Kinetics of Cyclohexane Oxidation

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Introduction

The oxidation of cyclohexane to cyclohexanone represents an important chemical reaction which is essential for the production of nylon. Despite its industrial importance, liquid phase oxidation of cyclohexane is considered to be an extremely complex reaction whose mechanism remains poorly understood to date. Over the past several decades, both kinetic modeling studies of various proposed reaction mechanisms as well as experimentations have been reported. Spielman[1] presented an analytical study of two reaction mechanisms postulated for liquid phase oxidation of hydrocarbon and applied the results obtained to experimental data on ordinary and boric acid modified air oxidation of cyclohexane. Alagy et al.[2] developed a mathematical model for cyclohexane oxidation based on the same reaction mechanism and included mass transfer considerations in their analyses. Pohorecki et al.[3] developed a new, comprehensive model of liquid phase catalytic cyclohexane oxidation with mass transfer and performed numerical simulations of industrial reactors using their model. More recently, Jhansi et al.[4,5] carried out liquid phase oxidation of cyclohexane using molecular oxygen and a zirconium and iron–copper complex catalyst, respectively. They proposed a new reaction mechanism based on the model of Pohorecki et al.[3] and showed that the pseudo-steady state approximation was invalid for the mechanism. The set of rate equations corresponding to the elementary steps in the reaction mechanism were integrated numerically and Genetic Algorithm was employed for curve fitting.

We will first discuss a few salient points relating to the reaction mechanism proposed by Jhansi et al.[4] which provided the motivation for the current work. The mechanism consists of eight elementary reaction steps (Figure 7 of [4]) with the rates of change of concentration for each component presented as Eqs. 1–7 of [4]. We note that the chemical equation depicted as step 4 of the reaction mechanism is not balanced stoichiometrically. Secondly, step 6 shows the reaction of half a molecule of oxygen which is unphysical for an elementary reaction. Further, the chemical formula for cyclohexanol in both of the above steps should have been $C_6H_{11}OH$ rather than $C_6H_{10}OH$. Finally, in summing up all the elementary reaction steps, it may be observed that the intermediate species $C_6H_{11}OO^*$ and $C_6H_{11}{}^*$ do not cancel exactly on each sides of the equations. In the next section, we present a reaction mechanism that is corrected of the above few points and show that the rate equation derived from this mechanism based on the pseudo-steady state hypothesis can describe fairly adequately the oxidation kinetics data reported by Jhansi et al.[4]

Model

We suggest that the formations of cyclohexanone and cyclohexanol from cyclohexane proceed in parallel but share a common preceding step in which the necessary intermediate species is produced. Following steps 1 and 2 of the reaction mechanism proposed by Jhansi et al.,[4] C_6H_{12} reacts with molecular oxygen on the zirconium complex catalyst to form the reactive intermediate, $C_6H_{11}OO^*$. Then, $C_6H_{11}OO^*$ can either undergo re-arrangement to produce cyclohexanone or react with another molecule of cyclohexane to produce cyclohexanol. In either case, the zirconium catalyst is regenerated at the end of the reaction. Figure 1 shows the two sets of elementary reaction steps which eventually lead to the formation of these two products of oxidation of cyclohexane, respectively. It may be observed that on summing these elementary steps, all intermediate species are cancelled away exactly and the following overall stoichiometric equation is obtained:

$$3C_6H_{12} + 2O_2 \rightarrow C_6H_{10}O + 2C_6H_{11}OH + H_2O \qquad (1)$$

On the basis of above suggested mechanism, the rate of reaction with respect to cyclohexane can be written as

$$\frac{d[C_6H_{12}]}{dt} = -2k_1[C_6H_{12}][O_2] - k_3[C_6H_{12}][C_6H_{11}OO^*] \qquad (2)$$

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$$\begin{cases} \mathrm{Al_2O_3 \bullet ZrZr\ C_6H_4 + C_6H_{12} + O_2 \xrightarrow{k_0} Al_2O_3 \bullet ZrZr^{-}\ C_6H_5{\cdots}C_6H_{11}OO^*} & \text{(step 1)} \\ \mathrm{Al_2O_3 \bullet ZrZr^{-}\ C_6H_5{\cdots}C_6H_{11}OO^* \xrightarrow{k_2} Al_2O_3 \bullet ZrZr\ C_6H_4 + C_6H_{10}O + H_2O} & \text{(step 2)} \end{cases}$$

$$\begin{cases} \mathrm{Al_2O_3 \bullet ZrZr\ C_6H_4 + C_6H_{12} + O_2 \xrightarrow{k_0} Al_2O_3 \bullet ZrZr^{-}\ C_6H_5{\cdots}C_6H_{11}OO^*} & \text{(step 1)} \\ \mathrm{Al_2O_3 \bullet ZrZr^{-}\ C_6H_5{\cdots}C_6H_{11}OO^* + C_6H_{12} \xrightarrow{k_3} Al_2O_3 \bullet ZrZr\ C_6H_4 + 2C_6H_{11}OH} & \text{(step 3)} \end{cases}$$

Figure 1. Proposed reaction mechanism for catalytic oxidation of cyclohexane.

where $k_1 = k_0[\mathrm{Al_2O_3 \cdot ZrZr\ C_6H_4}]$ and the concentration of the catalyst $[\mathrm{Al_2O_3 \cdot ZrZr\ C_6H_4}]$ is assumed to be constant. We apply the pseudo-steady state hypothesis to the rates of change of the intermediate species to obtain the following expression for its concentration:

$$[\mathrm{C_6H_{11}OO^*}] = \frac{2k_1[\mathrm{C_6H_{12}}][\mathrm{O_2}]}{k_2 + k_3[\mathrm{C_6H_{12}}]} \tag{3}$$

Thus, the rate equation in terms of $[\mathrm{C_6H_{12}}]$ is

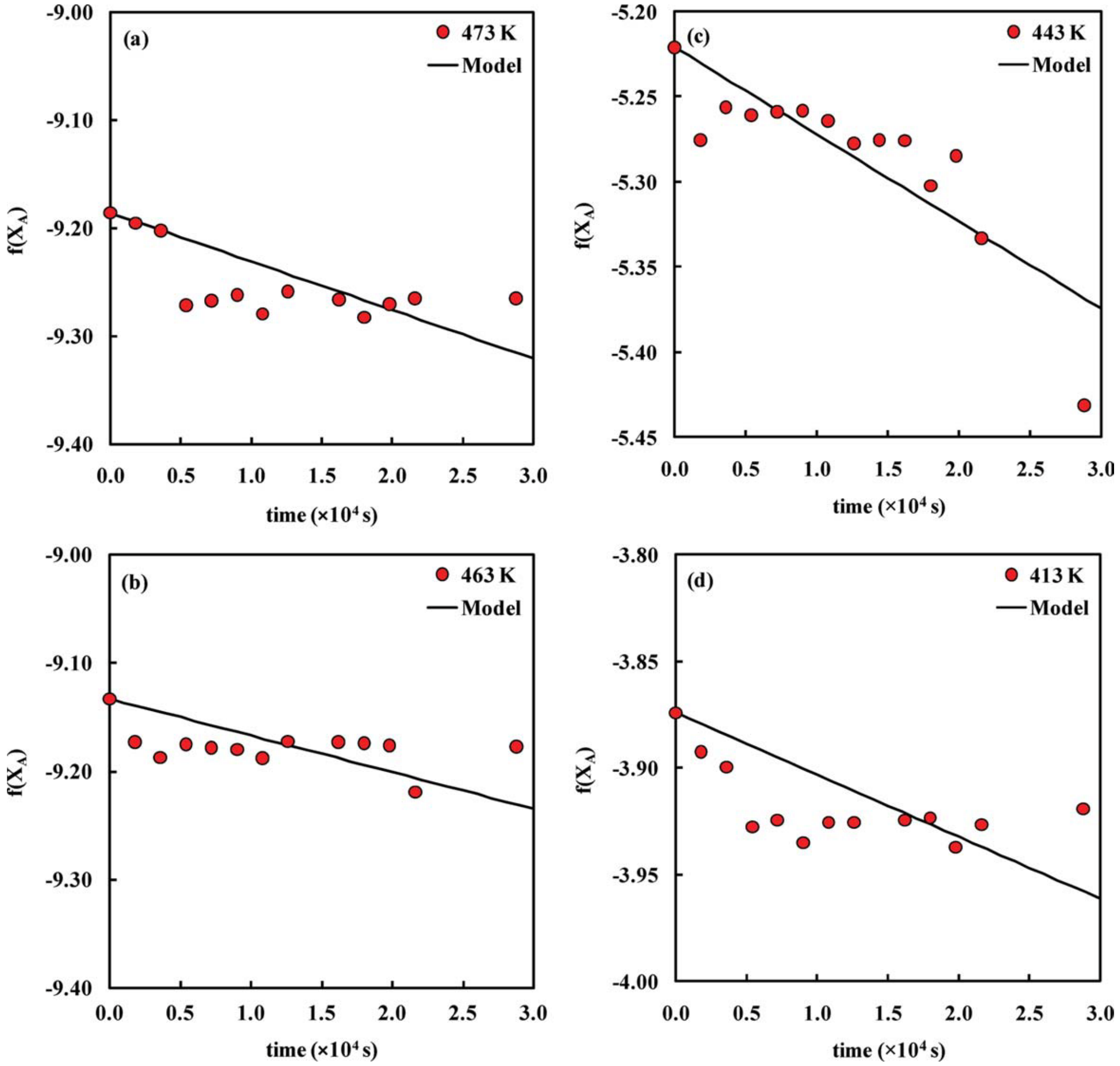

Figure 2. Comparisons of proposed kinetic model with experimental data[4] for cyclohexane oxidation using zirconium complex catalyst at (a) 473 K (b) 463 K (c) 443 K, and (d) 413 K.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 1. Rate Constants at Different Reaction Temperatures with Zr Catalyst

T (K)	k_1 (m^3 mol^{-1} s^{-1})	k_2 (s^{-1})	k_3 (m^3 mol^{-1} s^{-1})
473	1.61×10^{-8}	1.11×10^{-4}	0.527
463	1.11×10^{-8}	1.00×10^{-4}	0.500
443	1.68×10^{-8}	8.77×10^{-5}	0.010
413	9.50×10^{-9}	9.65×10^{-3}	2.60×10^{-3}

$$-\frac{d[C_6H_{12}]}{dt} = \frac{2k_1k_2[C_6H_{12}][O_2] + 4k_1k_3[C_6H_{12}]^2[O_2]}{k_2 + k_3[C_6H_{12}]} \qquad (4)$$

The rate equation can be integrated analytically to the following:

$$\ln\left\{\frac{[C_6H_{12}]^2\ k_2 + 2k_3[C_6H_{12}]_0}{[C_6H_{12}]_0^2\ k_2 + 2k_3[C_6H_{12}]}\right\} = -4k_1[O_2]t \qquad (5)$$

where, $[C_6H_{12}]_0$ is the initial concentration of C_6H_{12} at time $t = 0$. In the experimental work of Jhansi et al.,[4] 'neat' cyclohexane was used and so $[C_6H_{12}]_0$ may be calculated from the mass density of cyclohexane and its relative molecular mass. Despite the differences in reaction temperatures between the various sets of kinetics data to be analyzed in the next section and the expectation that density (and therefore concentration) is a strong function of temperature, $[C_6H_{12}]_0$ will be approximated as 9256 mol m^{-3} in the rest of this article. It is also assumed that the partial pressure of oxygen is maintained at 7 atm throughout the reaction[4] and $[O_2]$ remains constant. On the basis of the work of Suresh et al.,[6] the Henry's law constant for dissolution of oxygen in cyclohexane may be approximated as 10.9 mol m^{-3} bar^{-1}. This allows the value of $[O_2]$ to be calculated as 76.3 mol m^{-3}. It may also be stated at this point that the above proposed reaction mechanism was selected from among those that have been considered in the present work based on goodness of fit with the experimental data of Jhansi et al.[4,5] Although the proposed reaction mechanism involved only irreversible elementary steps, the various reaction mechanisms that have been considered included those with reversible ones, some of which required the application of numerical methods for integration of the rate equations derived.

Finally, the above integrated form of the rate equation can be expressed in terms of conversion of cyclohexane, X_A, which will be the most convenient form for comparison with the oxidation kinetics data presented in Table 2 of Ref. [4].

$$\ln\left\{\frac{(1-X_A)^2}{k_2 + 2k_3[C_6H_{12}]_0(1-X_A)}\right\} = -4k_1[O_2]t - \ln\left\{k_2 + 2k_3[C_6H_{12}]_0\right\} \qquad (6)$$

For brevity, we refer to the L.H.S. of Eq. (6) as $f(X_A)$. This quantity is plotted against t for the four sets of experimental data reported by Jhansi et al.[4] corresponding to the four reaction temperatures 473 K, 463 K, 443 K, and 413 K, respectively. Theoretically, the experimental data plotted in this manner should fall approximately on a straight line if the suggested reaction mechanism as well as the pseudo-steady state hypothesis were valid. Values of the rate constants can then be obtained by drawing the best fit line through the data points in a trial-and-error process. We present the result of such a curve-fitting procedure in the following section.

Results and Discussion

Figure 2 shows that the rate equation derived above can indeed describe fairly adequately, within the constraints of experimental accuracy, the oxidation kinetics data reported by the previous research workers. Despite the apparently unphysical fluctuations in conversion values, all four sets of experimental data do exhibit a linear and negative relationship with respect to time when plotted in the manner described above. This suggests that the reaction mechanism proposed in this article is valid and verifies the validity of the pseudo-steady state hypothesis applied in the derivation of the overall rate equation. Secondly, we note that rate constant values obtained via the trial-and-error and curve-fitting procedures do not exhibit a strictly monotonic, non-decreasing variation with increasing temperature and we attribute this to the noisy experimental data used for our calculations (Table 1). As such, we do not attempt to further calculate values of activation energy and pre-exponential factor for the reaction based on values of rate constants obtained but leave these to future work where higher quality experimental data may be available.

We next turn our attention to a more recent work reported by the same authors[5] where they have carried out cyclohexane oxidation using an iron–copper complex catalyst. We note that some of the points listed earlier pertaining to their reaction mechanism are also applicable to the one proposed in this latter work (Figure 13 of Ref. [5]). Here, to maintain generality and universality in the reaction mechanism of cyclohexane oxidation using metal complex catalysts, we suggest that the reaction follows the same set of elementary steps as those presented in Figure 1 earlier with the exception that the zirconium complex catalyst is replaced by the iron–copper counterpart for the present case. The experimental data presented by the authors in Table 4 of Ref. [5] are thus plotted in the same manner and the same curve-fitting procedure is applied.

As with the previous case, Figure 3a shows that the experimental data corresponding to oxidation of cyclohexane carried out at 443 K, 463 K, and 483 K are adequately

Table 2. Rate Constants at Different Reaction Temperatures with Fe-Cu Catalyst

T (K)	k_1 (m^3 mol^{-1} s^{-1})	k_2 (s^{-1})	k_3 (m^3 mol^{-1} s^{-1})
483	1.10×10^{-8}	2.74×10^{-4}	7.81×10^{-7}
463	9.88×10^{-9}	2.65×10^{-4}	4.79×10^{-7}
443	1.26×10^{-8}	2.65×10^{-4}	7.65×10^{-7}
423	1.63×10^{-8}	1.25×10^{-5}	4.37×10^{-7}
398	1.38×10^{-9}	2.74×10^{-4}	3.65×10^{-8}

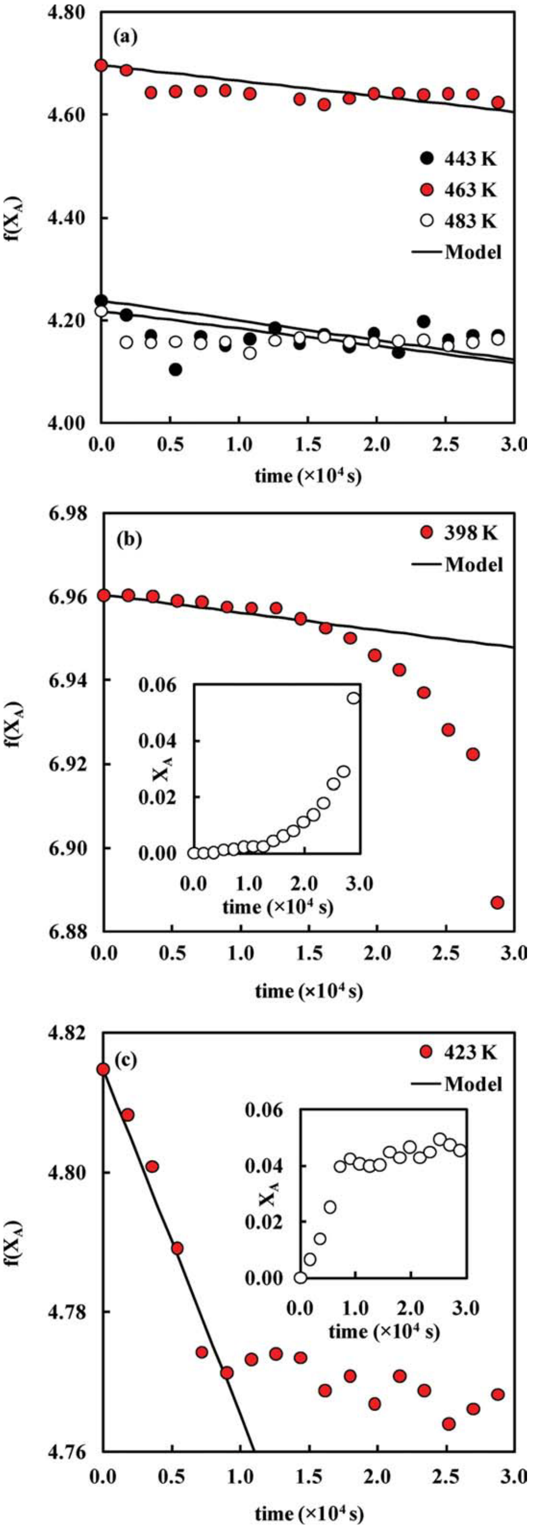

Figure 3. Comparisons of proposed kinetic model with experimental data[5] for cyclohexane oxidation using iron–copper complex catalyst at (a) 443 K, 463K, 483 K (b) 398 K and (c) 423 K.

Insets to panels (b) and (c) show cyclohexane conversions as functions of reaction times as reported by Jhansi et al.[5] at those two reaction temperatures, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

described by the rate equation derived based on the reaction mechanism proposed in the present study. It is interesting to note that, contrary to the claim of the previous authors, the pseudo-steady state hypothesis is once again verified to be valid in this case. However, at both 398 K and 423 K, this hypothesis seems to be valid only for the early parts of the reaction. Figures 3b, c show that the function f(X_A) in both these cases starts to deviate from a straight line beyond about 10^4 s. At these two temperatures, cyclohexane conversion either begins to increase exponentially or level off respectively after about 10^4 s, as depicted by the insets to these two panels. Because of this large qualitative difference in behavior of the same chemical reaction at two different temperatures, we are inclined to think that the observed deviation of the experimental data from the proposed kinetics model may be attributed to the nature of the experimental data. Although these two sets of data may not be adequate for testing of our theoretical model, we nevertheless present the comparisons between theory and experiments here for the sake of completeness. Table 2 shows the rate constant values calculated from the curve-fitting procedure which, like in the previous case, do not exhibit a strictly non-decreasing variation with increasing temperature and we again attribute this to the various uncertainties in the experimental data mentioned.

Conclusions

We have carried out a kinetics study of the catalytic oxidation of cyclohexane theoretically in this article. Various deficiencies in previous reaction mechanisms proposed for this reaction using different metal complex catalysts were identified and a new reaction mechanism was proposed in this study. Experimental data from the research literature were used to verify the proposed mechanism and it was found that the oxidation kinetics observed using two different metal complex catalysts could be adequately described by the rate equation derived based on the proposed reaction mechanism. Contrary to claims made by previous research workers, the pseudo-steady state hypothesis was found to be valid for the reaction. However, due to various unphysical characteristics of the experimental data and large qualitative differences in behavior of the reaction under different physical conditions, further verification of the proposed mechanism with higher quality data than those currently available in the literature would be necessary. It would also be important to verify whether the catalytic oxidation of cyclohexane with the use of other metal complexes as catalysts can be adequately modeled by the reaction mechanism proposed in the present study.

Acknowledgments

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