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Research on Oxidation of Phenanthrene to Phenanthrenequinone and its Kinetics

Key Words TBHP, phenanthrene, phenanthrenequinone, oxidation, kinetics

Abstract The oxidation of phenanthrene with TBHP into phenanthrenequinone and its kinetics have been studied. Reaction conditions were investigated by orthogonal test. For the oxidation of phenanthrene to phenanthrenequinone the optimum conditions as follows: molar ratio of TBHP to phenanthrene: 5:1; $MoO_2(acac)_2$ (catalyster) content: 0.05g(per 5g phenanthrene); reaction time: 4h.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 phenanthrenequinone.

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(or polycyclic aromatic hydrocarbons in the petroleum). 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 phenanthrenequinone[1-2]. Phenanthrenequinone can be used in organic synthesis. It itself is pesticides, and it can be used as fungicides and seed dressing agents to prevent corn smut, cotton seedling diseases. It can also be used as light guide materials, photosensitive solder preservative agents and paper etc. Thereby, the preparation of phenanthrenequinone from phenanthrene could reach the purposes of cleansing the environment and offering an effective way of commercial use of phenanthene.

The study described that phenanthrenequinone was made from phenanthrene with tert-butyl hydroperoxide (TBHP)as an oxidant. This oxidation method had the advantages of simple procedure, high efficiency, 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 phenanthrenequinone.

EXPERIMENTAL PROCEDURES

MATERIALS

Commercial phenanthrene and benzene were obtained by a local market. Tert-butyl hydroperoxide and Molybdenum (Ⅵ) acetylacetonate ($MoO_2(acac)_2$) were prepared by our Lab.

PROCEDURE

1) Preparation of TBHP

To a stired reactor which provided with a reflux condenser, tert-butyl alcohol, H_2O_2(30%by weight), 70% sulfuric acid (catalyst)and benzene (solvent) was proportionally added at room-temperature. Then the reaction temperature was kept at 40~70℃for 1~4h, and tert-butyl alcohol was oxidized into tert-butyl hydroperoxide . After the reaction was completed, the reaction mixtures were cooled to ambient temperature, and were introduced a separatory funnel. The down layer contained mainly H_2O, whereas the upper layer, which was organic layer and contained mainly TBHP and benzene, was used as oxidants for the oxidation of phenanthrene.

2) Oxidation of Phenanthrene

In a four-necked flash, which provided with a stirrer, thermometer and fractional column, phenanthrene, TBHP(in benzene) and $MoO_2(acac)_2$ were proportionally introduced. Then the reaction mixture was heated to boil for 4~16 h. The conversion of phenanthrene by oxidation into phenanthrenequinone.During the reactions the water was continuously distilled off in the form of the azeotropic mixture with benzene. Finally, tert-butyl alcohol was distilled off .

3) Kinetic experiments

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To a good stired reactor which provided with a reflux condenser and thermometer, phenanthrene, Tert-butyl hydroperoxide and benzene were proportionally added at room-temperature. Then the reaction temperature was kept at 40~75℃ for 3~12h, and phenanthrene was oxidized into phenanthrenequinone. At the end of experiments, concentration of TBHP, phenanthrene, phenanthrenequinone(PQ) and diphenic acid(DPA) in the oxidation reaction mixtures was determined.

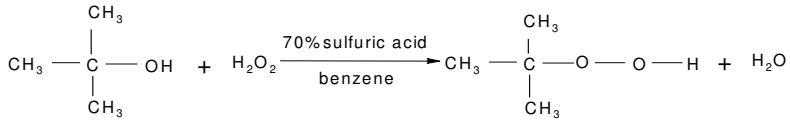
ANALYTICAL METHODS

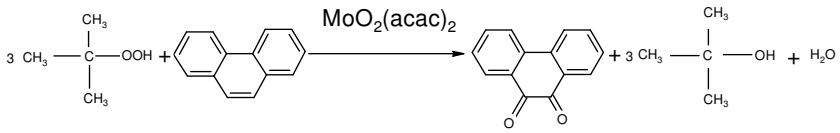
The quantitative analysis of tert-butyl hydroperoxide, phenanthrene, phenanthrenequinone and diphenic acid was performed by means of gas chromatography (Type: GC-2010, Shimadzu, Kyoto, Japan).

RESULTS AND DISCUSSION

1） Oxidation of Phenanthrene

First TBHP was prepared from our Lab. Tert-butyl alcohol was used as raw materials, 30%H_2O_2 as oxidants, and tert-butyl alcohol was oxidized into tert-butyl hydroperoxide. Then phenanthrene was oxidized into phenanthrenequinone with tert-butyl hydroperoxide.The reactions are presumed to be





For the oxidation of phenanthrene to phenanthrenequinone with TBHP the optimization was carried out with the orthogonal test[3]. Take the yields of PQ as the object function, the levels and factors in orthogonal test were given in Table 1, and the results are shown in Table 2. The optimum conditions were as below:

·reaction time: 4h;

·mass of $MoO_2(acac)_2$(per 5g phenanthrene): 0.05g;

·molar ratio of TBHP to phenanthrene: 5:1

Table1 Levels and factors in orthogonal test

Levels/ Factors	A: Raction time	B: molar ratio of TBHP : phenanthrene	C: Mass of $MoO_2(acac)_2$ (per 5g phenanthrene)
1	4h	6	0.05g
2	8h	5	0.35g
3	12h	4	0.2g
4	16h	3	0.1g

Table 2 Results of orthogonal test

No.	A	Blank1	B	Blank2	C	yields
1						0.4741
2						0.3208
3						0.3491
4						0.3458
5						0.3235
6						0.2701
7						0.1974
8						0.1429
9			$L_{16}(4^5)$			0.1169
10						0.1331
11						0.0485
12						0.1492
13						0.0845

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14	0.1428
15	0.1245
16	0.0695

The yields of PQ prepared through repeated experiments under the optimum conditions was no lower than 66%.

2) reaction kinetics

Phenanthrene was oxidized into phenanthrenequinone by tert-butyl hydroperoxide. The overall reaction is presumed to be

$$\text{phenanthrene} + 3\ \text{t-BuOOH} \xrightarrow{k_1} \text{phenanthrenequinone} + 3\ \text{t-BuOH} + H_2O$$

$$\text{phenanthrenequinone} + \text{t-BuOOH} + H_2O \xrightarrow{k_2} \text{diphenic acid} + \text{t-BuOH}$$

The chemical kinetic equations can be formulated as follows:

The rate of disappearance of phenanthrene:

$$(-r_A) = -dC_A/dt = k_1 C_A^{\alpha 1} C_B^{\alpha 2} \quad (1)$$

The rate of disappearance of t-BuOOH:

$$(-r_B) = -dC_B/dt = 3k_1 C_A^{\alpha 1} C_B^{\alpha 2} + k_2 C_B^{\alpha 3} C_C^{\alpha 4} C_E^{\alpha 5} \quad (2)$$

The rate of appearance of phenanthrenequinone:

$$r_C = dC_C/dt = k_1 C_A^{\alpha 1} C_B^{\alpha 2} - k_2 C_B^{\alpha 3} C_C^{\alpha 4} C_E^{\alpha 5} \quad (3)$$

The rate of appearance of diphenic acid:

$$r_D = dC_D/dt = k_2 C_B^{\alpha 3} C_C^{\alpha 4} C_E^{\alpha 5} \quad (4)$$

The rate of appearance of H_2O:

$$r_E = dC_E/dt = k_1 C_A^{\alpha 1} C_B^{\alpha 2} - k_2 C_B^{\alpha 3} C_C^{\alpha 4} C_E^{\alpha 5} \quad (5)$$

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: phenanthrene, B: t-BuOOH, C: phenanthrenequinone, D: diphenic acid, E: H_2O), α1, α2,…, α5are the order of the reaction, and k_1,k_2 are the rate constant.

Arrhenius' law: $k_i = k_{i0} EXP(E_i/RT)$, i=1,2 (6)

where k_{io} 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~ α5(the order of the reaction), k_{10}~k_{20}(pre-exponential factor) and E_1~ E_2(the activation energy) are 9 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 $L_{16}(4^5)$[3], whose levels and factors are shown in Table 3), the experimental data of chemical kinetics are shown in Table 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 3 Levels and factors in orthogonal test

Levels	A Reaction temperature(℃)	B Blank	C Reaction time(h)	D Blank	E t-BuOOH: phenanthrene (mol)
1	40		12		6
2	50		9		4
3	60		6		3
4	74		3		5

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Table 4 Experimental data of chemical kinetics

Test number	Reaction temperature (℃)	Reaction time (h)	Concentration				
			Phenanthrene ($mol.L^{-1}$)	t-BuOOH ($mol.L^{-1}$)	PQ ($mol.L^{-1}$)	DPA ($mol.L^{-1}$)	H_2O ($mol.L^{-1}$)
1	40	12	0.2225	1.3561	0.0118	0.0040	0.0118
2	40	9	0.3442	1.2188	0.0150	0.0360	0.0150
3	40	6	0.4510	1.1815	0.0147	0.0455	0.0147
4	40	3	0.2752	1.2729	0.0068	0.0285	0.0068
5	50	12	0.1761	1.2375	0.0082	0.0239	0.0082
6	50	9	0.2118	1.0875	0.0395	0.0379	0.0395
7	50	6	0.2423	1.2616	0.0131	0.0141	0.0131
8	50	3	0.1329	1.3070	0.0090	0.0058	0.0090
9	60	12	0.1719	0.9021	0.0517	0.0490	0.0517
10	60	9	0.1606	1.1750	0.0149	0.0083	0.0149
11	60	6	0.1356	0.9342	0.0260	0.0249	0.0260
12	60	3	0.2441	0.7424	0.0507	0.0543	0.0507
13	74	12	0.2275	0.8375	0.0428	0.0708	0.0428
14	74	9	0.0611	0.8241	0.0297	0.0839	0.0297
15	74	6	0.0393	0.8064	0.0202	0.0954	0.0202
16	74	3	0.0810	0.6401	0.0208	0.1366	0.0208

Table 5 Experimental and calculated data of kinetics

Test number	Measured value			Calculated value		
	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	0.2225	0.0118	0.0040	0.1267	0.0158	0.0078
2	0.3442	0.0150	0.0360	0.3114	0.0203	0.0494
3	0.4510	0.0147	0.0455	0.4554	0.0199	0.0409
4	0.2752	0.0068	0.0285	0.2826	0.0114	0.0245
5	0.1761	0.0082	0.0239	0.1244	0.0143	0.0294
6	0.2118	0.0395	0.0379	0.1775	0.0428	0.0458
7	0.2423	0.0131	0.0141	0.2416	0.0114	0.0205
8	0.1329	0.0090	0.0058	0.0920	0.0129	0.0033
9	0.1719	0.0517	0.0490	0.2168	0.0489	0.0329
10	0.1606	0.0149	0.0083	0.1559	0.0134	0.0066
11	0.1356	0.0260	0.0249	0.0749	0.0258	0.0158
12	0.2441	0.0507	0.0543	0.2655	0.0483	0.0494

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13	0.2275	0.0428	0.0708	0.3131	0.0414	0.0665
14	0.0611	0.0297	0.0839	0.1189	0.0329	0.0719
15	0.0393	0.0202	0.0954	0.0713	0.0153	0.0994
16	0.0810	0.0208	0.1366	0.1278	0.0198	0.1308

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 the kinetic parameters were obtained. The chemical kinetic equations as follows:

The rate of disappearance of phenanthrene:

$$(-r_A)=2.60\times10^3\exp(-\frac{1.78\times10^5}{RT})C_A^{0.912}C_B^{1.78}$$

The rate of appearance of phenanthrenequinone:

$$r_C=2.60\times10^3\exp(-\frac{1.78\times10^5}{RT})C_A^{0.912}C_B^{1.78}$$

$$-1.56\times10^3\exp(-\frac{6.26\times10^4}{RT})C_B^{1.14}C_C^{0.888}C_E^{0.447}$$

The rate of appearance of diphenic acid:

$$r_D=1.56\times10^3\exp(-\frac{6.26\times10^4}{RT})C_B^{1.14}C_C^{0.888}C_E^{0.447}$$

Calculated values of kinetic model are also shown in Table 5.

With residual analysis, the kinetic model was examined. The results are showed Figure 1~6. Figure1~6 indicate that C_{cal} versus $C_{measured}$ (phenanthrene or phenanthrenequinone or diphenic acid) are very near the diagonal, and $C_{measured}$- 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.

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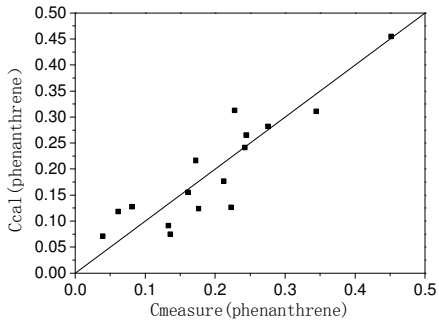

Fig. 1 Comparison between calculated and experimental concentration(phenanthrene)

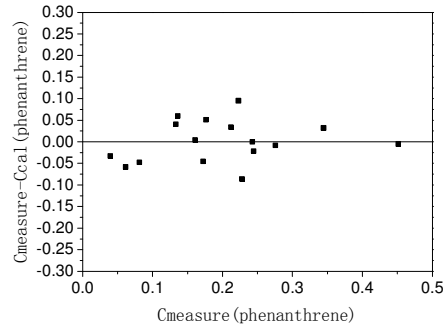

Fig. 2 Residual distribution of calculated and experimental concentration(phenanthrene)

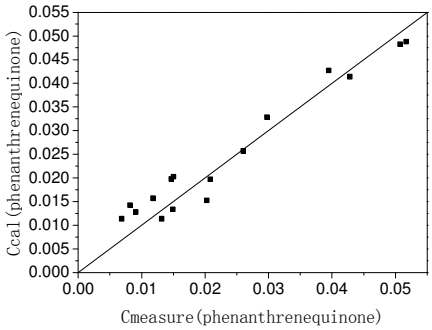

Fig. 3 Comparison between calculated and experimental concentration(quinone)

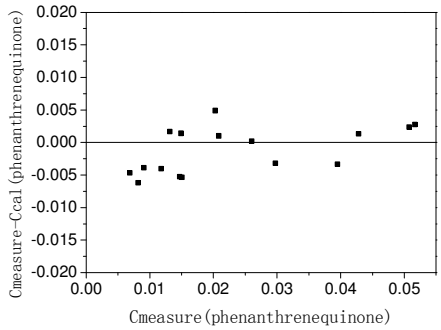

Fig. 4 Residual distribution of calculated and experimental concentration(quinone)

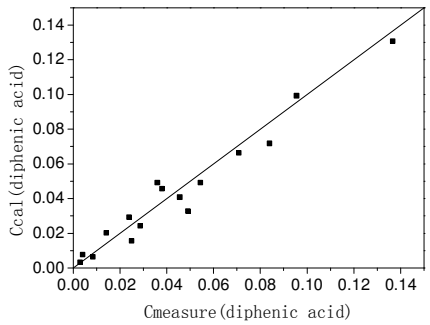

Fig. 5 Comparison between calculated and experimental concentration(diphenic acid)

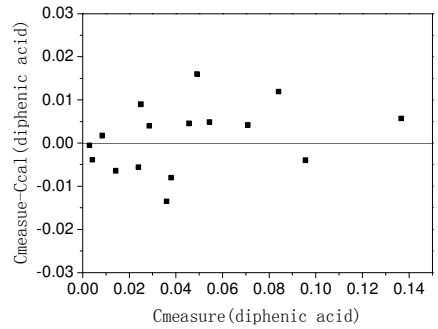

Fig. 6 Residual distribution of calculated and experimental concentration(diphenic acid)

CONCLUSIONS

By orthogonal test main technical parameters of preparing phenanthrenequinone were optimized. The optimum conditions were as follows: molar ratio of TBHP to phenanthrene: 5:1; $MoO_2(acac)_2$ (catalyster) content: 0.05g(per 5g phenanthrene); reaction time: 4h. This oxidation method had the advantages of simple procedure, high efficiency, and eco-friendly oxidation way. That the raw materials phenanthrene was used in making PQ could reach the purposes of cleansing the environment and offering an effective way of commercial use of phenanthene.

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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 obtained.The determination of kinetic parameters can be considered as a useful tool for the process design, operation and improvement of phenanthrene oxidation to phenanthrenequinone. 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.

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