Research on Kinetics for Oxidation of Phenanthrene to Diphenic Acid

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Authors’ contributions
This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

The reaction kinetics for oxidation of phenanthrene, with peracetic acid, into 2,2′-diphenic acid, was investigated. A laboratory scale completely mixed reactor was used for the study. By using the orthogonal test and mathematic ways, such as Runge-Kutta’s integral and revised simplex for optimization, estimation of kinetic parameters was conducted. And the chemical kinetic equations were obtained. These parameters could be utilized for the design, operation and optimization of the reactor in oxidation of phenanthrene to diphenic acid.

Keywords: Kinetics; phenanthrene; diphenic acid; oxidation.
1. INTRODUCTION

Next to naphthalene in terms of quantity, phenanthrene (C_{14}H_{10}), at the concentration of 4-5%, is the most abundant constituent in coal tar. Phenanthrene occurs in phenanthrene waste. Phenanthrene waste, which is a residue after isolation of anthracene and carbazole from crude anthracene, contains mainly phenanthrene (about 50±5%), and a small quantity of fluorene, anthracene, carbazole, etc. Because phenanthrene has not been found of sufficient commercial value to warrant the expense of its manufacture, the residue is commonly heaped in manufacturer as the form of a waste in China, seriously polluting the environment. Phenanthrene can be oxidized to 2,2'-diphenic acid [1-5], which is in growing demand in the world market due to its excellent performance in many newly developed applications, such as production of high temperature heat resistant resins, engineering plastics, liquid crystalline polymers, pharmaceuticals and agro-chemical industries etc. We had studied the oxidation of phenanthrene [6], with peracetic acid and by means of reaction distillation, into 2,2'-diphenic acid. Phenanthrene, 30% H$_2$O$_2$ and glacial acetic acid were used as raw materials, benzene was used as solvents, during the reactions the water formed and added with raw materials of 30% H$_2$O$_2$ was distilled off by using reaction distillation in the form of an azeotropic mixture with benzene, and phenanthrene was oxidized to diphenic acid with peracetic acid. The overall reaction is presumed to be:

$$
\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2 \xrightarrow{k_1} \text{CH}_3\text{COOOH} + \text{H}_2\text{O} $$

In the phenanthrene oxidation, in the presence of a large excess of H$_2$O$_2$ and acetic acid, the chemical kinetic equations can be formulated as follows:

$$
\text{phenanthrene} \xrightarrow{k_3} \text{phenanthrenequinone} \xrightarrow{k_4} \text{diphenic acid}
$$
The rate of disappearance of \( \text{H}_2\text{O}_2 \):

\[
(-r_A) = -\frac{dC_A}{dt} = k_1 C_A^{\alpha_1} - k_2 C_B^{\alpha_2}
\]

(1)

The rate of appearance of \( \text{CH}_3\text{COOOH} \):

\[
r_B = \frac{dC_B}{dt} = k_1 C_A^{\alpha_1} - k_2 C_B^{\alpha_2} - 3k_3 C_C^{\alpha_3} C_B^{\alpha_4} - k_4 C_D^{\alpha_5} C_B^{\alpha_6}
\]

(2)

The rate of disappearance of phenanthrene:

\[
(-r_C) = -\frac{dC_C}{dt} = k_3 C_C^{\alpha_3} C_B^{\alpha_4}
\]

(3)

The rate of appearance of phenanthrenequinone:

\[
r_D = \frac{dC_D}{dt} = k_3 C_C^{\alpha_3} C_B^{\alpha_4} - k_4 C_D^{\alpha_5} C_B^{\alpha_6}
\]

(4)

The rate of appearance of diphenic acid:

\[
r_E = \frac{dC_E}{dt} = k_4 C_D^{\alpha_5} C_B^{\alpha_6}
\]

(5)

where \( r \) is the reaction rate \( [\text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}] \), \( C_i \) is the concentration of component \( i \) (\( i=A, B, …, E \): \( \text{H}_2\text{O}_2 \), \( \text{B} \): \( \text{CH}_3\text{COOOH} \), \( C \): phenanthrene, \( D \): phenanthrenequinone, \( E \): diphenic acid), \( \alpha_1, \alpha_2, …, \alpha_6 \) are the order of the reaction, and \( k_1, k_2, k_3, k_4 \) are the rate constant.

Arrhenius’ law: \( k_i = k_{i0} \exp(\frac{E_i}{RT}) \), \( i=1,2,3,4 \) (6)

where \( k_{i0} \) is called the frequency or pre-exponential factor and \( E_i \) is called the activation energy of the reaction.

The kinetic equations ((1)~(5)) are nonlinear ordinary differential equations. \( \alpha_1~\alpha_6 \) (the order of the reaction), \( k_{10}~k_{40} \) (pre-exponential factor) and \( E_1~E_4 \) (the activation energy) are 14 kinetic parameters. Generally, in the estimation of kinetic parameters, graphing method and linear or non-linear fitting can be used. But these methods are not fit for the parameter estimation of complex reactions. In the study, the simplex optimization method was used. Firstly, the kinetic experiments were performed with the orthogonal test (the orthogonal table of \( L_{16}(4^5) \) [8], whose levels and factors are shown in Table 1), the orthogonal test and experimental data of chemical kinetics are shown in Tables 2-3. Then by using the Runge-Kutta method and revised simplex, estimation of kinetic parameters was carried out, the results are shown in Table 4.

### Table 1. Levels and factors in orthogonal test

| Levels | A | B | C | D | E | C<sub>i0</sub>(mol·L<sup>-1</sup>), Ph | H<sub>2</sub>O<sub>2</sub> |
|--------|---|---|---|---|---|-----------------|----------------|
| 1      | 1:10 | 1:8 | 6 | 80 |
| 2      | 1:15 | 1:10 | 8 | 85 |
| 3      | 1:20 | 1:4 | 10 | 90 |
| 4      | 1:25 | 1:6 | 12 | 95 |

* \( C_{i0} \) is the initial concentration of reactants

### Table 2. Orthogonal test

| Test number | A | B | C | D | E | C<sub>i0</sub> (mol·L<sup>-1</sup>) | Phenanthrene | \( \text{H}_2\text{O}_2 \) |
|-------------|---|---|---|---|---|-----------------|----------------|----------------|
| 1           | 1 | 1 | 1 | 1 | 1 | 0.59             | 5.35           |
| 2           | 1 | 2 | 2 | 2 | 2 | 0.51             | 6.02           |
| 3           | 1 | 3 | 3 | 3 | 3 | 0.82             | 3.84           |
| 4           | 1 | 4 | 4 | 4 | 4 | 0.67             | 4.72           |
| 5           | 2 | 1 | 2 | 3 | 4 | 0.50             | 4.53           |
| 6           | 2 | 2 | 1 | 4 | 3 | 0.44             | 5.20           |
| 7           | 2 | 3 | 4 | 1 | 2 | 0.64             | 2.99           |
| 8           | 2 | 4 | 3 | 2 | 1 | 0.56             | 3.92           |
| 9           | 3 | 1 | 3 | 4 | 2 | 0.43             | 3.86           |
| 10          | 3 | 2 | 4 | 3 | 1 | 0.38             | 4.51           |
| 11          | 3 | 3 | 1 | 2 | 4 | 0.52             | 2.46           |
| 12          | 3 | 4 | 2 | 1 | 3 | 0.47             | 3.29           |
| 13          | 4 | 1 | 4 | 2 | 3 | 0.38             | 3.46           |
| 14          | 4 | 2 | 3 | 1 | 4 | 0.35             | 4.09           |
| 15          | 4 | 3 | 2 | 4 | 1 | 0.46             | 2.15           |
| 16          | 4 | 4 | 1 | 3 | 2 | 0.41             | 2.92           |
Table 3. Experimental data of chemical kinetics

| Test number | Reaction time (h) | Reaction temperature (°C) | Phenanthrene (mol.L⁻¹) | PQ (mol.L⁻¹) | DPA (mol.L⁻¹) | H₂O₂ (mol.L⁻¹) | Peracetic acid (mol.L⁻¹) |
|-------------|------------------|---------------------------|------------------------|--------------|--------------|----------------|------------------------|
| 1           | 10               | 95                        | 0.3724                 | 0.0204       | 0.1202       | 0.08           | 7.6×10⁻³               |
| 2           | 8                | 90                        | 0.391                  | 0.0175       | 0.0568       | 0.49           | 9.8×10⁻⁴               |
| 3           | 12               | 80                        | 0.7424                 | 0.0285       | 0.0161       | 0.15           | 3.0×10⁻⁴               |
| 4           | 6                | 85                        | 0.6012                 | 0.0177       | 0.0158       | 0.47           | 9.4×10⁻⁴               |
| 5           | 8                | 85                        | 0.4729                 | 0.0149       | 0.0159       | 0.20           | 4.0×10⁻⁴               |
| 6           | 10               | 80                        | 0.4016                 | 0.0104       | 0.0133       | 0.34           | 6.8×10⁻⁴               |
| 7           | 6                | 90                        | 0.5741                 | 0.0228       | 0.0134       | 0.13           | 2.6×10⁻⁴               |
| 8           | 12               | 95                        | 0.4418                 | 0.0219       | 0.1487       | 0.10           | 2.0×10⁻⁴               |
| 9           | 12               | 90                        | 0.3651                 | 0.0176       | 0.0601       | 0.14           | 2.8×10⁻⁴               |
| 10          | 6                | 95                        | 0.3512                 | 0.0141       | 0.0529       | 0.08           | 1.6×10⁻⁴               |
| 11          | 10               | 85                        | 0.4419                 | 0.0155       | 0.00717      | 0.03           | 6.0×10⁻⁵               |
| 12          | 8                | 80                        | 0.4181                 | 0.0072       | 0.00215      | 0.15           | 3.0×10⁻⁴               |
| 13          | 6                | 80                        | 0.3217                 | 0.0036       | 0.00773      | 0.42           | 8.4×10⁻⁴               |
| 14          | 12               | 85                        | 0.2947                 | 0.0129       | 0.0192       | 0.14           | 2.8×10⁻⁴               |
| 15          | 8                | 95                        | 0.3961                 | 0.0189       | 0.1562       | 0.03           | 6.0×10⁻⁵               |
| 16          | 10               | 90                        | 0.3512                 | 0.0161       | 0.0271       | 0.06           | 1.2×10⁻⁴               |

Table 4. Experimental and calculated data of kinetics

| Test number | Measured value Cᵢ (mol.L⁻¹) | PQ (mol.L⁻¹) | DPA (mol.L⁻¹) | Calculated value Cᵢ′ (mol.L⁻¹) | PQ (mol.L⁻¹) | DPA (mol.L⁻¹) |
|-------------|-------------------------------|--------------|--------------|--------------------------------|--------------|--------------|
| 1           | 0.3724                        | 0.0181       | 0.1202       | 0.4011                         | 0.0196       | 0.1593       |
| 2           | 0.371                         | 0.0175       | 0.0568       | 0.4213                         | 0.0184       | 0.07035      |
| 3           | 0.7424                        | 0.0219       | 0.0161       | 0.7772                         | 0.0278       | 0.01504      |
| 4           | 0.5812                        | 0.0177       | 0.0158       | 0.6405                         | 0.0194       | 0.01008      |
| 5           | 0.5029                        | 0.0149       | 0.0159       | 0.4683                         | 0.0161       | 0.01543      |
| 6           | 0.3516                        | 0.0104       | 0.0133       | 0.4191                         | 0.0116       | 0.00925      |
| 7           | 0.5141                        | 0.0228       | 0.0134       | 0.6064                         | 0.0217       | 0.01184      |
| 8           | 0.4718                        | 0.0219       | 0.1487       | 0.4079                         | 0.0228       | 0.1293       |
| 9           | 0.3851                        | 0.0176       | 0.0601       | 0.3249                         | 0.0165       | 0.05327      |
| 10          | 0.3012                        | 0.0141       | 0.0529       | 0.3602                         | 0.0134       | 0.04161      |
| 11          | 0.4119                        | 0.0167       | 0.00717      | 0.4988                         | 0.0145       | 0.00666      |
| 12          | 0.3881                        | 0.0082       | 0.00215      | 0.4618                         | 0.0066       | 0.00153      |
| 13          | 0.4217                        | 0.0046       | 0.00073      | 0.3764                         | 0.0032       | 0.00046      |
| 14          | 0.3647                        | 0.0129       | 0.0192       | 0.3175                         | 0.0113       | 0.02112      |
| 15          | 0.3261                        | 0.0189       | 0.1562       | 0.4216                         | 0.0196       | 0.1876       |
| 16          | 0.5312                        | 0.0171       | 0.0271       | 0.3724                         | 0.0158       | 0.02173      |

The laboratory scale reactor was used for the kinetic study and the fluid flow of the reactor was presumed to be complete mixing. With the kinetic experiments, experimental values of concentration Cᵢ (i=A, B,...,E; j= 1,2,...,16) were obtained. And with solving nonlinear ordinary differential equations ((1)~(5)), the calculated values of concentration Cᵢ′ could be obtained by using Runge-Kutta method. Thereby we had objective function $F$.

$$F = \sum_{j=1}^{M} (C_{ij} - C_{ij}' )^2 = \sum_{j=1}^{M} \left[ (C_{A_i})^2 + (C_{B_i} - C_{B_{i,j}})^2 + (C_{C_i} - C_{C_{i,j}})^2 + (C_{D_i} - C_{D_{i,j}})^2 + (C_{E_i} - C_{E_{i,j}})^2 \right]$$

4
By the aid of modified simplex, model parameter adjustment and optimization was conducted. From calculation, and the kinetic parameters were found to be as follows:

\[ k_{10} = 5.0 \times 10^{10}, \quad k_{20} = 1.1 \times 10^{11}, \quad k_{30} = 4.0 \times 10^{11}, \quad k_{40} = 3.5 \times 10^{11} \]

\[ \alpha_1 = 0.75, \quad \alpha_2 = 2.05, \quad \alpha_3 = 1.32, \quad \alpha_4 = 1.72, \quad \alpha_5 = 0.815, \quad \alpha_6 = 2.15 \]

\[ E_1 = 8.9 \times 10^4, \quad E_2 = 1.0 \times 10^5, \quad E_3 = 1.1 \times 10^5, \quad E_4 = 1.05 \times 10^5 \text{ [J/mol]} \]

Calculated values of kinetic model are also shown in Table 4.

With residual analysis, the kinetic model was examined. The results are showed Figs. 1-6. Figs. 1-6 indicate that \( C_{\text{cal}} \) versus \( C_{\text{measured}} \) (phenanthrene or phenanthrenequinone or diphenic acid) are very near the diagonal, and \( C_{\text{measured}} - C_{\text{cal}} \) versus \( C_{\text{measured}} \) are near the abscissa, which shows that the model and parameter estimation are dependable, the model fitting better, and the way used feasible.
4. CONCLUSIONS

The laboratory scale completely mixed reactor was used for the kinetic study. By using the Runge-Kutta method and modified simplex, estimation of kinetic parameters was conducted. The kinetic parameters were found to be: pre-exponential factor: \( k_1 = 5.0 \times 10^{10}, \ k_2 = 1.1 \times 10^{11}, \ k_3 = 4.0 \times 10^{11}, \ k_4 = 3.5 \times 10^{11} \); the activation energy: \( E_1 = 8.9 \times 10^{4}, \ E_2 = 1.0 \times 10^{5}, \ E_3 = 1.1 \times 10^{5}, \ E_4 = 1.05 \times 10^{5} \); the order of the reaction: \( \alpha_1 = 0.75, \ \alpha_2 = 2.05, \ \alpha_3 = 1.32, \ \alpha_4 = 1.72, \ \alpha_5 = 0.815, \ \alpha_6 = 2.15, \) respectively. The determination of kinetic parameters can be considered as a useful tool for the process design, operation and improvement of phenanthrene oxidation to diphenic Acid. Residual analysis showed that the model and parameter estimation were dependable, the model fitting better, and the way used feasible. This method had the advantages of simple, dependable and accurate.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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