Kinetic and mechanistic studies of the hydroformylation of 1-octene with $[RhH(PPh_3)_3CO]$ as a catalyst.

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The aim of this poster is to show that reaction progress kinetic analysis (RPKA) [1] can be modified to elucidate kinetic information from, catalysed reactions that incorporate gases.

- Gas uptake signals have been utilised as effective *in-situ* methods in RPKA. [2]
- Reactions incorporating more than one gas have not been studied in this way.
- RPKA can give a complete kinetic and hence mechanistic picture of a reaction from a minimal number of experiments.
- The reaction focused on is the hydroformylation of 1-octene using $[RhH(PPh_3)_3CO]$.

Kinetic study of the hydroformylation of 1-octene using $[Rh(CO)_2(acac)]$ and PPh_3

A known reaction was studied to determine whether gas uptake can be used as a principle technique for investigation. The reaction chosen was the hydroformylation of 1-octene using $[RhH(PPh_3)_3CO]$ because:

- Well established and accepted dissociative reaction mechanism, (fig1).[3]
- Reaction contains three simultaneously changing reacting components.
- Results could be compared to previous kinetic and mechanistic studies in the literature.

A homogeneous batch reactor was used throughout this study (fig 2):

- Ability for efficient gas/liquid mixing.
- Can run both constant pressure (open) and constant volume (closed) experiments.
- Fitted with PicoLog software to allow for continual and accurate monitoring of pressure.

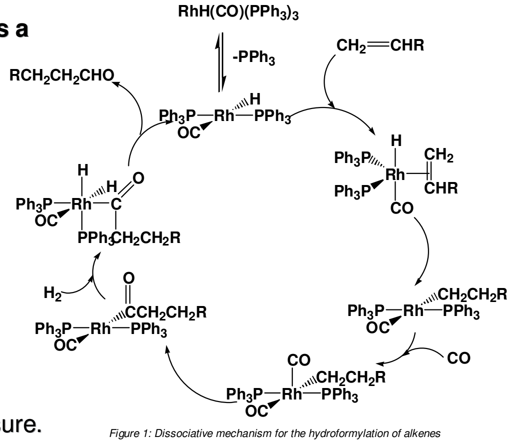


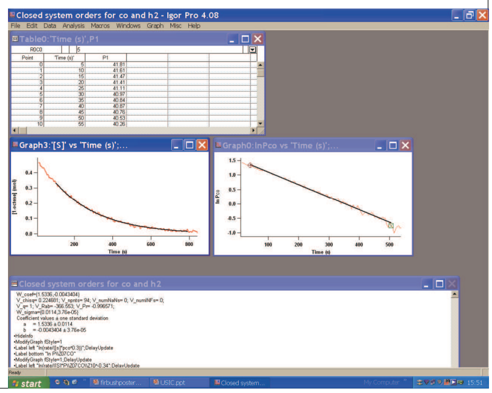
Figure 1: Dissociative mechanism for the hydroformylation of alkenes

The data collected is exported into a curve fitting software package, Igor (fig 3):

- Easy way to manipulate and present data
- Allows data to be fitted to several mathematical models

Figure 2: (left) Homogeneous batch reactor setup capable of efficient gas/liquid mixing and the ability for kinetic measurements at constant pressure and volume.

Figure 3: (right) Screen shot of Igor showing a: the imported data (in table one) b: data being manipulated (text box, bottom left) c: data presented in graphs (graphs 3 and 0) and d: two examples of data being fitted to mathematical models; graph 3 shows and exponential fit and graph 0 shows a linear fit.



Order in 1-octene and total gas pressure

- Open and closed experiments ran to determine the order in substrate and overall gas pressure

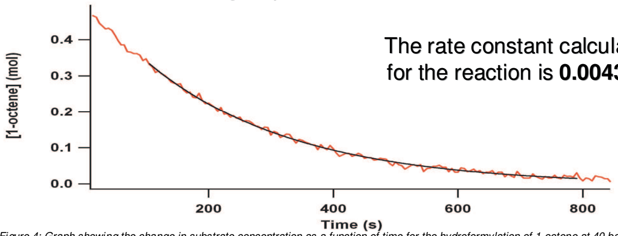


Figure 4: Graph showing the change in substrate concentration as a function of time for the hydroformylation of 1-octene at 40 bar and 80°C

- Open system shows first order in substrate concentration

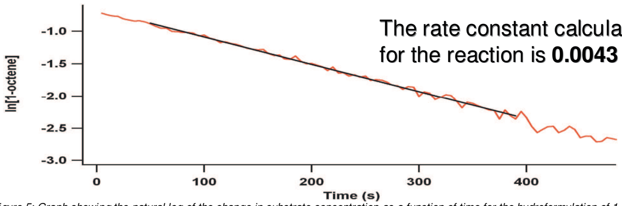
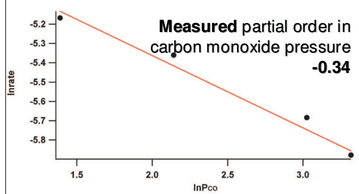


Figure 5: Graph showing the natural log of the change in substrate concentration as a function of time for the hydroformylation of 1-octene at 40 bar and 80°C in a closed system.

- Closed system shows zero order in overall gas pressure
- Previous studies show partial orders in both hydrogen and carbon monoxide pressure [4]

Order in hydrogen and carbon monoxide

- Series of experiments run to determine order in gas pressure
- 5 reactions run with H_2 pressure between 5 and 25 bar
- Closed system used to calculate order with respect to PCO



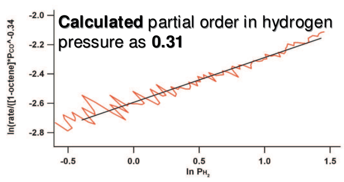
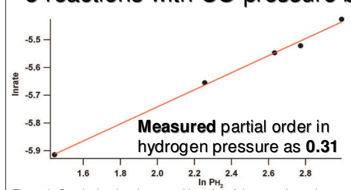


Figure 6: Graph showing the natural log plot of the rate of reaction as a function of time for the natural log of the carbon monoxide pressure
Figure 7: Graph showing the natural log plot of the rate of reaction divided by the octene concentration and carbon monoxide pressure to their respective powers as a function of time for the natural log of the hydrogen pressure

- To check to see if opposite experiments are comparable
- 5 reactions with CO pressure between 5 and 25 bar



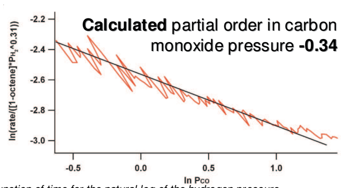


Figure 8: Graph showing the natural log plot of the rate of reaction as a function of time for the natural log of the hydrogen pressure
Figure 9: Graph showing the natural log plot of the rate of reaction divided by the octene concentration and hydrogen pressure to their respective powers as a function of time for the natural log of the carbon monoxide pressure

- Results show **Rate α $[1\text{-octene}]^1[PH_2]^{0.31}[PCO]^{-0.34}$** shown by 7 experiments: open, closed and 5 variable pressure experiments.
- Combining variable pressure data with closed system data allows for calculation of order in CO/H_2 pressure (shown experimentally)

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4) Kamer, P.C.J., *et al.*, Coord. Chem. Rev., 2004. **248,** p. 2409–2424