

Supporting Information

Instrumentation. Reactions were carried out in an Omnical Super CRC reaction calorimeter, which allows continuous monitoring of the instantaneous enthalpy balance around the vessel. The sample vessel is a 6 ml septum-cap vial equipped with a shaft and stirring blade. Sample volume did not exceed 3.5 ml. The system operates as a differential scanning calorimeter by comparing the heat released or consumed in a sample vessel compared with that from a reference compartment at intervals of 2-6 seconds over the course of the reaction.

An energy balance around the vessel for the case of a single reaction occurring demonstrates that the reaction heat flow, q , is proportional to the reaction rate, r , where ΔH_{rxn} is the heat of reaction and V is the reaction volume.

$$q = \Delta H_{\text{rxn}} \cdot V \cdot r$$

If the units of reaction heat flow are given in watts ($\text{mJ}\cdot\text{s}^{-1}$), the heat of reaction in $\text{J}\cdot\text{mol}^{-1}$, and the reaction volume in l, the reaction rate will be given in $\text{M}\cdot\text{s}^{-1}$.

The observed heat flow profiles may also be used to obtain the fractional conversion of substrate by calculation of the fractional area under the temporal heat flow curve as given below, where the numerator represents the area under the heat flow curve to any time point t and the denominator represents the total area under the heat flow curve to reaction completion at time t_f .

$$\text{fractional conversion} = \frac{\int_0^t q \cdot dt}{\int_0^{t_f} q \cdot dt}$$

Conversion determined from heat flow was compared to conversion by HPLC measurement to confirm that the observed heat flow represents an accurate measure of rate of the reaction under study.

The heat flow signal is calibrated to account for time lag through the reactor walls via mathematical correction of a constant applied heat flow signal to produce the square wave that would result in the ideal case; the same correction is then applied to the experimental heat flow data.

Materials and Methods.

The catalyst Poly-L-leucene-polyethylene glycol monomethyl ether was purchased commercially (Lancaster) and used as obtained.

Preparation of H_2O_2 in acetonitrile; 400 mg of urea- H_2O_2 (Lancaster) was taken and 3 ml of acetonitrile was added and stirred for 1 hr. After the stirring was stopped the solid particles were allowed to settle down and required amount of clear solution was taken. To determine the concentration of H_2O_2 , known amount of this H_2O_2 -acetonitrile solution was taken in a 10 ml volumetric flask and to that added 2ml saturated aqueous KI solution, 2 ml of concentrated acetic acid and made up to 10 ml with distilled water. This solution was kept for 30 minutes and titrated against known standard concentration solution of sodium thiosulfate.

In a typical reaction, required amount of catalyst was added to the reaction vessel with 2 ml of dry THF (Lancaster) along with a non amount of an internal std for HPLC analysis (Benzophenone). Then required amount of H_2O_2 solution of acetonitrile is added to this vessel. This vial was placed in the calorimeter and stirred until thermal equilibration was reached (ca. 1 hr). A syringe containing known amount of base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Lancaster, Distilled prior to reaction) was placed in the sample injection port of the calorimeter and was allowed to reach thermal equilibration. Once thermal equilibrium was reached, DBU was injected into the reaction mixture. The deprotonation of H_2O_2 by DBU was found to be exothermic and gave rise to heat flow. Known amount of chalcone (Lancaster) was dissolved in known amount of THF and required amount of this chalcone solution was taken in a syringe and placed in the sample injection port of the calorimeter and was allowed to reach thermal equilibration. Once thermal equilibrium was achieved after the deprotonation reaction, reaction was initiated by injecting the chalcone solution into the stirred solution. After known time reaction sample was taken using a syringe and

the reaction was quenched by aqueous sodium sulphite solution. The organic phase was extracted in ethyl acetate and ether and was analyzed using HPLC.

Analytical Conditions for Chalcone epoxidation

Column: DAICEL CHIRALPAK AD

Mobile phase: Hexane/ethanol (90:10)

Wavelength = 254 nm

Flow rate = 1ml/min

Analytical Conditions for Chloro chalcone epoxidation

Column: DAICEL CHIRALPAK AD

Mobile phase: Hexane/iso-propanol (95:5)

Wavelength = 254 nm

Flow rate = 1ml/min

Analytical Conditions for p-methoxy chalcone epoxidation

Column: DAICEL CHIRACEL OD

Mobile phase: Hexane/iso-propanol (95:5)

Wavelength = 254 nm

Flow rate = 1ml/min

The reaction conditions of reactions shown in Figure 3 - 1a, are

For both the experiments; Temperature: 26 C, Catalyst loading : 10.58 gm/l (since exact molecular wt is not known, the wt of catalyst is used instead of mol), Volume of THF; 2ml, volume of acetonitrile ; 1 ml. The initial concentrations of substrates were

Run1; [Chalcone] = 0.061 M, [H₂O₂] = 0.102 M

Run2; [Chalcone] = 0.043 M, [H₂O₂] = 0.085 M

The reaction conditions of reactions shown in Figure 3 - 1b, are

For both the experiments; Temperature: 26 C, Catalyst loading : 10.3 gm/l, Volume of THF; 2ml, volume of acetonitrile; 1 ml. The initial concentrations of substrates were

Run1; [p-chloro Chalcone] = 0.064 M, [H₂O₂] = 0.098 M

Run2; [p-chloro Chalcone] = 0.046 M, [H₂O₂] = 0.081 M

The reaction conditions of reactions shown in Figure 3 - 1c, are

For both the experiments; Temperature: 26 C, Catalyst loading : 16.068 gm/l, Volume of THF; 2ml, volume of acetonitrile; 1 ml. The initial concentrations of substrates were

Run1; [p-methoxy Chalcone] = 0.058 M, [H₂O₂] = 0.102 M

Run2; [p-methoxy Chalcone] = 0.040 M, [H₂O₂] = 0.083 M

The reaction conditions of reactions shown in Figure 4 a are

For all the experiments; Temperature: 26 C, Catalyst loading : 10.58 gm/l, Volume of THF; 2ml, volume of acetonitrile; 1 ml. The initial concentrations of substrates were

Legend	[Chalcone], M	[H₂O₂], M	[DBU], M
[Excess] = 0.041 M	0.061	0.102	0.24
[Excess] = 0.015 M	0.085	0.1	0.24
[Excess] = 0.062 M	0.041	0.103	0.24

The reaction conditions of reactions shown in Figure 4 b are

For all the experiments; Temperature: 26 C, Catalyst loading : 10.3 gm/l, Volume of THF; 2ml, volume of acetonitrile; 1 ml. The initial concentrations of substrates were

Legend	p- Chloro [Chalcone], M	[H₂O₂], M	[DBU], M
[Excess] = 0.034 M	0.064	0.0978	0.23
[Excess] = 0.055 M	0.045	0.10	0.23
[Excess] = 0.006 M	0.091	0.097	0.23

The reaction conditions of reactions shown in Figure 4 c are

For all the experiments; Temperature: 26 C, Catalyst loading : 16.1 gm/l, Volume of THF; 2ml, volume of acetonitrile; 1 ml. The initial concentrations of substrates were

Legend	p-methoxy [Chalcone], M	[H ₂ O ₂], M	[DBU], M
[Excess] = 0.044 M	0.058	0.102	0.23
[Excess] = 0.061 M	0.042	0.104	0.23

Tools used for rate parameter determination

Kinetic parameters were determined by fitting the reaction rate data obtained from the heat flow to an analytical rate equation using the Solver program in Excel (Microsoft). Non-linear statistical analysis for about 2650 total data points were carried out using “solvstat” (Excel for chemists by Prof. E. Joseph Billo) to determine the confidence limit of the kinetic parameters thus obtained.

Competition Reaction between chalcone and methoxy chalcone

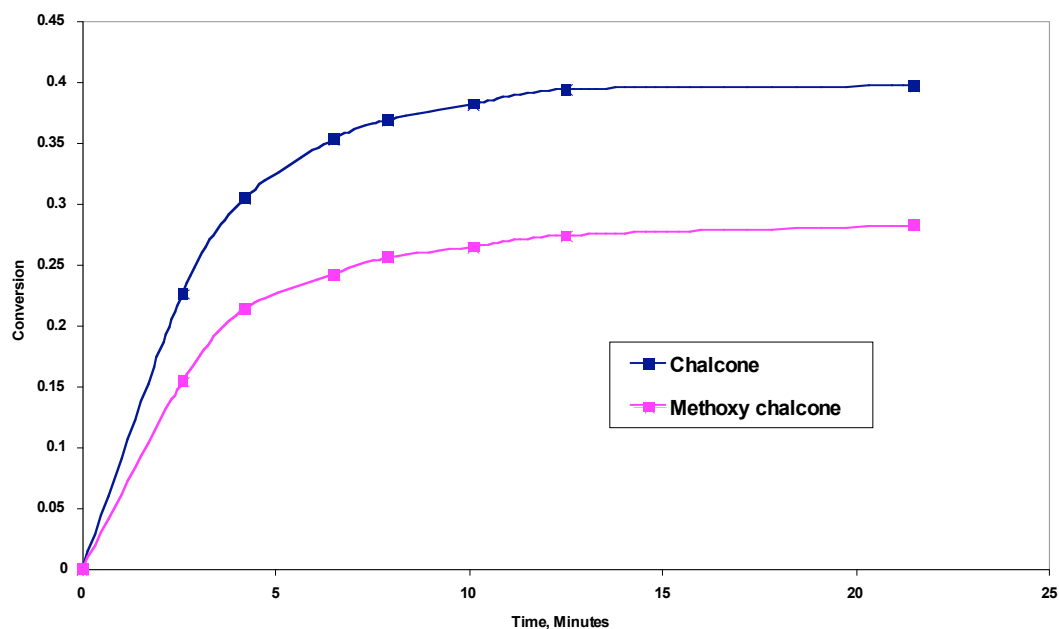


Figure 1; Conversion of Chalcone and Methoxy chalcone as a function of time

Reaction conditions; [Chal] = [p-Methoxy chal] = 0.0775 M, [H₂O₂] = 0.0525 M, [Cata] = 10.53 g/l

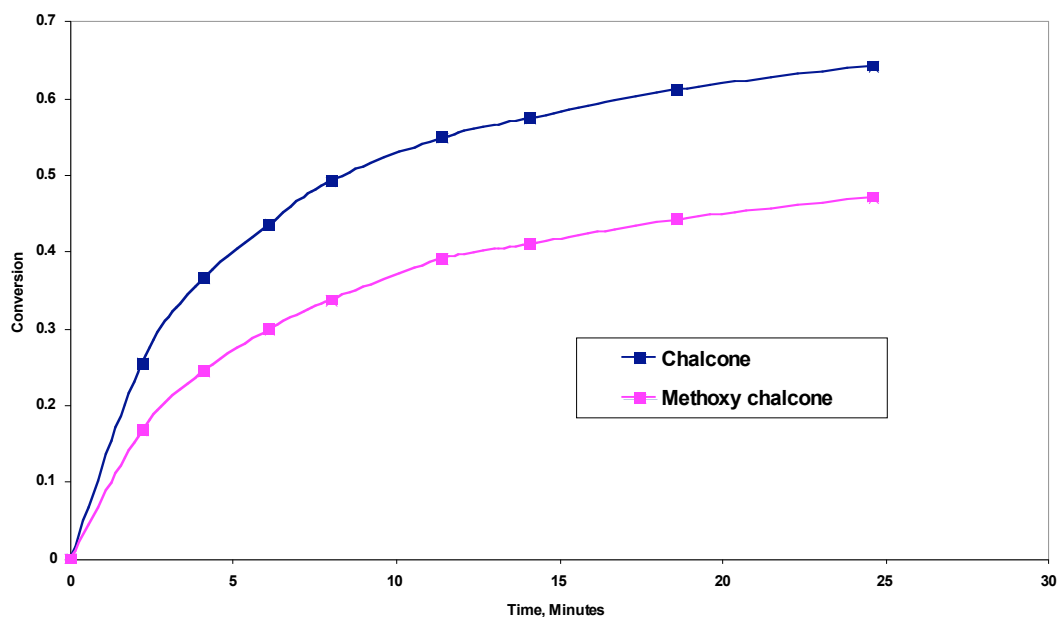


Figure 2; Conversion of Chalcone and Methoxy chalcone as a function of time
 Reaction conditions; [Chal] = [p-Methoxy chal] = 0.0776 M, [H₂O₂] = 0.1021 M,
 [Cata] = 10.65 g/l

Competition Reaction between chalcone and chloro chalcone

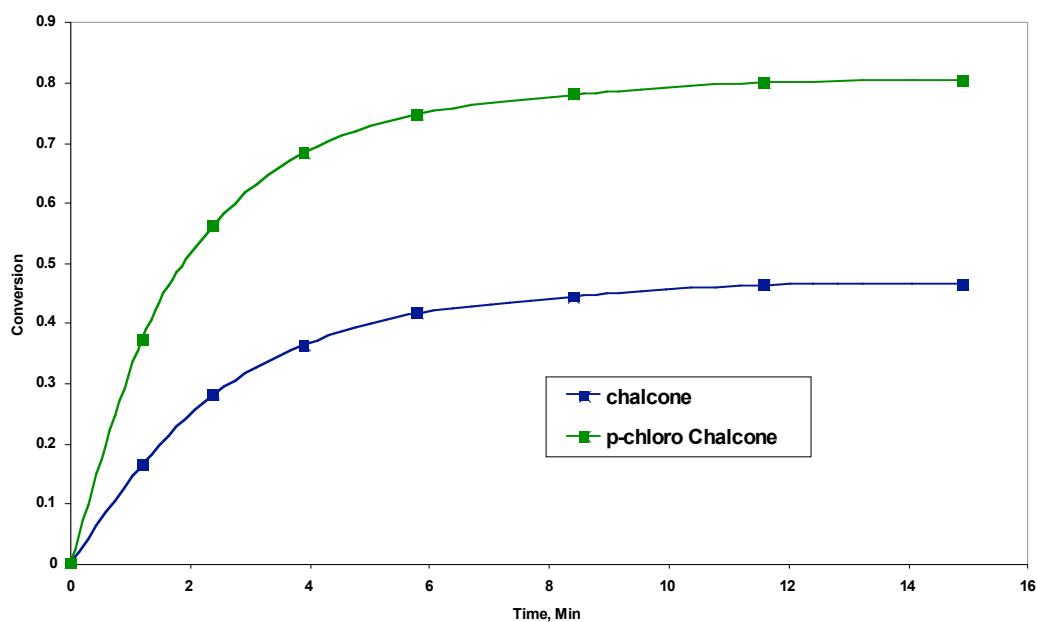


Figure 3; Conversion of Chalcone and p-chloro chalcone as a function of time
 Reaction conditions; [Chal] = [p-Chloro chal] = 0.075 M, [H₂O₂] = 0.0962 M, [Cata]
 = 10.05 g/l

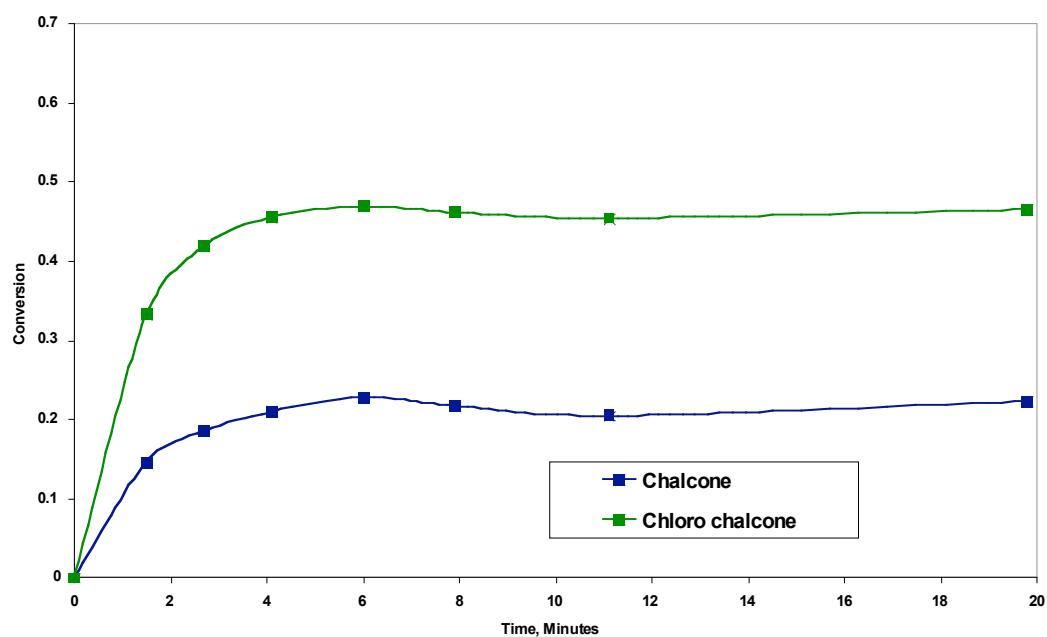


Figure 4; Conversion of Chalcone and p-chloro chalcone as a function of time

Reaction conditions; [Chal] = [p-Chloro chal] = 0.075 M, [H₂O₂] = 0.0487 M, [Cata] = 10.03 g/l