online Library on [26/10/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/doi/10.1002/ajoc.201700406 by CochraneChina, Wiley Online Library on [26/10/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/doi/10.1002/ajoc.201700406 by CochraneChina, Wiley Online Library on [26/10/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/doi/10.1002/ajoc.201700406 by CochraneChina, Wiley Online Library on [26/10/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/doi/10.1002/ajoc.201700406 by CochraneChina, Wiley Online Library on [26/10/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/doi/10.1002/ajoc.201700406 by CochraneChina, Wiley Online Library on [26/10/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/doi/10.1002/ajoc.201700406 by CochraneChina, Wiley Online Library on [26/10/2023]. See the Terms and Conditions (https://onlineLibrary.wiley.com/doi/10.1002/ajoc.201700406 by CochraneChina, Wiley Online Library on [26/10/2023]. See the Terms and Conditions (https://onlineLibrary.wiley.com/doi/10.1002/ajoc.201700406 by CochraneChina, Wiley Online Library on [26/10/2023]. See the Terms and Conditions (https://onlineLibrary.wiley.com/doi/10.1002/ajoc.201700406 by CochraneChina, Wiley Online Library.wiley.com/doi/10.1002/ajoc.20



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Figure 1. A) Schematic of the measurement system. B) Photograph of the installed mass flow measurement system.

#### Mass Flow Meter

The gas delivered by the pressure controller then passes through a digital mass flow meter before entering the reaction vessel. The mass flow meter directly reads the absolute mass flow of the reactant gas, regardless of its temperature and pressure. Thus, no calibration is required for individual experiments. A bypass pipeline with a stop valve (valve 2, Figure 1) is configured to protect the mass flow meter during the gas replacement procedure before performing the reaction.

Two key parameters of the mass flow meter are important for setting up a successful measurement system: the scale and the pressure drop. Concerning the scale, we chose a mass flow meter with a scale of 0 to 2 standard cubic centimeters per minute (sccm), which corresponds to 0 to  $1.5 \times 10^{-6} \text{ mol s}^{-1}$  of the gaseous reactant flow. This is a suitable range for most catalytic reactions involving gases at millimole scale.

The pressure drop of the mass flow meter also needs to be taken into consideration. The flow of gas through the mass flow mater causes a drop in pressure compared with the inlet pressure, which is proportional to the rate of gas flow; this is the working principle of a mass flow meter. A significant pressure drop caused by the mass flow meter not only causes the actual gas pressure to deviate

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**Figure 2.** Simulations of the gas uptake kinetics of a first-order reaction involving a gaseous reactant under constant pressure. Data points represent the theoretical gas uptake profile; the blue and red curves represent the gas uptake profiles measured by low- and normal-pressure-drop mass flow meters, respectively. Inset: data from the initial period. Details of the simulation are given in the Supporting Information.

from the set point during the reaction, but also biases the determined reaction kinetics. Our simulation showed that (Figure 2), a low-pressure-drop mass flow meter (0.207 kPasccm<sup>-1</sup>) is able to follow the reaction progress well, whereas a mass flow meter with a normal pressure drop (3.45 kPasccm<sup>-1</sup>) produced a distorted gas uptake profile. Therefore, the former should be used in the measurement system.

#### **Reaction Vessel**

The designed reaction vessel (Figure 3), in which the gas uptake reaction takes place, is a thick-walled glass vessel that can work at elevated pressures (up to 6 atm). The top of the vessel is connected to the measurement system (pipeline from valve 3, Figure 1) through a Teflon screw cap. Temperature control and agitation of the vessel are provided by a magnetic stirrer equipped with a thermostat. A side arm with a Teflon screw valve and a 14/10 glass joint is designed to facilitate the addition of materials if the vessel is connected to the gas line. According to the scale of the reaction under study, reaction vessels with different volumes can be used. Because the system measures the absolute mass flow of the gaseous reactant, no calibration is needed if using different reaction vessels. To ensure best performance of the measurement system, the smallest reaction vessel should be used for a specified reaction.



Figure 3. The designed reaction vessel, illustrating the addition of material through the side arm by a needle.

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To enable replacement of gas in the vessel before the reaction, two stop valves (valves 3 and 4, Figure 1) are installed between the mass flow meter and the reaction vessel.

#### Method for the Measurements

Using this measurement system, the catalytic reaction of interest can be performed in the reaction vessel under specified conditions. In a general procedure, the vessel charged with the reaction solution under the desired atmosphere is first allowed to reach thermal equilibrium, and then a component to trigger the reaction (a solution of a reagent or a catalyst) is injected by syringe needle through the side arm. The Teflon screw valve is then sealed and data acquisition is started. A representative gas uptake profile of such a system is presented in Figure 4, which shows that the method is able to yield high-quality rate data.



Figure 4. A representative gas uptake profile acquired by the designed measurement system.

The plot shows the mass flow of gas compensation as a function of time. The rate profile of a reaction with respect to substrate or product could be easily obtained from the mass flow data by considering the stoichiometry. The rate profile provides an abundance of information of a catalytic process. First, the rate profile throughout the full reaction is presented directly, which is of good quality and is appropriate for analysis of reaction progress kinetics. Second, the initial rate of the reaction could be easily obtained from the maximum of the rate curve, and is suitable for initial rate analysis. Third, the integral of the rate profile (the area under the curve in Figure 4) provides total gas consumption, which is proportional to the progress of the reaction.

To ensure the best performance of the measurement system, the following points are worth noting: 1) the scale of the reaction should be adjusted so that the initial gas uptake is 40–90% of the capacity of the mass flow meter; 2) good agitation should be applied to exclude a phase-transfer-limiting scenario; 3) the rate of the reaction should be appropriate, that is, the full time-course of the reaction should exceed 20 min.

## **Results and Discussion**

With this system in hand, we performed a series of experiments to validate the accuracy, reproducibility, and applicability of the proposed method for studying kinetics. A range of catalytic aerobic oxidation reactions, which were conducted in organic solvents of a homogeneous nature, were used as model reactions.

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#### **Test of Accuracy**

Because the gas uptake data comes directly from the mass flow meter, we first tested the accuracy of the total gas flow measured during a catalytic reaction. Palladium-catalyzed aerobic oxidation of alcohols to aldehydes, previously studied by Stahl and co-workers, was selected as a suitable model (Figure 5).<sup>[11b]</sup> In the presence of catalytic amount of Pd(OAc)<sub>2</sub> and pyridine, benzyl alcohol was oxidized to benzaldehyde by oxygen. By conducting the reaction on various scales with different conversions, we found that the total oxygen uptake (obtained by integration of the rate data) correlated well with the amount of benzaldehyde produced. A regression analysis of the acquired data afforded a good linear relationship, which is in agreement with the stoichiometry of the reaction.

Next, the accuracy of the initial rate determined by this system was tested by performing a similar Pd<sup>II</sup>-catalyzed aerobic oxidation reaction (Figure 6). The reaction was conducted on different scales, and the initial rate for oxygen consumption exhibited an excellent linear relationship with the scale of the reaction. Therefore, the accuracy of the determined initial rate was also verified. Both results indicated that this measurement system has good accuracy, which might meet the requirements of a quantitative kinetics study.

#### Kinetics Study Using the Initial Rate Method

Because the measurement system proved to be accurate, we performed a kinetics study on a model catalytic aerobic oxidation reaction using the initial rate method to determine if this system could reproduce the experimental results obtained by other methods. The Pd<sup>II</sup>-catalyzed aerobic oxidation reaction of benzyl alcohol (Figure 6) has been studied in detail by Stahl and co-workers.<sup>[11c]</sup> Using the mea-

surement system described here, kinetic data were acquired and compared with the literature report on the same reaction. First, the dependence of the initial rate on the pressure of oxygen was investigated (Figure 7 A). A set of initial rates were measured under different oxygen pressures. It was found that the initial rate exhibited zero-order with respect to oxygen pressure if that exceeded 60 kPa. By performing the experiment at a low pressure of O2, Pd black was observed, indicating the deactivation of catalyst. This was in full agreement with the result reported by the Stahl lab, which was acquired by measuring the decrease of oxygen pressure in a sealed vessel. Second, the dependence of the initial rate on concentration of the alcohol was studied (Figure 7B). A set of initial rates were measured at different alcohol concentration, which exhibited saturation kinetics and fit well to the deduced rate law. This is also in agreement with a previous study.<sup>[11c]</sup>These results demonstrated that the present method is suitable for



**Figure 5.** Plot of oxygen consumed versus amount of produced benzaldehyde in the model reaction. Reaction conditions:  $Pd(OAc)_2$  (37.5 mm), pyridine (150 mm), PhCH<sub>2</sub>OH (750 mm) in toluene, 80 °C, 103 kPa O<sub>2</sub>.



**Figure 6.** Plot of the determined initial O<sub>2</sub> uptake versus the scale of the reaction. Reaction conditions:  $Pd(OAc)_2$  (2.5 mm), 1-phenylethanol (520 mm) in DMSO, 80 °C, 103 kPa O<sub>2</sub>.

initial rate study of gas uptake reactions. This is convenient, because for each reaction only the kinetic data of the first several minutes need to be acquired, and the initial rate could be obtained directly from the rate profile, without the need for linear regression, as is typically required with other kinetic measurement methods.

#### **Application in Reaction Progress Kinetic Analysis**

As mentioned above, RPKA can provide valuable information about a reaction mechanism with a limited number of experiments if high-quality full course rate data is available. The present method is able to acquire rate data of a catalytic reaction directly, and herein we demonstrate the advantage of using this method in RPKA.



**Figure 7.** Dependence of the initial rate on A) oxygen pressure and B) concentration of alcohol in the catalytic aerobic oxidation of 1-phenylethanol. The initial rates with respect to  $O_2$  consumption are reported. Reaction conditions: Pd(OAc)<sub>2</sub> (2.5 mM) in DMSO (2 mL total volume), 80 °C; A: 1-phenylethanol (0.52 M), 0–150 kPa  $O_2$ ; B: 1-phenylethanol (0.1–1.4 M), 103 kPa  $O_2$ .

#### **General Method**

To perform the analysis, the measured rate profile (reaction rate as a function of time) should be converted to the schematic rate law (reaction rate as a function of substrate concentration). For a given reaction  $aS + bGas \rightarrow cP$ , where S, Gas, and P represent the substrate, the gaseous reactant, and the product, respectively, and *a*, *b*, and c describe the stoichiometry of the reaction, the rate  $[mM min^{-1}]$  with respect to substrate S is [Eq. (1)]:

$$rate = -\frac{d[S]}{dt} = \frac{a}{b} \cdot \frac{1}{22.4 \cdot V_{\text{soln}}} \cdot \frac{dV_{gas}}{dt}$$
(1)

where  $V_{soln}$  is the volume of the reaction solution [L], and  $dV_{gas}/dt$  is the measured mass flow of gas [sccm]. Then, the substrate concentration as a function of time is expressed as follows [Eq. (2)]:

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$$[S]_t = [S]_0 - \frac{a}{b} \cdot \frac{1}{22.4 \cdot V_{\text{soln}}} \cdot \frac{dV_{gas}}{dt}$$
(2)

where  $[S]_0$  is the initial concentration of the substrate [mM]; the integral term could be calculated by numerical integration of the mass flow data. The rate–concentration relationship, that is, the "schematic rate law", could be established by plotting the rate against  $[S]_r$ .

By following this method, the acquired rate profiles can be converted to schematic rate laws conveniently by applying only basic mathematics. Overlaying schematic rate laws obtained from different initial conditions can provide mechanistic information such as reaction order, catalyst deactivation, and product inhibition.

#### Comparison with the Operando IR Spectroscopic Method

Because operando IR spectroscopy is a standard method for full-course kinetics study used by organic chemists, we compared the kinetic data acquired by operando IR spectroscopy and the present method to demonstrate the advantage of direct rate data acquisition with RPKA.

In this context, the Pd<sup>II</sup>-catalyzed aerobic oxidation of benzyl alcohol to benzaldehyde<sup>[11b]</sup> was used as a model reaction for the kinetics study. For the operando IR spectroscopy study, we measured the product concentration (by monitoring the intensity of the peak at 1700 cm<sup>-1</sup>) to acquire the raw concentration data (Figure 8A), and then numerical differentiation was applied to obtain rate data (Figure 8B) for the construction of the schematic rate law (Figure 8C). For the gas uptake measurement, we directly measured the gas uptake rate to acquire the raw

rate data (Figure 9A). It was clear that although operando IR spectroscopy could provide a concentration profile of sufficient quality, numerical differentiation of the raw concentration data afforded rate data with a low signal-to-noise ratio, because differentiation greatly amplifies fluctuations in the raw data. This is a common problem that any concentration-based kinetic measurement method will create. As a result, the schematic rate law derived from such rate data (Figure 8C) exhibited insufficient quality for RPKA. Therefore, significant smoothing or curve fitting should be performed on the raw kinetic data obtained by operando IR spectroscopy to reduce data fluctuation prior to use in kinetic analysis. On the contrary, the raw rate data obtained by the gas uptake measurement was of good quality, which ensured the good quality of the derived schematic rate law (Figure 9B) for kinetic analysis. This rendered the present measurement method more suitable for RPKA of organic reactions involving gas uptake.

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**Figure 8.** Kinetic data for the Pd<sup>II</sup>-catalyzed aerobic oxidation of benzyl alcohol acquired by operando IR spectroscopy. A) Raw concentration data of the benzaldehyde product; B) rate profile obtained by numerical differentiation of the raw concentration data without smoothing or curve fitting; C) the schematic rate law derived from the rate profile. Reaction conditions: PhCH<sub>2</sub>OH (390 mM), Pd(OAc)<sub>2</sub> (25 mM) and pyridine (100 mM) in toluene, 80 °C, 103 kPa O<sub>2</sub>.

#### Application 1: Probing Catalyst Deactivation and Product Inhibition

Stahl and co-workers performed a detailed mechanistic study on the aforementioned Pd<sup>II</sup>-catalyzed aerobic oxidation of benzyl alcohol using pressure-based gas uptake kinetics measurements.<sup>[11b]</sup> Their findings revealed that catalyst deactivation occurred during the reaction, but it was unclear whether or not product inhibition played a role. We performed a more detailed kinetic study using the present gas uptake measurement system. The full-course rate data of the reaction with respect to oxygen consumption were acquired at different initial substrate concentrations (Figure 9A). The corresponding rate-concentration profiles were obtained by applying Equations (1) and (2) (Figure 9B).

Rate-concentration profiles provide important mechanistic information about a catalytic process. For reactions conducted at initial substrate concentrations of 0.39 and 0.31 M, the rate-concentration profiles do not overlay (Figure 9B, blue and red curves), indicating that either catalyst deactivation or product

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**Figure 9.** Reaction progress kinetic analysis of the Pd<sup>II</sup>-catalyzed aerobic oxidation of benzyl alcohol. A) Rate profiles of the reaction with respect to O<sub>2</sub> consumption; B) overlay of the schematic rate laws derived from the rate profiles. Reaction conditions: Pd(OAc)<sub>2</sub> (25 mm) and pyridine (100 mm) in toluene (total volume 8 mL), 80 °C, 103 kPa O<sub>2</sub>.

inhibition occurred as the reaction proceeded. At this stage, another rate profile acquired at 0.31 M substrate together with 0.08 M product was used to distinguish these two scenarios (Figure 9B, green curve). The observation that the corresponding curve lies between the original two confirms both catalyst deactivation and product inhibition,<sup>[8]</sup> which adds important new information to the original mechanistic understanding.<sup>[11b]</sup> Notably, this key mechanistic information was obtained from just three full-course kinetic measurements, which could be performed conveniently using the present method.

# Application 2: Probing the Reaction Order with Respect to Substrate Concentration

Another example studied using the present method was the Cu<sup>1</sup>-catalyzed aerobic oxidative homocoupling of phenylacetylene (the Glaser–Hay reaction).<sup>[13]</sup> We noted that controversial conclusions had been reached on the order of reaction with respect to the concentration of acetylene derivatives. Zero-,<sup>[14]</sup> first-,<sup>[15]</sup> and second-order<sup>[13c, 16]</sup> reactions have all been reported in the literature for different catalytic systems. Our interest was attracted by two reports showing a second-order rate dependence,<sup>[13c, 16]</sup> and we hoped to reinvestigate the kinetic features of the reaction by using our gas uptake measurement system. Full-course rate data were recorded for three experiments starting with different substrate concentrations (Figure 10 A), and the corresponding schematic rate laws were established according to Equations (1) and (2) (Figure 10 B). Again, the rate data was of good and sufficient quality for RPKA.

In this case, three rate-concentration profiles overlay well with each other, revealing that the reaction suffers from neither catalyst deactivation nor product inhibition. The schematic rate laws clearly demonstrate a first-order kinetics with respect to concentration of phenylacetylene for this specific catalytic system, which corrected previous conclusions.<sup>[13c, 16]</sup>

These successful examples highlighted the utility of mass flow measurements for RPKA. The ability to reproducibly acquire good quality real-time rate data renders the present method unique in mechanistic studies; this allows us to access sufficient mechanistic information on homogeneous catalytic reactions with the least experimental endeavor.



**Figure 10.** Reaction progress kinetic analysis of the copper-catalyzed oxidative homocoupling of phenylacetylene. A) Rate profiles of the reaction with respect to  $O_2$  consumption; B) overlay of the schematic rate laws derived from the rate profiles. Reaction conditions: CuCl (30 mm), PhC=CH (blue: 590 mm, green: 510 mm, red: 390 mm) in pyridine (total volume 5 mL), 30 °C, 103 kPa  $O_2$ .

## Conclusions

In this article, we demonstrate that gas uptake measurements could be used as a precise and reliable method for the acquisition of kinetic rate data of homogeneous catalytic organic reactions on a millimole scale. The quality of the acquired rate data is remarkably superior to that of the rate data derived from concentration data. The instruments are easily available and inexpensive (total cost < 8000 USD), and the measurement system can be easily operated by well-trained organic chemists. The method is compatible with both initial rate studies and reaction progress kinetics studies, and requires no calibration of individual experiments.

The limitation of the present method is the same as other kinetic methods based on gas uptake measurements, that is, the reaction under study should have sufficiently high selectivity. Because gas uptake is measured as the only parameter to describe the kinetics of the reaction, other side reactions involving the consumption of the same gaseous reactant will interfere. Therefore, control experiments should be performed to verify the selectivity of the reaction prior to studying the kinetics of gas uptake. Despite this, the method described here provides a good complement to the current toolbox for kinetic study.

This method is expected to facilitate mechanistic studies on related organic reactions, and its further application in the studies of hydrogenation, carbonylation, and hydroformylation reactions is anticipated.

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## **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** gas mass flow  $\cdot$  homogeneous catalysis  $\cdot$  kinetics  $\cdot$  reaction mechanisms  $\cdot$  reaction rates

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