Kinetics of CO_x Formation in MC Oxidation of *p*-Xylene

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Outline

- Introduction
- Mechanism & Kinetic Model
- Experimental
- Results
- Conclusion

Introduction

The Amoco MC method is defined by:

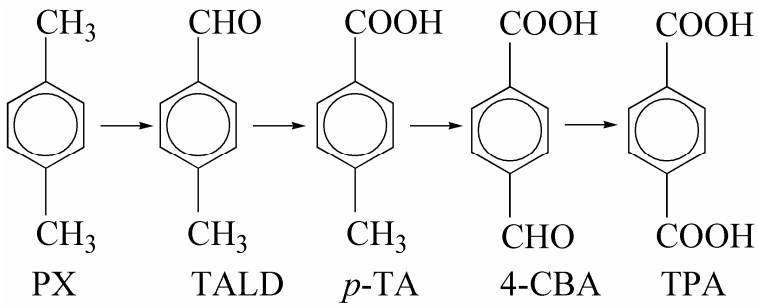
$$Hydrocarbon + O_2 \xrightarrow[solvent]{metals/bromide} oxygenate + H_2O$$

$$Ar - n(CH_3) + O_2 \xrightarrow[HOAC]{\substack{Co(OAC)_2 \\ Mn(OAC)_2 \\ HBr}} Ar - n(COOH) + nH_2O \qquad n = 1\text{-}4$$

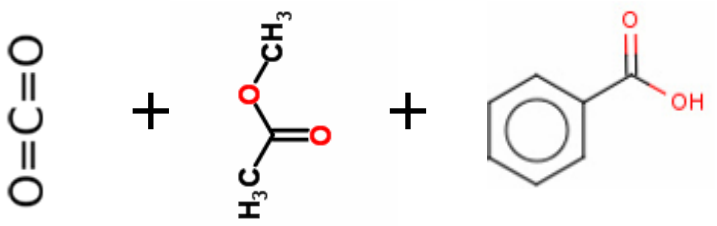
- **High activity**
- **High selectivity**
- **Easy separation**

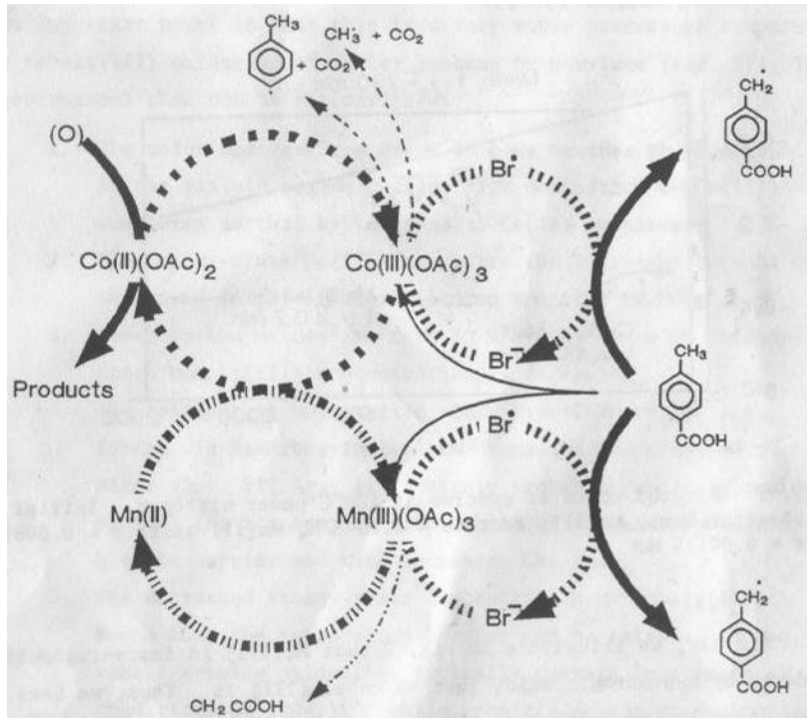
Introduction

Oxidation of PX to TPA



Major by-products (>0.1% yield)





Catalytic cycles for PX oxidation suggested by Partenheimer.

The formation of COx (CO_2 and CO) can be used to estimate side reactions in PX oxidation.

Partenheimer, W. ***Catalysis of Organic Reactions***, (Ed.: D. W. Blackburn): 321-346, Marcel Dekker: New York, 1990.

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Mechanism & Kinetic Model

(*i*) Formation of CO_2

$$Ar-COOH+Co^{III}\xrightarrow{k_I}Ar^{\cdot}+CO_2+Co^{II} \quad (1)$$

$$CH_3COOH+ROO^{\cdot}\xrightarrow{k_{II}}ROOH+CH_3COO^{\cdot} \quad (2)$$

$$CH_3COO^{\cdot}\rightarrow CH_3^{\cdot}+CO_2 \quad (3)$$

$$Ar-COOH+ROO^{\cdot}\xrightarrow{k_{III}}ROOH+Ar-COO^{\cdot} \quad (4)$$

$$r_{CO_2}=k_I\cdot[Ar-COOH]\cdot[Co^{III}]+k_{II}\cdot[CH_3COOH]\cdot[ROO^{\cdot}] \quad (5)$$

Kinetic Model of CO_2 Formation:

$$r_{CO_2}=k_1\cdot[Ar-COOH]+k_2\cdot[ROO^{\cdot}] \quad (6)$$

Partenheimer, W. ***Catalysis of Organic Reactions***, (Ed.: D. W. Blackburn): 321-346, Marcel Dekker: New York, 1990.
Kenigsberg, T. P.; Ariko, N. G.; Agabekov, V. ***Energy Convers. Mgmt.,*** 1995, 677-680.

Mechanism & Kinetic Model

(*ii*) Formation of CO

$$Ar-CHO+Co^{III} \xrightarrow{k_{IV}} Ar^{\bullet}+CO+Co^{II} \qquad (7)$$

$$Ar-CO^{\bullet} \xrightarrow{k_{V}} Ar^{\bullet}+CO \qquad (8)$$

$$r_{CO}=k_{IV}\cdot[Ar-CHO]\cdot[Co^{III}]+k_{V}\cdot[Ar-CO^{\bullet}] \qquad (9)$$

Kinetic Model of CO Formation:

$$\boxed{r_{CO}=k_{3}\cdot[Ar-CHO]+k_{4}\cdot[Ar-CO^{\bullet}]} \qquad (10)$$

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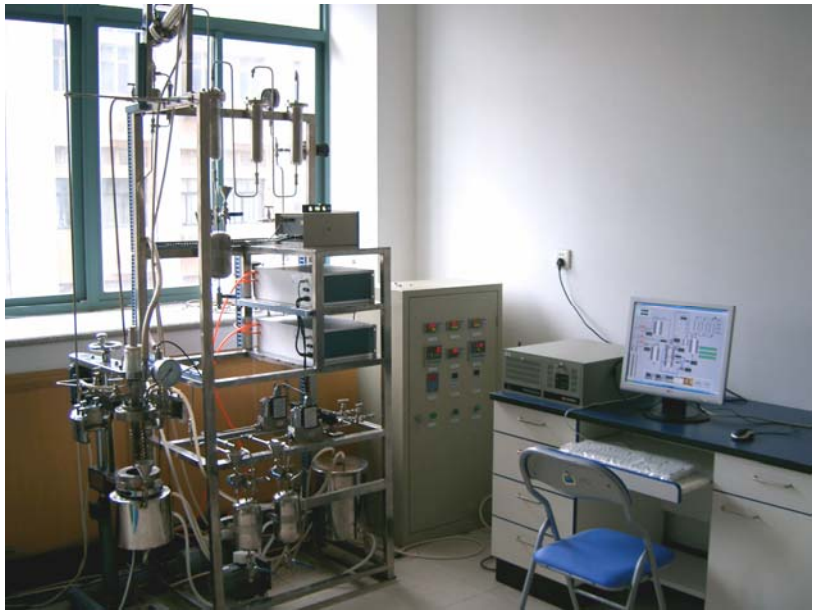
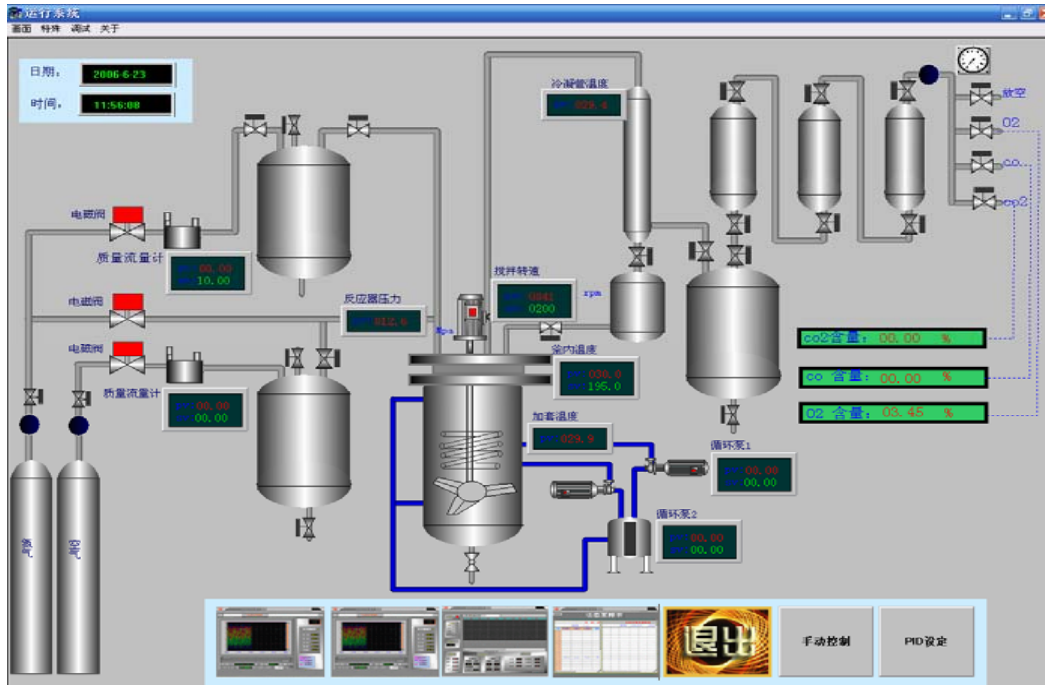
Experimental

Experimental setup





$$r_{CO_x} = \frac{[CO_x] \cdot Q_{Air} \cdot 0.79}{(1-[O_2]-[CO_x]) \cdot 22.4 \cdot M_{sol}} \qquad (11)$$

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Results

Determination of intermediates and free radicals

$$\frac{dC_{PX}}{dt} = -k_1 C_{PX} - k_2 C_{[O]} C_{PX} \tag{12}$$

$$\frac{dC_{[O]_{PX}}}{dt} = k_1 C_{PX} + k_2 C_{[O]} C_{PX} - CC_{[O]_{PX}} - k_6 C_{[O]_{PX}} (C_{[O]} + C_{[O]_{PX}}) \tag{13}$$

$$\frac{dC_{TALD}}{dt} = CC_{[O]_{PX}} - k_1 C_{TALD} - k_3 C_{[O]} C_{TALD} \tag{14}$$

$$\frac{dC_{[O]_{TALD}}}{dt} = k_1 C_{TALD} + k_3 C_{[O]} C_{TALD} - CC_{[O]_{TALD}} - k_6 C_{[O]_{TALD}} (C_{[O]} + C_{[O]_{TALD}}) \tag{15}$$

$$\frac{dC_{p-TA}}{dt} = CC_{[O]_{TALD}} - k_1 C_{p-TA} - k_4 C_{[O]} C_{p-TA} \tag{16}$$

Weizhen Sun, Ling Zhao. ***Ind. Eng. Chem. Res.***, 2011, 50: 2548-2553.
Weizhen Sun, Yi Pan, Ling Zhao, Xinggui Zhou. ***Chem. Eng. Technol.***, 2008, 31: 1402-1409.

Results

Determination of intermediates and free radicals

$$\frac{dC_{[O]_{p-TA}}}{dt} = k_1 C_{p-TA} + k_4 C_{[O]} C_{p-TA} - CC_{[O]_{p-TA}} - k_6 C_{[O]_{p-TA}} (C_{[O]} + C_{[O]_{p-TA}}) \quad (17)$$

$$\frac{dC_{4-CBA}}{dt} = CC_{[O]_{p-TA}} - k_1 C_{4-CBA} - k_5 C_{[O]} C_{4-CBA} \quad (18)$$

$$\frac{dC_{[O]_{4-CBA}}}{dt} = k_1 C_{4-CBA} + k_5 C_{[O]} C_{4-CBA} - CC_{[O]_{4-CBA}} - k_6 C_{[O]_{4-CBA}} (C_{[O]} + C_{[O]_{4-CBA}}) \quad (19)$$

$$\frac{dC_{TPA}}{dt} = CC_{[O]_{4-CBA}} \quad (20)$$

$$\frac{dC_{i-O_4-j}}{dt} = k_6 (C_{[O]}{}^2 - C_{[O]_{PX}} C_{[O]_{TALD}} - C_{[O]_{PX}} C_{[O]_{p-TA}} - C_{[O]_{PX}} C_{[O]_{4-CBA}} - C_{[O]_{TALD}} C_{[O]_{p-TA}} - C_{[O]_{TALD}} C_{[O]_{4-CBA}} - C_{[O]_{p-TA}} C_{[O]_{4-CBA}}) \quad (21)$$

where

$$C_{[O]} = (C_{[O]_{PX}} + C_{[O]_{TALD}} + C_{[O]_{p-TA}} + C_{[O]_{4-CBA}})$$
$$C = (k_2 C_{PX} + k_3 C_{TALD} + k_4 C_{p-TA} + k_5 C_{4-CBA})$$

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Results

Model parameters for main reaction

Table 1a. Estimated rate constants (kg/mol/min)

$k_2\times10^{-3}$	$k_3\times10^{-3}$	$k_4\times10^{-3}$	$k_5\times10^{-3}$	k_6
15.88±0.62	17.09±0.53	3.28±0.13	9.81±0.28	0.54±0.02

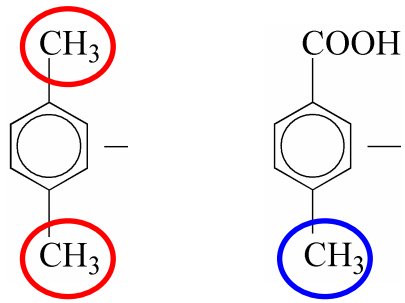
Table 1b. Initiation rate constants

Initiation rate constants	Case 1	Case 2	Case 3
k_1, 10^{-5}min^{-1}, for PX oxidation	6.29	5.50	4.03

$$k_2 / k_4 = 4.8$$

Hammett structure-reactivity relationship:

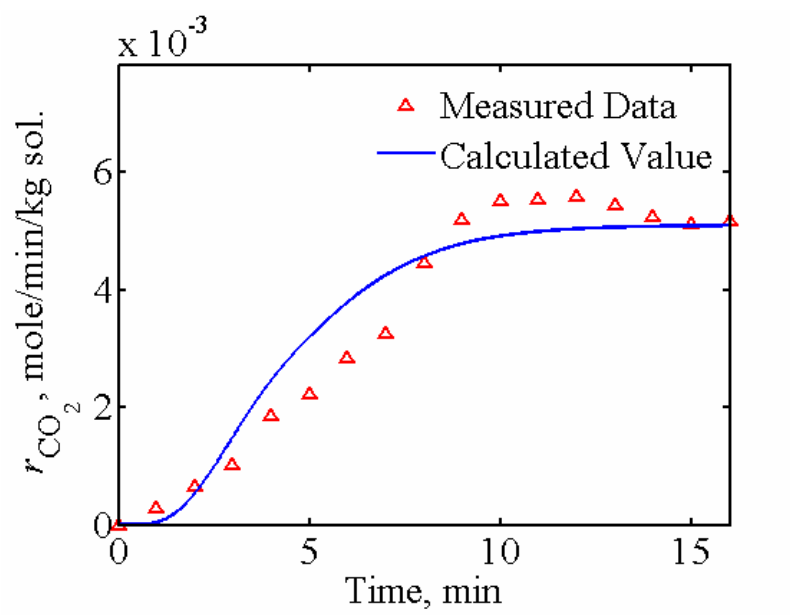
$$\log(k / k_0) = \sigma \cdot \rho \Rightarrow k_2 / k_4 = 4.9$$



Results

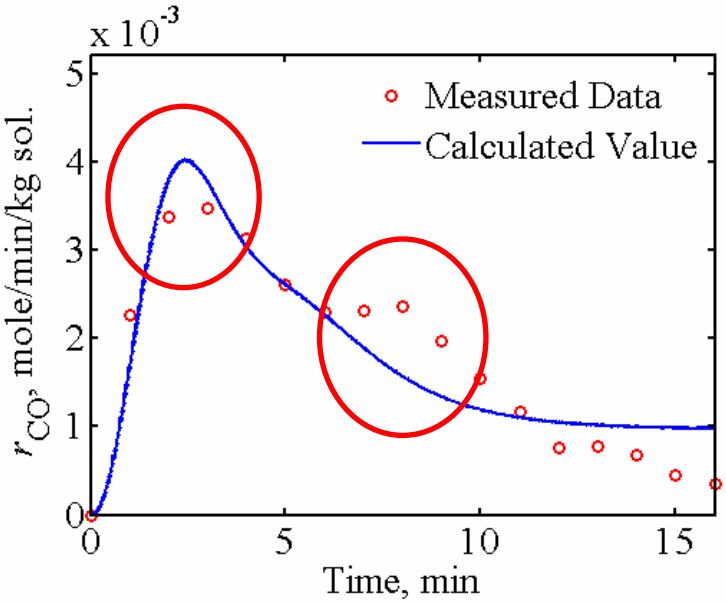
Preliminary fitting

$$r_{CO_2} = k_1 \cdot [Ar - COOH] + k_2 \cdot [ROO^{\cdot}] \quad (6)$$



Model fitting to the formation rate of CO_2

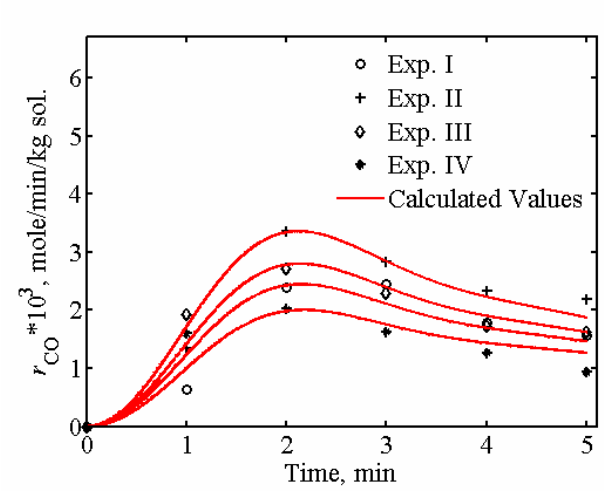
$$r_{CO} = k_3 \cdot [Ar - CHO] + k_4 \cdot [Ar - CO^{\cdot}] \quad (10)$$



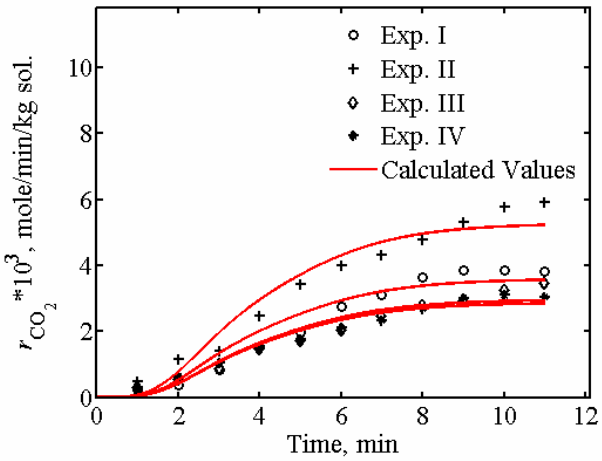
Model fitting to the formation rate of CO

Results

Revised fitting



Model fitting to the formation rate of CO



Model fitting to the formation rate of CO_2

Table 2. Summary of Rate Constants

Co/Mn/Br, 10^{-6} kg/kg	k_1 *10^3, min^{-1}	k_3 *10^3, min^{-1}	k_4, min^{-1}
350/350/700	3.8±0.5	12.9±2.5	5.4±4.0
700/350/700	5.6±0.7	18.1±2.1	
350/700/700	3.2±0.4	14.9±2.0	
350/350/1400	3.1±0.1	10.3±2.4	

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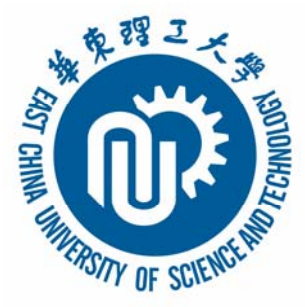
Conclusion

1. The MC oxidation of PX was carried out semi-continuously and the formation kinetics of COx was measured. The simplified elementary steps of COx formation were summarized, on the basis of which the kinetic model of COx formation was established.

2. For the formation of CO_2, the fitting curve is in agreement with the experiments. The rate constants of elementary step for decarboxylation of alkyl aromatics were determined with narrow confidence intervals.

3. There are two peaks for the formation rate of CO as a function of time, in which the first is captured successfully by the model. In initial stage, the CO formation has two main sources, including the decarbonylation of aldehyde group and the direct decarbonylation of carbonyl radical. The rate constants of these two elementary steps were determined.



The End!

Thank you for your attentions!