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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.

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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 entironment. 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_2O_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_2O_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. This oxidation method had the advantages of high yields, simple procedure, repeat use of solvents, economy, and eco-friendly oxidation way. And based on the oxidation, the reaction kinetics had further been investigated. A laboratory scale completely mixed reactor was used for the study. The orthogonal test and mathematic ways, such as Runge-Kutta's integral and revised simplex for optimization, were used for estimating the kinetic parameters. The kinetic equations obtained could be used for the design, operation and optimization of the reactor in oxidation of phenanthrene to diphenic acid.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

Commercial phenanthrene, which was obtained by a local market, 30% H_2O_2 (A.R) and glacial acetic acid (A.R) were used for oxidation of phenanthrene to 2,2'-diphenic acid.

2.2 Kinetic Experiments

To a good stired reactor which provided with a reflux condenser and thermometer, phenanthrene, glacial acetic acid and 30% H_2O_2 were proportionally added at room-temperature. Then the reaction temperature was kept at 80-95℃ for 6-12 h, and phenanthrene was oxidized into diphenic acid. At the end of experiments, concentration of H_2O_2, CH_3COOOH, phenanthrene, phenanthrenequinone (PQ) and diphenic acid (DPA) in the oxidation reaction mixtures was determined.

2.3 Analytical Methods

H_2O_2 and CH_3COOOH were determined by titration according to GB/T19108 — 2003 [7]. The quantitative analysis of phenanthrene, phenanthrenequinone and diphenic acid was performed by means of High Perfect Liquid Chromatogram (Type: LC-10A, Shimadzu, Kyoto, Japan).

3. RESULTS AND DISCUSSION

Phenanthrene, 30% H_2O_2 and glacial acetic acid were used as raw materials, and phenanthrene was oxidized into diphenic acid by peracetic acid. The overall reaction is presumed to be:

$$CH_3COOH + H_2O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CH_3COOOH + H_2O$$

$$\text{phenanthrene} \xrightarrow[CH_3COOOH]{k_3} \text{phenanthrenequinone} \xrightarrow[CH_3COOOH]{k_4} \text{diphenic acid}$$

In the phenanthrene oxidation, in the presence of a large excess of H_2O_2 and acetic acid, the chemical kinetic equations can be formulated as follows:

The rate of disappearance of H_2O_2:

$$(-r_A) = -dC_A/dt = k_1C_A^{\alpha 1} - k_2C_B^{\alpha 2} \quad (1)$$

The rate of appearance of CH_3COOOH:

$$r_B = dC_B/dt = k_1C_A^{\alpha 1} - k_2C_B^{\alpha 2} - 3k_3C_C^{\alpha 3}C_B^{\alpha 4} - k_4C_D^{\alpha 5}C_B^{\alpha 6} \quad (2)$$

The rate of disappearance of phenanthrene:

$$(-r_C) = -dC_C/dt = k_3C_C^{\alpha 3}C_B^{\alpha 4} \quad (3)$$

The rate of appearance of phenanthrenequinone:

$$r_D = dC_D/dt = k_3C_C^{\alpha 3}C_B^{\alpha 4} - k_4C_D^{\alpha 5}C_B^{\alpha 6} \quad (4)$$

The rate of appearance of diphenic acid:

$$r_E = dC_E/dt = k_4C_D^{\alpha 5}C_B^{\alpha 6} \quad (5)$$

where r is the reaction rate [$mol \cdot L^{-1} \cdot min^{-1}$], C_i is the concentration of component i (i=A,B,…,E. A: H_2O_2, B: CH_3COOOH, C: phenanthrene, D: phenanthrenequinone, E: diphenic acid), α1, α2,…, α6 are the order of the reaction, and k_1,k_2,k_3,k_4 are the rate constant.

Arrhenius' law: $k_i = k_{i0}EXP(E_i/RT)$, 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. α1~ α6 (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 phenanthrene: acetic acid (mol)	B phenanthrene: H_2O_2 (mol)	C reaction time (h)	D blank	E reaction temperature (℃)
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

Table 2. Orthogonal test

Test number	A	B	C	D	E	C_{i0} ($mol.L^{-1}$)*	
						Phenanthrene	H_2O_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

** C_{i0} is the initial concentration of reactants*

Table 3. Experimental data of chemical kinetics

Test number	Reaction time (h)	Reaction temperature (℃)	Concentrations C_{ij}				
			Phenanthrene ($mol.L^{-1}$)	PQ ($mol.L^{-1}$)	DPA ($mol.L^{-1}$)	H_2O_2 ($mol.L^{-1}$)	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	0.00073	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 C_{ij}			Calculated value C_{ij}'		
	Phenanthrene ($mol.L^{-1}$)	PQ ($mol.L^{-1}$)	DPA ($mol.L^{-1}$)	Phenanthrene ($mol.L^{-1}$)	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 C_{ij} (i=A, B,…,E; j= 1,2,…,16) were obtained. And with solving nonlinear ordinary differential equations ((1)~(5)), the calculated values of concentration C_{ij}' could be obtained by using Runge-Kutta method. Thereby we had objective function *F.*

$$F = \sum_{j=1}^{M} (Cij - Cij')^2 == \sum_{j=1}^{M} [(C_{Aj}— C_{Aj}')^2 +(C_{Bj}— C_{Bj}')^2 +(C_{Cj}— C_{Cj}')^2 +(C_{Dj}— C_{Dj}')^2 +(C_{Ej}— C_{Ej}')^2]$$

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:

$k_{1o}=5.0\times10^{10}$, $k_{20}=1.1\times10^{11}$, $k_{30}=4.0\times10^{11}$, $k_{40}=3.5\times10^{11}$

α_1 =0.75, α_2=2.05, α_3=1.32, α_4=1.72, α_5=0.815, α_6=2.15

$E_1=8.9\times10^4$, $E_2=1.0\times10^5$, $E_3=1.1\times10^5$, $E_4=1.05\times10^5$ [$J\cdot mol^{-1}$].

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_{cal} versus $C_{measured}$ (phenanthrene or phenanthrenequinone or diphenic acid) are very near the diagonal, and $C_{measured}$- C_{cal} versus $C_{measured}$ are near the abscissa, which shows that the model and parameter estimation are dependable, the model fitting better, and the way used feasible.

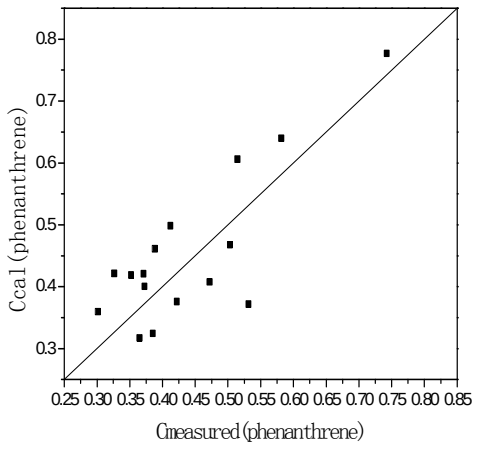

Fig. 1. Comparison between calculated and experimental concentration (phenanthrene)

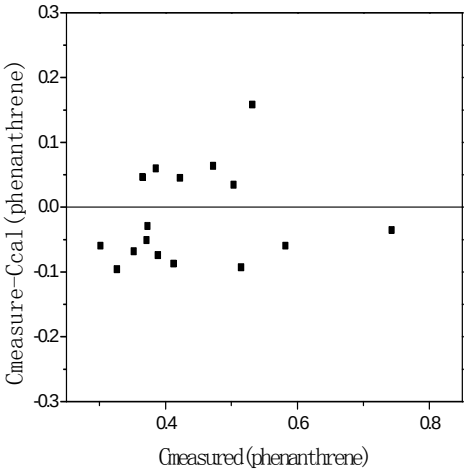

Fig. 2. Residual distribution of calculated and experimental concentration (phenanthrene)

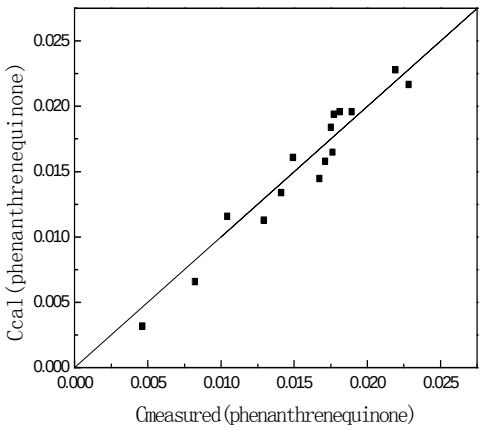

Fig. 3. Comparison between calculated and experimental concentration (quinone)

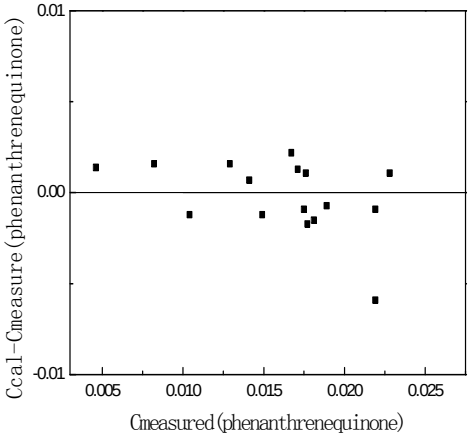

Fig. 4. Residual distribution of calculated and experimental concentration (quinone)

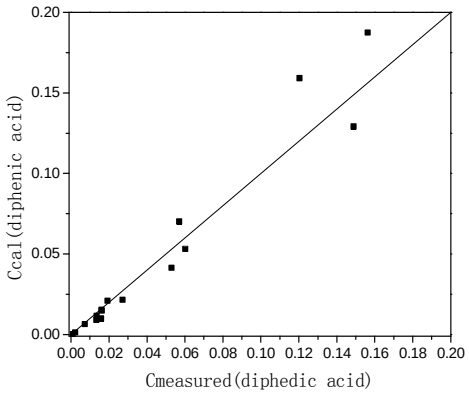

Fig. 5. Comparison between calculated and experimental concentration (diphenic acid)

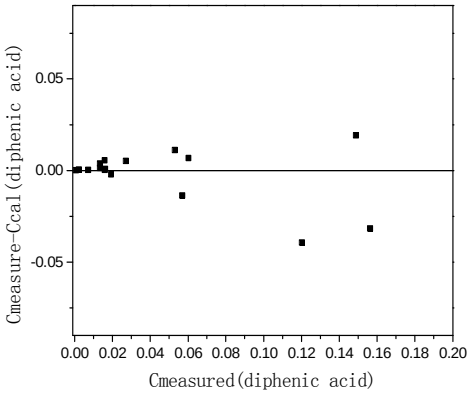

Fig. 6. Residual distribution of calculated and experimental concentration (diphenic acid)

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: $k_{10}=5.0\times10^{10}$, $k_{20}=1.1\times10^{11}$, $k_{30}=4.0\times10^{11}$, $k_{40}=3.5\times10^{11}$; the activation energy: $E_1=8.9\times10^4$, $E_2=1.0\times10^5$, $E_3=1.1\times10^5$, $E_4=1.05\times10^5$; 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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