

Experimental Study and Modeling of Homogenous Catalytic Oxidation of *m*-Xylene to Isophthalic Acid

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ABSTRACT: The homogeneous oxidation of *m*-xylene (MX) to isophthalic acid (IPA) with acetic acid as solvent catalyzed by Co–Mn–Br catalyst was investigated at temperatures from 448.2 to 466.2 K by semicontinuous and continuous experiments. Based on the free radical chain reaction mechanism of hydrocarbon, one simplified kinetic model of MX oxidation with six parameters was developed involving MX, IPA, and important intermediates. The kinetic model fitted experimental data well, in which there was only one adjustable parameter, i.e., chain initiation rate constant corresponding to various temperatures, while other parameters were kept constant. It was found that the oxidation rate constants concerning the methyl on the benzene ring of MX was well consistent with the predictions by the Hammett structure–reactivity relationship. Through reasonable assumptions, the well-mixed reactor model of MX oxidation was further developed, by which successful predictions of the continuous MX oxidation process under different operating conditions were performed. Hopefully the kinetic experiments and related models may bring fundamental data and some valuable insights to industrial MX oxidation.

1. INTRODUCTION

Isophthalic acid (IPA) is a commercially important aromatic dicarboxylic acid, which is used as precursor to the fire-resistant material called Nomex with excellent thermal, chemical, and radiation resistance.¹ Mixed with terephthalic acid (TPA), IPA can be used in the manufacture of resins for drink bottles. Another high performance polymer, polybenzimidazole, is also produced from IPA.² Currently, the commercial production of IPA is from the liquid phase oxidation of *m*-xylene (MX) under the Co–Mn–Br catalyst system.³ Such a liquid phase oxidation technique of hydrocarbon using air or oxygen is of great importance to industrialized economies, by which one relatively cheap petroleum hydrocarbon is converted into high-value-added industrial organic chemicals important in polymer and petrochemical industries.⁴ To avoid the use of bromide, some bromide-free catalyst systems have been put forward to promote the xylene oxidation.^{5–7} However, none of these methods has been put into commercial application for the quick deactivation of catalyst.⁸ Therefore, in a quite long period of time for the future, the dominating technology to manufacture IPA will be the liquid phase oxidation of MX using Co–Mn–Br as catalyst.

Given that MX has much similarity in molecular structure with respect to *p*-xylene (PX), they share quite a lot common characteristics, from their productions to applications in polyester industries, to the oxidation reaction mechanism.^{9,10} In the past half century, much attention has been paid to the liquid phase oxidation of PX to TPA, including the oxidation mechanism, reaction kinetics, process simulation, and so on.^{9–22} However, to the best of our knowledge there is far less literature focusing on the liquid phase oxidation of MX to IPA. This may be owing to that the scale of commercial production of IPA is relatively small compared with that of TPA. But with the fast growth of the global market of purified terephthalic acid (PTA) in the past decades, the commercial competition is becoming more and more intense.²³ Some small PTA plants are being forced to shut down or turn to the

production of more value-added IPA since they share a similar manufacture process.

However, there are at least two different points between the catalytic oxidation of MX and PX to their corresponding aromatic dicarboxylic acids. One lies in the fact that the IPA from the oxidation of MX has large solubility in the solvent acetic acid,^{10,24} while the solubility of TPA in acetic acid is very small even at elevated temperature.²⁵ As a result, the MX oxidation to IPA is generally a homogeneous reaction system, and on the contrary for the PX oxidation to PTA it is a slurry solution with the precipitation of TPA.¹⁴ The other point is that the methyl groups on the benzene ring have different reaction activities according to their sites and/or the situation whether other sites are occupied.¹⁰ For example, the relative reactivity of the methyl groups of PX will be 3.9 if that of toluene is supposed to be 1.0, and after one methyl is oxidized to carboxylic acid the reactivity of the other will decrease to be 0.39.¹⁰ For MX, the reactivity of methyl groups is 2.5, and it will drop to 0.49 when one methyl is converted into carboxylic acid. Therefore, the kinetic information and process modeling for the liquid phase oxidation of MX to IPA are necessary for its industrial process optimization and scale-up. However, to the best of our knowledge there is far less literature concerning the reaction kinetics and modeling of MX oxidation compared with extensive investigation of PX oxidation.

In this work, the reaction kinetics of liquid phase oxidation of MX to IPA using Co–Mn–Br as catalyst was measured by semicontinuous experiments under conditions of industrial interest such as temperature, catalyst, and pressure. The kinetic model was established based on the free radical chain reaction mechanism of hydrocarbon oxidation. The reliability of the

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kinetic model was further verified by modeling the continuous experimental process of MX oxidation.

2. EXPERIMENTAL SECTION

In this work, the semicontinuous experiments were performed to measure the liquid phase oxidation kinetics of MX to IPA. The semicontinuous experiments mean that the gas oxidant air was introduced into the reactor continuously while the liquid reactant was put into the reactor at the beginning. To verify the modeling of the industrial continuous process of MX oxidation, the continuous experiments were carried out, in which both the oxidant air and liquid reactant were introduced into the reactor continuously. The detailed description regarding the semicontinuous and continuous experimental apparatus and method can be referred to our previous work.^{21,22,26,27} Here we give a brief introduction about the semicontinuous experiment, as well as the continuous one.

2.1. Semicontinuous Experiments. In a typical semicontinuous experiment, about 550 mL of reactant mixture, including MX, acetic acid (HAc), water, and catalyst was put into the reactor. Catalyst used in this work is composed of cobalt acetate, manganese acetate, and bromide hydride. The chromatography-grade N₂ is introduced into the reactor to replace air, and stirring with an agitation rate of 800 rpm and heating were started simultaneously. When the temperature inside the reactor became stable at the setting value, the air was then introduced into the reactor to start the reaction.

2.2. Continuous Experiments. For the continuous process, the mixture of the solvent, reactants, and air are continuously fed into and the reaction solution is discharged out of the reactor. The reaction conditions are close to those of the industrial MX oxidation process, which are listed in Table 1.

Table 1. Reaction Conditions for Continuous Experiments

press. inside reactor, bar	composn of catal, ppm of Co/Mn/Br	mass concn of inlet liq, MX/acetic acid/water
13	800/400/1200	0.25/0.67/0.08

Different from PX oxidation, there is no mass precipitation of IPA due to a large solubility of IPA in acetic acid. During each reaction, strong agitation was performed together with baffles installed inside the reactor to eliminate the influence of mass transfer. Thermal resistance thermometers were inserted into the reactor to monitor the temperature changes during the whole reaction.

2.3. Analytical Method. The sample was collected and put into a volumetric flask by washing the sampling tube with dimethyl sulfoxide (DMSO). A high performance liquid chromatography (HPLC) method with an ion exchange column was used to analyze all of the reactants, intermediates, and products, i.e., MX, *m*-tolualdehyde (*m*-TALD), *m*-toluic acid (*m*-TA), 3-carboxybenzaldehyde (3-CBA), and IPA. The analytical method regarding the products of MX oxidation is the same as that of PX oxidation, which was described in detail in the literature.²⁸

3. KINETIC MODEL

The autoxidation of hydrocarbons catalyzed by metal/bromide follows a free radical chain mechanism, which has been well summarized in the literature.^{10,13,29,30} To apply this comprehensive mechanism to an industrial process, some trivial reaction steps concerning branched chain should not be taken

into account. Based on this, the simplified oxidation kinetics for PX oxidation have been developed by Wang et al.³¹ and in our previous work,²¹ respectively. Referring to the oxidation kinetics of PX, a simplified oxidation reaction sketch for MX oxidation can be formulated as Figure 1.

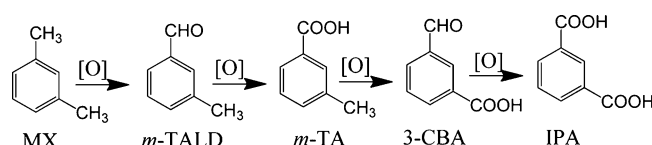
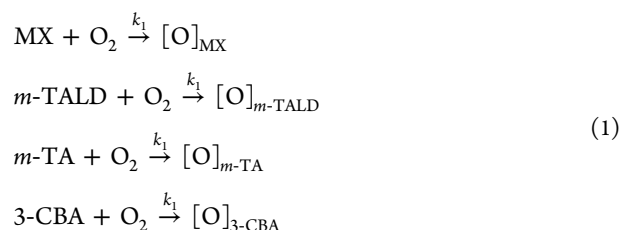


Figure 1. Simplified oxidation reaction sketch for MX oxidation to IPA.

Although MX and other intermediates are assumed to be oxidized according to the sequence shown in Figure 1, essentially all the elementary reactions involving MX, intermediates, and free radicals proceed simultaneously, which to some extent makes the reaction pathway complicated. Taking PX oxidation as an example, there are as many as 35 elementary reaction steps in Wang et al.'s work, 29 of which are rate controlling.³¹ However, there are quite a few free radicals involved in this reaction network, which are very unstable and thus hard to determine. Also, the number of measurable components is very limited. In this sense, fitting the kinetic model to experimental data may lead to inaccurate results, namely overfitting.³² In view of this, Sun et al. proposed a simplification strategy regarding the PX oxidation kinetics catalyzed by cobalt and manganese acetate and bromide in acetic acid under conditions close to those of an industrial process.^{21,22} First, it was assumed that the reactivities of different free radicals for removing the α -H atom of a certain substrate were identical. Second, it was approximated that all of the substrates have equivalent initiation rate constants. Third, the differences in the termination rate constants between various peroxy radicals were assumed to be neglected. Given that MX shares a common oxidation reaction mechanism and similar molecular structure with PX, they should have similar reaction networks. Therefore, according to the above-mentioned simplification strategy, the reaction pathway of MX oxidation to IPA can be formulated as follows.

chain initiation:



chain propagation:

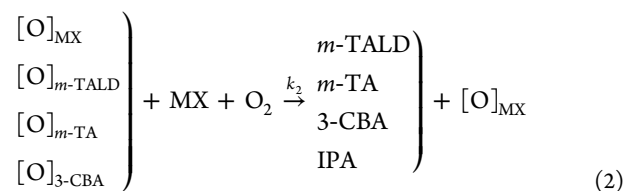
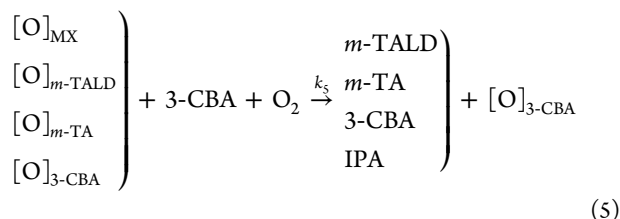
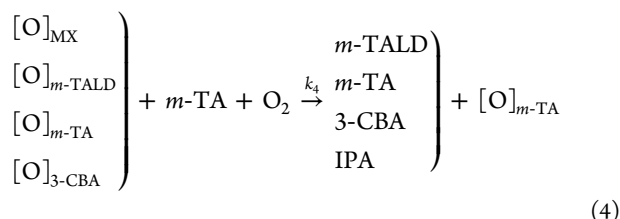
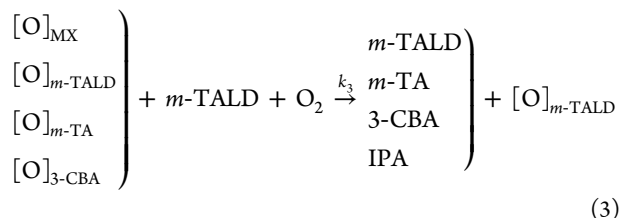
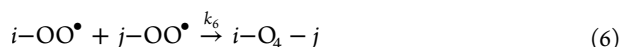


Table 2. Estimated Rate Constants and Corresponding Confidence Intervals with Confidence Level of 95%

temp, K	$k_1, 10^{-5} \text{ min}^{-1}$	$k_2, 10^4 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$	$k_3, 10^4 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$	$k_4, 10^3 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$	$k_5, 10^4 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$	$k_6, \text{ kg}^2 \cdot \text{mol}^{-2} \cdot \text{min}^{-1}$
448.2	2.77 ± 0.18					
453.2	3.25 ± 0.22					
458.2	4.54 ± 0.32	1.21 ± 0.08	1.83 ± 0.14	4.77 ± 0.18	1.85 ± 0.09	0.55 ± 0.06
463.2	6.05 ± 0.43					



chain termination:



In the reaction pathway of MX oxidation given by eqs 1–6, $[\text{O}]_{\text{MX}}$, $[\text{O}]_{m\text{-TALD}}$, $[\text{O}]_{m\text{-TA}}$, and $[\text{O}]_{3\text{-CBA}}$ represent the corresponding peroxy radicals derived from MX, *m*-TALD, *m*-TA, and 3-CBA, respectively. After suitable simplification, clearly we can see that there are only six rate constants to be determined. Correspondingly, five components can be used to fit these rate constants, i.e. MX, *m*-TALD, *m*-TA, 3-CBA, and IPA. Based on mass balance in a semicontinuous process, the kinetic model for MX oxidation to IPA can be readily written as follows.

$$\frac{dC_{\text{MX}}}{dt} = -k_1 C_{\text{MX}} - k_2 C_{[\text{O}]} C_{\text{MX}} \quad (7)$$

$$\frac{dC_{m\text{-TALD}}}{dt} = CC_{[\text{O}]_{\text{MX}}} - k_1 C_{m\text{-TALD}} - k_3 C_{[\text{O}]} C_{m\text{-TALD}} \quad (8)$$

$$\frac{dC_{m\text{-TA}}}{dt} = CC_{[\text{O}]_{m\text{-TALD}}} - k_1 C_{m\text{-TA}} - k_4 C_{[\text{O}]} C_{m\text{-TA}} \quad (9)$$

$$\frac{dC_{3\text{-CBA}}}{dt} = CC_{[\text{O}]_{m\text{-TA}}} - k_1 C_{3\text{-CBA}} - k_5 C_{[\text{O}]} C_{3\text{-CBA}} \quad (10)$$

$$\frac{dC_{\text{IPA}}}{dt} = CC_{[\text{O}]_{3\text{-CBA}}} \quad (11)$$

$$\frac{dC_{[\text{O}]_{\text{MX}}}}{dt} = k_1 C_{\text{MX}} + k_2 C_{[\text{O}]} C_{\text{MX}} - CC_{[\text{O}]_{\text{MX}}} - k_6 C_{[\text{O}]_{\text{MX}}} (C_{[\text{O}]} + C_{[\text{O}]_{\text{MX}}}) \quad (12)$$

$$\frac{dC_{[\text{O}]_{m\text{-TALD}}}}{dt} = k_1 C_{m\text{-TALD}} + k_3 C_{[\text{O}]} C_{m\text{-TALD}} - CC_{[\text{O}]_{m\text{-TALD}}} - k_6 C_{[\text{O}]_{m\text{-TALD}}} (C_{[\text{O}]} + C_{[\text{O}]_{m\text{-TALD}}}) \quad (13)$$

$$\frac{dC_{[\text{O}]_{m\text{-TA}}}}{dt} = k_1 C_{m\text{-TA}} + k_4 C_{[\text{O}]} C_{m\text{-TA}} - CC_{[\text{O}]_{m\text{-TA}}} - k_6 C_{[\text{O}]_{m\text{-TA}}} (C_{[\text{O}]} + C_{[\text{O}]_{m\text{-TA}}}) \quad (14)$$

$$\frac{dC_{[\text{O}]_{3\text{-CBA}}}}{dt} = k_1 C_{3\text{-CBA}} + k_5 C_{[\text{O}]} C_{3\text{-CBA}} - CC_{[\text{O}]_{3\text{-CBA}}} - k_6 C_{[\text{O}]_{3\text{-CBA}}} (C_{[\text{O}]} + C_{[\text{O}]_{3\text{-CBA}}}) \quad (15)$$

$$\frac{dC_{i\text{-O}_4-j}}{dt} = k_6 (C_{[\text{O}]}^2 - C_{[\text{O}]_{\text{MX}}} C_{[\text{O}]_{m\text{-TALD}}} - C_{[\text{O}]_{\text{MX}}} C_{[\text{O}]_{m\text{-TA}}} - C_{[\text{O}]_{\text{MX}}} C_{[\text{O}]_{3\text{-CBA}}} - C_{[\text{O}]_{m\text{-TALD}}} C_{[\text{O}]_{m\text{-TA}}} - C_{[\text{O}]_{m\text{-TALD}}} C_{[\text{O}]_{3\text{-CBA}}} - C_{[\text{O}]_{m\text{-TA}}} C_{[\text{O}]_{3\text{-CBA}}}) \quad (16)$$

$$C_{[\text{O}]} = C_{[\text{O}]_{\text{MX}}} + C_{[\text{O}]_{m\text{-TALD}}} + C_{[\text{O}]_{m\text{-TA}}} + C_{[\text{O}]_{3\text{-CBA}}} \quad (17)$$

$$C = k_2 C_{\text{MX}} + k_3 C_{m\text{-TALD}} + k_4 C_{m\text{-TA}} + k_5 C_{3\text{-CBA}} \quad (18)$$

The initial conditions are

$$\begin{aligned} t = 0, \quad C_{\text{MX}} &= C_{\text{MX}}^0, \quad C_{m\text{-TALD}} = 0, \quad C_{m\text{-TA}} = 0, \\ C_{3\text{-CBA}} &= 0, \quad C_{\text{IPA}} = 0, \quad C_{[\text{O}]_{\text{MX}}} = 0, \\ C_{[\text{O}]_{m\text{-TALD}}} &= 0, \quad C_{[\text{O}]_{m\text{-TA}}} = 0, \quad C_{[\text{O}]_{3\text{-CBA}}} = 0, \\ C_{i\text{-O}_4-j} &= 0 \end{aligned} \quad (19)$$

4. RESULTS AND DISCUSSION

4.1. Estimation of Rate Constants. Four runs of experiments under various temperatures were carried out and used to fit the kinetic model and to estimate model parameters. The rate constants k_1 through k_6 are obtained by minimizing the residual sum of the squares as follows:

$$S = \sum_{i=1}^m \sum_{j=1}^5 (y_{ij}^{\text{cal}} - y_{ij}^{\text{exp}})^2 \quad (20)$$

where y_{ij}^{cal} and y_{ij}^{exp} are the calculated and experimental concentrations of the *j*th component, respectively. Ordinal numbers 1, 2, 3, 4, and 5 represent MX, *m*-TALD, *m*-TA, 3-CBA, and IPA, respectively, and *m* represents the total runs of the experiments. A Matlab function, *lsqnonlin*, is employed to find the minimum of function *S*.

There are six parameters to be estimated in the kinetic model, while we have only five observable components that can be measured. Therefore, directly fitting the model to experimental data may result in an overfitting problem.³² Fortunately, it can be found from the formulation of the kinetic model that the rate constants are independent of catalyst, except k_1 . Furthermore, preliminary fitting results showed that the rate constants changed little with different temperatures within the investigated temperature range in this work, except k_1 . Accordingly, we fixed the values of k_2 through k_6 when fitting experiments under various temperatures. As a consequence of this, four runs of experiments listed in Table 2 can share the common parameters, i.e., k_2 through k_6 , and only k_1 acts as the only alterable parameter. It can be seen from Table 2 that all the confidence intervals are at least 1 order of magnitude less than the corresponding rate constants, which indicates that the rate constants are definite and reliable. Moreover, compared with chain initiation and termination steps, chain propagation steps proceed much faster, which accords with the characteristic of the typical free radical chain reactions. In particular, the rate constant of the chain initiation step has the order of magnitude of 10^{-5} and it is more sensitive to temperature variation. The comparison between experimental data and predictions based on the kinetic model is shown in Figure 2. Clearly we can see that there are very good agreements between experimental data and model calculations from reactant to intermediates to main product.

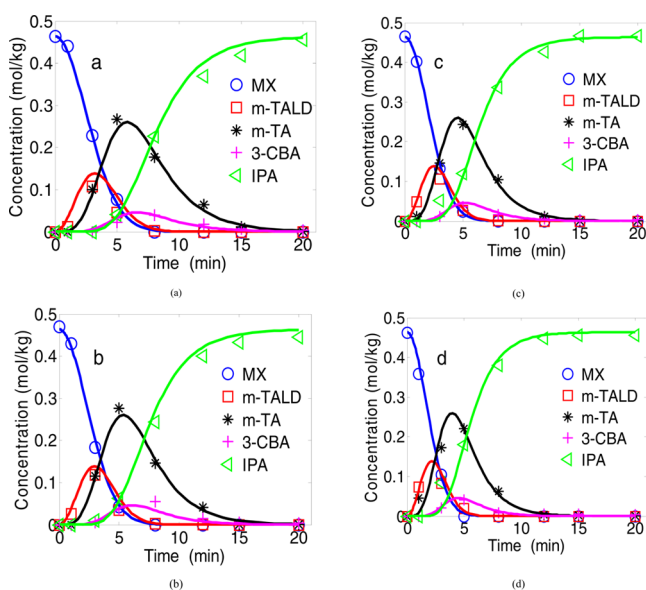


Figure 2. Concentration profiles of reactant and products as a function of time under various temperatures. Symbols, experimental data; line, calculated values by kinetic model in this work. Temperature: (a) 448.2, (b) 453.2, (c) 458.2, and (d) 463.2 K. Pressure: 13 bar. $[\text{Co}]/[\text{Mn}]/[\text{Br}] = 800/400/1200$ ppm. Water concentration in solution: 8% (mass concentration).

4.2. Validation of Kinetic Model. For most methyl aromatic compounds, their oxidation reaction rates follow the Hammett structure–reactivity equation:¹⁰

$$\log\left(\frac{k}{k_0}\right) = \sigma\rho \quad (21)$$

This equation essentially comes from the Gibbs free energy relationship.^{14,33} In eq 21, k and k_0 represent the rate constant for the oxidation of a given compound and that of toluene, respectively. The σ and ρ stand for the constant characteristic of the substituent on the ring and that for a given set of conditions. In the literature many values of ρ have been reported for metal/bromine catalyzed oxygenations, which are similar and range from -0.60 to -1.34 .^{10,34} Since the MX oxidation experiments in this work were carried out in an acetic acid solution of 8% water, we adopt the ρ value of -0.95 recommended by Partenheimer because it was measured in acetic acid solution with the water content of 10%.¹⁰

Concerning the values of σ for the meta position on a benzene ring, when a methyl group becomes oxidized to a carboxylic acid, it will change from -0.10 to 0.32 .³⁵ Therefore, the ratio of the oxidation rate of MX to that of *m*-TA can be readily calculated from eq 21, and the result is 2.51. On the other hand, the value of k_2/k_4 (they are the oxidation rate constants corresponding to the oxidations of MX and *m*-TA, respectively, listed in Table 2) can be computed to be 2.54. It is clear that the reaction rate constant estimated in this work has a very good agreement with the predicted value based on the Hammett relationship. This indicates that the kinetic model of MX oxidation developed in this work is well-established. Moreover, the Arrhenius relationship between the chain initiation rate constant k_1 and temperature T was plotted in Figure 3, in which a good linearity can be noticed. Meanwhile, the pre-exponential factor and activation energy were obtained to be $1.53 \times 10^6 \text{ min}^{-1}$ and 92.3 kJ/mol , respectively.

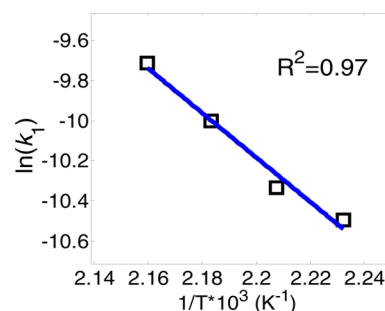


Figure 3. Arrhenius relationship between k_1 and $1/T$.

4.3. Modeling of Continuous Process. The commercial production of IPA is a continuous process, among which the reactions happening in the oxidation reactor to convert MX to IPA are the key procedure. It is necessary to establish the mathematical model of the oxidation reactor to predict the industrial MX oxidation. To establish the model of the MX oxidation reactor, the following assumptions are made. First, due to very strong agitation the reactants inside the reactor should be mixed well, so the hypothesis of a well-mixed reactor is met with. Next, the crystallization process of solid phase IPA inside the reactor is neglected given that there is no massive crystal precipitation owing to the considerably large solubility of IPA in acetic acid aqueous solution.¹⁰ Finally, the gas–liquid mass transfer is also assumed sufficient because of good mixing inside the reactor. Based on the aforementioned assumptions, the mass balance equations describing the concentrations of liquid phase reactants can be written as follows:

$$c_{i,0} - c_i + \tau R_i = 0 \quad (22)$$

Table 3. Model Prediction against Continuous Experiments

exptl run	temp, K	τ , min	conv of MX, exptl/calcd	yield of IPA, exptl/calcd	3-CBA in liq phase, exptl/calcd, 10^{-6} kg/kg	<i>m</i> -TA in liq phase, exptl/calcd, 10^{-6} kg/kg
1	450.2	90	>99.5/99.4	97.1/97.3	1294/1244	4156/4401
2	456.2	90	>99.5/99.5	98.1/97.6	1198/1085	3536/3837
3	461.2	95	>99.5/99.6	98.6/98.1	901/884	2869/3127
4	466.2	95	>99.5/99.7	98.5/98.3	813/779	2345/2754
5	466.2	70	>99.5/99.5	97.6/97.8	943/1052	2529/3223
6	466.2	52	>99.5/99.3	97.4/97.1	1375/1407	3831/4675
7	439.2	15	~96.4/95.4	78.1/79.8	10131/8857	28070/32173
8	463.2	15	~98.4/97.7	88.8/89.2	5631/4924	15050/17613

where R_i represents the net formation rate of the component i , and $c_{i,0}$ and c_i stand for the inlet and outlet concentrations of liquid component i , respectively. When the residence time τ is specified, combining the oxidation kinetics R_i obtained previously, the nonlinear equation set can be solved by using the Matlab function *fsolve*.

Comparisons between experiments and model predictions concerning various temperatures and residence time (τ) are listed in Table 3. It can be seen from the experiments that with the increase of temperature and residence time the conversion of MX, as well as the yield of IPA, is enhanced, while the intermediates 3-CBA and *m*-TA obviously go down. Meanwhile, the model calculations gave reasonable predictions regarding these experimental results. It is worth noting that for the experimental runs 4–7 in Table 3 the temperatures are out of the investigated range of the kinetic model. However, the predictions are still satisfactory. This further demonstrates the reliability of the kinetic model proposed in this work.

5. CONCLUSIONS

The homogeneous catalytic oxidation kinetics of MX to IPA has been investigated under conditions of industrial interest such as temperature, pressure, and catalyst by semicontinuous experiments. One simplified kinetic model for MX oxidation was developed on the basis of the free radical chain reaction mechanism. The model calculated values regarding reactants, intermediates, and desired products matched experimental data well under different temperature conditions. For various conditions, it was found that there was only one parameter required to be adjusted, i.e., the chain initiation rate constant. Furthermore, the rate constants concerning oxidation of the methyl in the benzene ring can well conform to the Hammett structure–reactivity prediction relationship on hydrocarbon oxidation. The continuous experiments were further performed under conditions of industrial interest. According to the kinetic model developed in this work and reasonable assumptions, the well-mixed reactor model was established. The calculations based on the reactor model can well predict the continuous experiments. It is hopeful that the kinetic experiments and related models may provide fundamental data and some insights to the industrial oxidation of MX to IPA.

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Notes

The authors declare no competing financial interest.

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