

Study of Oxidation of Phenanthrene to Diphenic Acid and its Kinetics

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Abstract—The oxidation of phenanthrene, with peracetic acid and by means of reaction distillation, into 2,2'-diphenic acid and its kinetics have been studied. For the oxidation of phenanthrene, reaction conditions were investigated by orthogonal test, and the optimum conditions were as follows: molar ratio of phenanthrene to acetic acid: 1.0:25.0; molar ratio of phenanthrene to H₂O₂: 1.0:8.0; dropping time of 30% H₂O₂: 9h; reaction time: 18h; solvent: benzene; reaction temperature: about 90°C (boil). Experimental results showed that the yields of diphenic acid could reach to 60%~67%. And for its kinetics, a laboratory scale completely mixed reactor was used. 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. 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

I. INTRODUCTION

Next to naphthalene in terms of quantity, phenanthrene, 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 agrochemical industries etc. Thereby, the preparation of diphenic acid from phenanthrene could reach the

purposes of cleansing the environment and offering an effective way of commercial use of phenanthrene.

The study described the oxidation of phenanthrene, with peracetic acid and by means of reaction distillation, into 2,2'-diphenic acid. Phenanthrene, 30% H₂O₂ 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% H₂O₂ 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 work 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 have 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.

II. EXPERIMENTAL PROCEDURES

A. MATERIALS

Commercial phenanthrene, which was obtained by a local market, 30% H₂O₂ (A.R) and glacial acetic acid (A.R) were used for oxidation of phenanthrene to 2,2'-diphenic acid.

B. EXPERIMENTAL PROCEDURE

1) Oxidation of Phenanthrene Oxidation

In a four-necked flask, which provided with a stirrer, thermometer, fractional column and dropping funnel, phenanthrene, glacial acetic acid and benzene were proportionally introduced, and the mixture was heated to boil. Then 30% H₂O₂ was gradually added drop by drop for 3h~12h. The water was continuously distilled off in the form of the azeotropic mixture with benzene during the reactions. The conversion of phenanthrene by oxidation into diphenic acid

Recovery of phenanthrene, acetic acid and solvent

After the reaction was completed, acetic acid and the solvent benzene, which could be repeatedly used for making 2,2'-diphenic acid, distilled off under reduced pressure. Then 10% of sodium hydroxide was added in the residue. The undissolved materials, which contained

mainly un-reacted phenanthrene and could be used again for oxidation of phenanthrene, were separated by filtration, whereas diphenic acid as a salt, which was formed by reaction of diphenic acid with sodium hydroxide, was dissolved in the filtrate.

Separation of diphenic acid

Finally, the filtrate was acidified with concentrated hydrochloric acid, diphenic acid precipitated in crystalline form and the diphenic acid was obtained by filtration. Neutralization by adding base and acidifying by adding acid was repeated several times till the products of purer diphenic acid were obtained.

2) Kinetic experiments

To a good stirred reactor which provided with a reflux condenser and thermometer, phenanthrene, glacial acetic acid and 30% H₂O₂ were proportionally added at room-temperature. Then the reaction temperature was kept at 80~95 °C for 6~12h, and phenanthrene was oxidized into diphenic acid. At the end of experiments, concentration of H₂O₂, CH₃COOOH, phenanthrene, phenanthrenequinone(PQ) and diphenic acid(DPA) in the oxidation reaction mixtures was determined.

C. ANALYTICAL METHODS

H₂O₂ and CH₃COOOH were determined by titration according to GB/T19108 – 2003^[6]. The quantitative analysis of phenanthrene, phenanthrenequinone and diphenic acid was performed by means of High Perfect Liquid Chromatogram (Type: LC-10A, Shimadzu, Kyoto, Japan).

III. RESULTS AND DISCUSSION

A. Oxidation of phenanthrene

Taking the yields of diphenic acid as the object function, and the conditions such as molar ratio of phenanthrene to acetic acid, molar ratio of phenanthrene to H₂O₂, dropping time of 30%H₂O₂, reaction time as variable factors, we evaluated the effects of these four factors on the function. Experiments were carried out by using the orthogonal table of L16(4⁵)^[7] [i.e., an orthogonal table of 16 rows (16 times of test), 5 columns (4 factors and a vacant arrange: A= molar ratio of phenanthrene to acetic acid, B=molar ratio of phenanthrene to H₂O₂, C= reaction time, D=vacant arrange, E=dropping time of 30%H₂O₂), and 4 levels: 1:10, 1:15, 1:20, 1:25 ; 1:8, 1:10, 1:4, 1:6 ; 12h, 21h, 18h, 15h ; 9h, 6h, 12h, 3h]. The results are shown in Table 1. The optimum conditions were as follows:

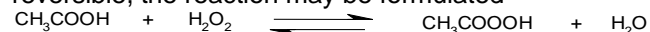
- molar ratio of phenanthrene to acetic acid: 1:25.0;
- molar ratio of phenanthrene to H₂O₂: 1:8.0;
- reaction time: 18h ;
- dropping time of 30%H₂O₂: 9h;
- solvent: benzene;
- reaction temperature: about 90°C(boil).

With variance analysis of effects of each factor on the yields of diphenic acid, we found that there were no notable factors for influencing yields of diphenic acid except A factor, that is, molar ratio of phenanthrene to acetic acid was the dominant factor for influencing the yields of diphenic acid.

Table 1 Orthogonal test and results

Test number	A	B	C	D	E	Yields (%)
1						27.67
2						26.09
3						23.72
4						28.46
5						41.11
6						20.55
7						24.51
8			L ₁₆ (4 ⁵)			48.22
9						53.75
10						59.29
11						27.67
12						29.25
13						47.43
14						64.03
15						27.67
16						41.90

Because the reaction to form peracetic acid is reversible, the reaction may be formulated



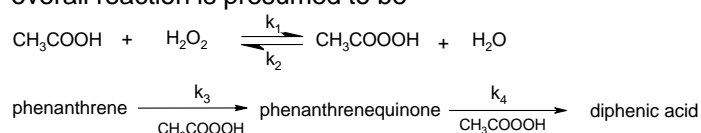
It makes the reaction reverse and the consumption of the acetic acid increase that the acetic acid can be diluted by water formed and added with raw materials (30%H₂O₂). In order to decrease the consumption, reaction distillation was utilized for making diphenic acid. In the work, Phenanthrene, 30%H₂O₂ and glacial acetic acid were used as raw materials, benzene was used as solvents, the water distilled off in the form of the azeotropic mixture with benzene, and phenanthrene was oxidized into diphenic acid by peracetic acid.

As acetic acid is the most expensive ingredient in the oxidation process, this reduction of the amount of acetic acid means savings. Experiments showed that, under the optimum conditions, 1 mol of phenanthrene 25 moles of acetic acid was needed for making

diphenic acid. Through repeated experiments under the optimum conditions, the yields of diphenic acid could reach 60~67%, the purity of diphenic acid prepared was 96~98%, and the melting point of the products was 232~233°C.

B. Reaction kinetics

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



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 ($i=A, B, \dots, E$. A: H_2O_2 , B: CH_3COOOH , C: phenanthrene, D: phenanthrenequinone, E: diphenic acid), $\alpha_1, \alpha_2, \dots, \alpha_6$ are the order of the reaction, and k_1, k_2, k_3, k_4 are the rate constant.

Arrhenius' law: $k_i = k_{i0} \exp(E_i/RT), i=1, 2, 3, 4$

$$(6)$$

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. $\alpha_1 \sim \alpha_6$ (the order of the reaction), $k_{10} \sim k_{40}$ (pre-exponential factor) and $E_1 \sim E_4$ (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 $L_{16}(4^5)$, whose levels and factors are shown in Table 2), the orthogonal test and experimental data of chemical kinetics are shown in Table 3~4. Then by using the Runge-Kutta method and revised simplex, estimation of kinetic parameters was carried out, the results are shown in Table 5.

Table 2 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 (°C)
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 3 Orthogonal test

Test number						C_{i0} ($mol \cdot L^{-1}$)*	
	A	B	C	D	E	Phenanthrene	H_2O_2
1						0.59	5.35
2						0.51	6.02
3						0.82	3.84
4						0.67	4.72
5						0.50	4.53
6						0.44	5.20
7						0.64	2.99
8			$L_{16}(4^5)$			0.56	3.92
9						0.43	3.86
10						0.38	4.51
11						0.52	2.46
12						0.47	3.29
13						0.38	3.46
14						0.35	4.09
15						0.46	2.15
16						0.41	2.92

* C_{i0} is the initial concentration of reactants

Table 4 Experimental data of chemical kinetics

Test number	Reaction time (h)	Reaction Temperature (°C)	Concentrations C_{ij}				
			Phenanthrene (mol.L ⁻¹)	PQ (mol.L ⁻¹)	DPA (mol.L ⁻¹)	H ₂ O ₂ (mol.L ⁻¹)	Peracetic acid (mol.L ⁻¹)
1	10	95	0.3724	0.0181	0.1202	0.08	7.6×10 ⁻³
2	8	90	0.371	0.0175	0.0568	0.49	9.8×10 ⁻⁴
3	12	80	0.7424	0.0219	0.0161	0.15	3.0×10 ⁻⁴
4	6	85	0.5812	0.0177	0.0158	0.47	9.4×10 ⁻⁴
5	8	85	0.5029	0.0149	0.0159	0.20	4.0×10 ⁻⁴
6	10	80	0.3516	0.0104	0.0133	0.34	6.8×10 ⁻⁴
7	6	90	0.5141	0.0228	0.0134	0.13	2.6×10 ⁻⁴
8	12	95	0.4718	0.0219	0.1487	0.10	2.0×10 ⁻⁴
9	12	90	0.3851	0.0176	0.0601	0.14	2.8×10 ⁻⁴
10	6	95	0.3012	0.0141	0.0529	0.08	1.6×10 ⁻⁴
11	10	85	0.4119	0.0167	0.00717	0.03	6.0×10 ⁻⁵
12	8	80	0.3881	0.0082	0.00215	0.15	3.0×10 ⁻⁴
13	6	80	0.4217	0.0046	0.00073	0.42	8.4×10 ⁻⁴
14	12	85	0.3647	0.0129	0.0192	0.14	2.8×10 ⁻⁴
15	8	95	0.3261	0.0189	0.1562	0.03	6.0×10 ⁻⁵
16	10	90	0.5312	0.0171	0.0271	0.06	1.2×10 ⁻⁴

Table 5 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

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

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:

$k_{10}=5.0 \times 10^{10}$, $k_{20}=1.1 \times 10^{11}$, $k_{30}=4.0 \times 10^{11}$,
 $k_{40}=3.5 \times 10^{11}$
 $\alpha_1=0.75$, $\alpha_2=2.05$, $\alpha_3=1.32$, $\alpha_4=1.72$, $\alpha_5=0.815$,
 $\alpha_6=2.15$
 $E_1=8.9 \times 10^4$, $E_2=1.0 \times 10^5$, $E_3=1.1 \times 10^5$,
 $E_4=1.05 \times 10^5$ [J·mol⁻¹]
 Calculated values of kinetic model are also shown in Table 5.

The kinetic model was examined with

Statistical Test^[8](the decisive index ρ^2 : $\rho^2=1 - \sum_{j=1}^M$

$$(y_j - y'_j)^2 / \sum_{j=1}^M y_j^2 ; F_{\text{examination}} : F = \left[\sum_{j=1}^M y_j^2 - \right.$$

$$\left. \sum_{j=1}^M (y_j - y'_j)^2 / M_p \right] / \left\{ \sum_{j=1}^M (y_j - y'_j)^2 / (M - M_p) \right\} ; \text{residual analysis). With the}$$

calculation: $\rho^2 > 0.9$ and $F > 10FT$. Residual analysis is showed in Figure 1~6. Figure1~6 indicate that C_{cal} versus C_{measured} (phenanthrene or phenanthrenequinone or diphenic acid) are very near the diagonal, and $C_{\text{measured}} - C_{\text{cal}}$ versus C_{measured} are near the abscissa. $\rho^2 > 0.9$, $F > 10FT$ and residual analysis show that the model and parameter estimation are dependable, the model fitting better, and the way used feasible.

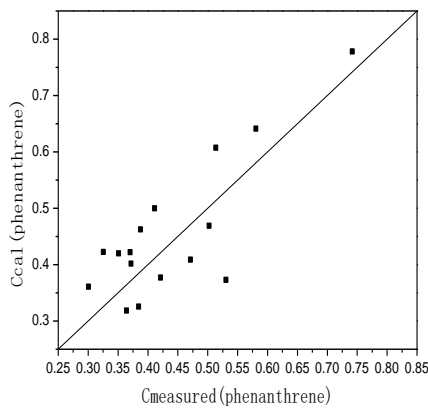


Fig. 1. Comparison between calculated and experimental concentration (phenanthrene)

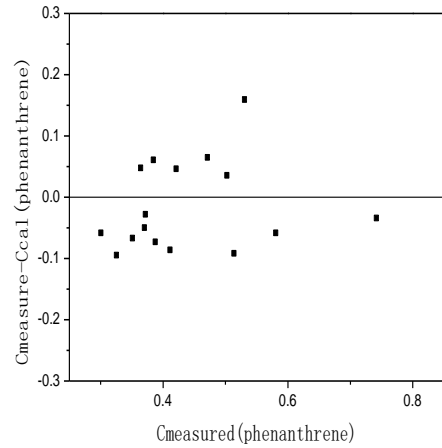


Fig. 2. Residual distribution of calculated and experimental concentration (phenanthrene)

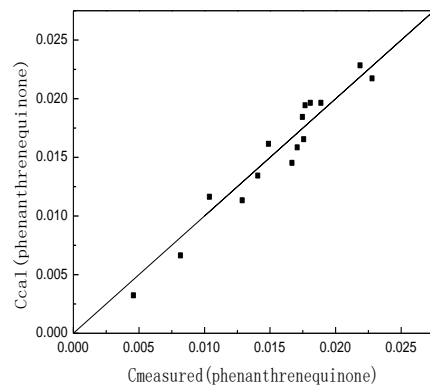


Fig. 3. Comparison between calculated and experimental concentration (quinone)

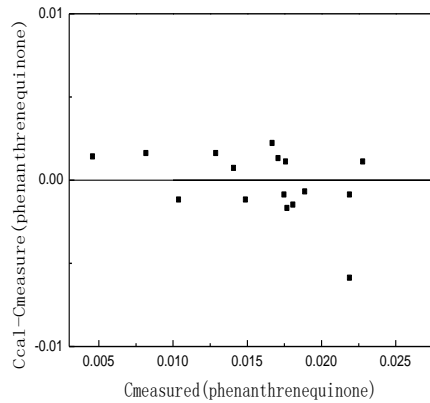


Fig. 4. Residual distribution of calculated and experimental concentration (quinone)

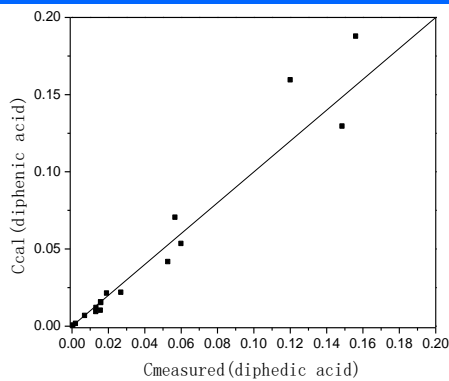


Fig. 5. Comparison between calculated and experimental concentration(diphenic acid)

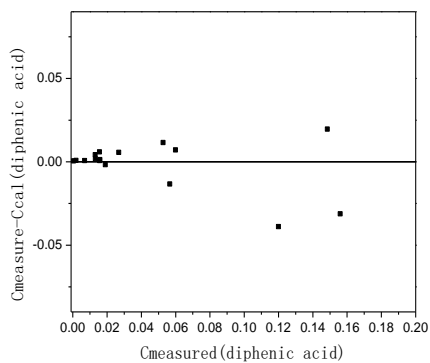


Fig. 6. Residual distribution of calculated and experimental concentration (diphenic acid)

IV. CONCLUSIONS

For the oxidation of phenanthrene, main technical parameters were optimized by orthogonal test. The optimum conditions were as follows: molar ratio of phenanthrene to acetic acid: 1.0:25.0; molar ratio of phenanthrene to H₂O₂: 1.0:8.0; dropping time of 30% H₂O₂: 9h; reaction time:18h ; solvent: benzene; reaction temperature: about 90°C(boil). The study showed that, under the optimum conditions, the yields of diphenic acid could reach 60%~67%. By using reaction distillation, the water formed and added with raw materials of 30% H₂O₂ was distilled off in the form of an azeotropic mixture with benzene, so that no dilution of the acetic acid took place, which made the consumption of acetic acid decrease. The study had the advantages of simple procedure, repeated use of benzene and acetic acid, economy, and eco-friendly oxidation way.

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 determination of kinetic parameters can be considered as a useful tool for the process design, operation and improvement of phenanthrene oxidation to diphenic Acid. Statistical Test showed that the model and parameter estimation were dependable, the model fitting better, and the way used feasible.

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