

Kinetics and Mechanism of Quaternary Ammonium Salts as Phase-Transfer Catalysts in the Liquid–Liquid Phase for Oxidation of Thiophene

Dishun Zhao,^{*,†,‡} Hongwei Ren,[†] Jianlong Wang,[‡] Yu Yang,[†] and Ying Zhao[†]

College of Chemistry and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang Hebei 050018, P.R.C., and School of Chemical Engineering, Tianjin University, Tianjin 300072, P.R.C

Received March 27, 2007. Revised Manuscript Received June 25, 2007

Owing to the insolubility of the binary phase system for oxidative desulfurization, a formic acid/H₂O₂ system with quaternary ammonium salts as phase-transfer catalysts was employed in the oxidation of thiophene. Four catalytic systems with ultrasound were carried out, tetrabutyl ammonium bromide behaved as the optimum active catalyst, and the desulfurization rate was 94.67%. Dispersion of phase-transfer catalyst between the organic and aqueous phases was related to the extraction constant. When the amount of catalyst exceeded 0.0019 mol L⁻¹, quaternary ammonium salts would serve well to transfer the polar substance of oxidant [HCOOO⁻] to the nonpolar environment of the organic phase. In the transfer process, complexation [HCOOO–Q–X] resulted from the interaction of oxidant and phase-transfer catalyst, which could decrease the polarity of the oxidant and the apparent activation energy. With the extractive equilibrium and oxidative reaction, a dynamic model was developed. From the study of kinetics, it could be shown that the reaction order was pseudo-first-order.

Introduction

As environmental concern increases, much research work has been carried out on the oxidative desulfurization (ODS) with hydrogen peroxide to reduce the amount of organosulfur compound in petroleum. Various catalysts such as acetic acid,¹ formic acid,^{2–3} cobalt salts,⁴ titanium silicate,⁵ sodium carbonate,⁶ and phosphotungstic acid^{7–8} are applied in this novel liquid–liquid phase system. However, in the process of ODS, there are still some problems owing to the insolubility of the polar aqueous phase and nonpolar organic phase. The insolubility of the oxidant and substrate of organosulfur is an obstacle to ODS, and it makes them react with each other only at the interface. As a consequence, the reaction rate is decreased and the conversion of organosulfur in this two-phase system is too low.

The quaternary ammonium salts with their unique capability to dissolve in both aqueous and organic liquids have been used

extensively in a variety of chemical applications such as phase-transfer catalysts (PTC).^{9–11} They can incorporate with the oxidant and transport it from the interface phase to the reaction phase, thereby enhancing the reaction rate. There are several advantages of the PTC system, such as an increased reaction rate and mild reaction temperature and pressure, avoiding the employment of expensive anhydrous or aprotic solvents.

So here, quaternary ammonium salts have been used in oxidative desulfurization, and a new method to remove organosulfur compound in petroleum is developed. Earlier work has demonstrated its process efficiency, safety, and reduced environmental impact.^{12–14} In this paper, we exploited four catalytic systems under an ultrasonic field to remove thiophene and had an insight study into the mechanism of oxidative desulfurization by quaternary ammonium salts. We attempted to clarify the behavior of quaternary ammonium salts in the liquid–liquid phase system. Some important questions were the following: How did the quaternary ammonium salts interact with the oxidant to form a certain kind of complexation, how did the complexation transport the oxidant across the interface to the organic phase, and how did the oxidant react with thiophene in organic phase. On the basis of this study, the cycling model and dynamic model of quaternary ammonium salts for oxidation of thiophene were developed respectively.

* To whom correspondence should be addressed. Tel.: +86-0311-88632009. Fax: +86-0311-88632009. E-mail address: dishunzhao@yahoo.com.cn.

[†] Hebei University of Science and Technology.

[‡] Tianjin University.

(1) Shiraishi, Y.; Tachibana, K.; Hirai, T.; Komasa, I. *Ind. Eng. Chem. Res.* **2002**, *41* (17), 4362–4375.

(2) Filippis, P. D.; Scarsella, M. *Energy Fuels* **2003**, *17*, 1452–1455.

(3) Yu, G. X.; Lu, S. X.; Chen, H.; Zhu, Z. N. *Energy Fuels* **2005**, *19*, 447–452.

(4) Shiraishi, Y.; Hirai, T.; Komasa, I. *J. Chem. Eng. Jpn.* **2002**, *35*, 1305–1311.

(5) Kong, L. Y.; Li, G.; Wang, X. S.; Wu, B. *Energy Fuels* **2006**, *20*, 896–902.

(6) Deshpande, A.; Bassi, A.; Prakash, A. *Energy Fuels* **2005**, *19*, 28–34.

(7) Yazu, K.; Yamamoto, Y.; Furuya, T.; Miki, K.; Ukegawa, K. *Energy Fuels* **2001**, *15*, 1535–1536.

(8) Yazu, K.; Furuya, T.; Miki, K.; Ukegawa, K. *Chem. Lett.* **2003**, *32*, 920–921.

(9) Koch, H. F.; Shen, J. Y.; Roundhill, D. M. *Sep. Sci. Technol.* **2000**, *35* (4), 623–629.

(10) Yadav, G. D.; Jadhav, Y. B. *Clean Technol. Environ. Policy* **2003**, *6*, 32–42.

(11) Jin, G.; Morgner, H.; Ido, T.; Goto, S. *Catal Lett.* **2003**, *86*, 207–210.

(12) Zhao, D. S.; Ren, H. W.; Ma, S. G.; Liu, C. W. *Acta Chim. Sinica* **2006**, *64* (20), 2086–2090.

(13) Zhao, D. S.; Ren, H. W.; Zhou, E. P.; Li, L. *J. Fuel Chem. Technol.* **2007**, *35* (1), 47–50.

(14) Zhao, D. S.; Ma, S. G.; Liu, C. W.; Ren, H. W. *Chem. J. Chin. Univ.* **2006**, *27* (1), 144–146.

Table 1. Effects of PTC on the Desulfurization Rate^a

PTC	no PTC	TMAB	TEAB	TPAB	TBAB
thiophene conversion (%)	28.37	42.37	70.02	86.57	94.67

^a Reaction condition 323 K; amount of catalyst 0.0116 mol L⁻¹.

Table 2. Log E_{Q+Y-} of Phase-Transfer Catalyst

PTC	TMAB	TEAB	TPAB	TBAB
log E_{Q+Y-}	0.16	2.32	4.48	6.64

Experimental Section

Materials. Thiophene, analytical grade, from China was used without any further treatment. Hydrogen peroxide (aqueous solution 30%, China) was used as oxidant. Its concentration was determined by iodometric titration, and its consumption was not monitored during the reaction. Formic acid, analytical grade (China); *n*-heptane, analytical grade (China); silver nitrate, analytical grade (China); and four different quaternary ammonium salts were used. Tetrabutyl ammonium bromide (TBAB), tetrapropyl ammonium bromide (TPAB), tetraethyl ammonium bromide (TEAB), and tetramethyl ammonium bromide (TMAB) were procured from China and used without any purification.

A typical reaction run was as follows: the water under ultrasonic field was first heated up and stabilized to one desired reaction temperature of 323 K. Then, 0.028 mL of thiophene was dissolved in 24 mL of *n*-heptane, used as the model compound, and added to the reactor. A 0.03–0.25 g portion of the catalyst, 12 mL of hydrogen peroxide, and 12 mL of formic acid were added to the reactor too. The resulting mixture was reacted for 1.5 h at the reaction temperature and analyzed periodically. The oxidant in the aqueous phase was separated by tap funnel, and H₂O₂ was added for a new ODS process. The organic phase was subjected to gas chromatographic analysis with an FPD detector on a capillary column (SE – 54, 15 m × 0.25 mm, 0.33 μm film thickness). Oxidation products were identified through GC-MS analysis and FIR analysis. The retention of the phase-transfer anion was detected with titration analysis of silver nitrate.

Results and Discussion

1. Behavior of Quaternary Ammonium Salts in the Liquid–Liquid Phase. *1.1. Dispersion of Phase-Transfer Catalyst between the Organic and Aqueous Phases.* Four different catalytic systems were investigated to determine the optimum active catalyst. The experiment data of the different catalysts is shown in Table 1.

As it is shown in Table 1, it is obvious that the oxidative reaction is a transfer-rate-limited reaction, and the reaction rate is determined by the transportation of oxidant [HCOOO⁻]. With the presence of quaternary ammonium salts, [HCOOO⁻] is transported to the organic phase quickly, so the reaction becomes an organic-phase-limited reaction.

With the extraction constant log E_{Q+Y-} (Table 2), it is concluded that an increase in the number of atoms surrounding the central N atom of an ammonium cation may increase the lipophilic property. Therefore, TBAB behaves as the optimum active catalyst, which can transfer sufficient oxidant from the aqueous phase to the organic phase.

1.2. Formation of the Complexation [HCOOO–Q–X]. The effect of the TBAB amount on the desulfurization rate was explored (Figure 1). It is indicated that the conversion of thiophene increased with the increasing amount of TBAB. But when the amount exceeded a critical value, 0.0093 mol L⁻¹, the conversion of thiophene did not increase any longer, which meant the transport function of phase-transfer catalyst could serve the reaction well at this moment.

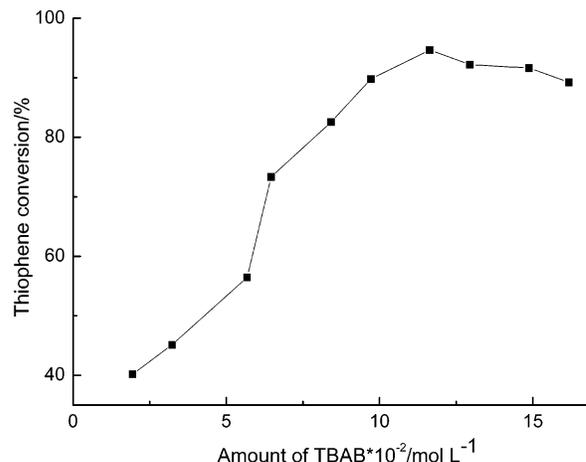


Figure 1. Changing of thiophene concentration during the reaction as a function of the amount of TBAB: (reaction condition) 323 K.

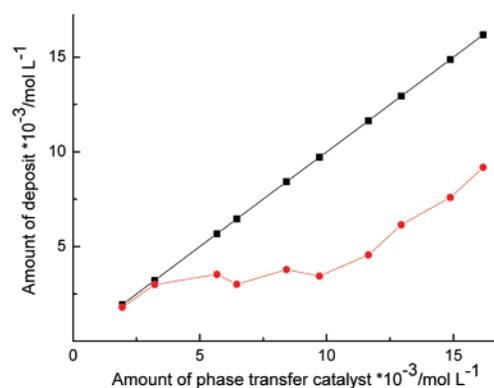


Figure 2. Changing of deposit of $n_{[AgBr]}$ in organic phase and aqueous phase for different amounts of TBAB after reaction: (reaction condition) 323 K; (♦) amount of TBAB added to reaction; (●) deposit of $n_{[AgBr]}$.

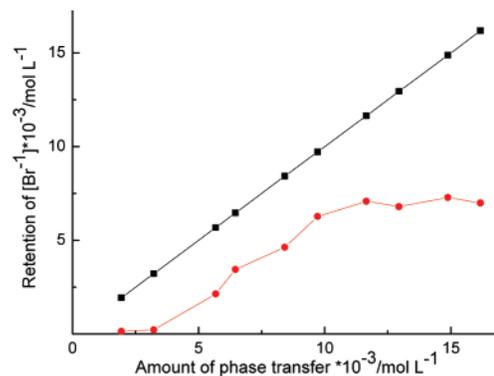


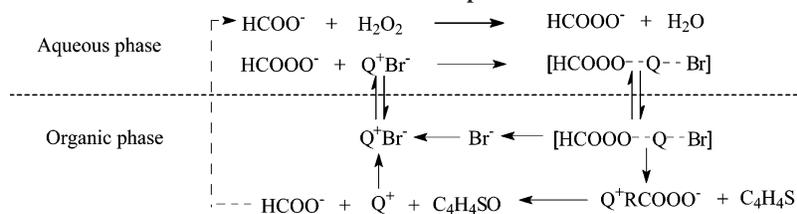
Figure 3. Changing of undetected $n_{[Br^-]}$ in organic phase and aqueous phase for different amount of TBAB after reaction: (reaction condition) 323 K; (♦) amount of TBAB added to reaction; (●) deposit of $n_{[AgBr]}$.

Table 3. Available Radius of PTC

PTC	TMAB	TEAB	TPAB	TBAB
$r(Q^+)$ (Å)	2.85	3.48	4.01	4.37

The retention data of $n_{[Br^-]}$ after oxidation (Figure 2) was detected with titration analysis to gain insight into the behavior of the phase-transfer catalyst in the liquid–liquid phase system. It was shown that the amount of deposit of $n_{[AgBr]}$ nearly remained constant until 0.0093 mol L⁻¹. But with more catalyst-transfer catalyst, the amount of deposit would increase in a linear way. Amounts of $n_{[Br^-]}$ undetected during the reaction at various amounts of catalyst are also shown in Figure 3. When the amount of catalyst was small 0.0019–0.0032 mol L⁻¹, the

Scheme 1. Cycling Model of Quaternary Ammonium Salts as Phase-Transfer Catalysts in the Liquid-Liquid-Phase System for Oxidation of Thiophene



undetected $n_{[\text{Br}^-]}$ was small as well. As the amount increased from 0.0057 to 0.0116 mol L⁻¹, the undetected $n_{[\text{Br}^-]}$ increased from 0.0022 to 0.0071 mol L⁻¹. However, from 0.0129 to 0.0162 mol L⁻¹, the undetected $n_{[\text{Br}^-]}$ became parallel. This indicated that the undetected $n_{[\text{Br}^-]}$ existed in another form in the liquid-liquid phase system. With the conclusions of Figures 2 and 3, we can conclude that there was some kind of complexation resulting from the interaction of phase-transfer cation [Q⁺], phase-transfer anion [Br⁻], and oxidant [HCOOO⁻]. We can also conclude that little complexation was formed when the catalyst amount was small and the conversion of thiophene was low. With more catalyst added to the reaction system, more complexation was formed and oxidant [HCOOO⁻] was transported to the organic phase sharply, resulting in an increased reaction rate. When the catalyst amount was 0.0129 mol L⁻¹, the complexation was sufficient for the reaction, so the reaction rate would be parallel.

The complexation can be indicated as



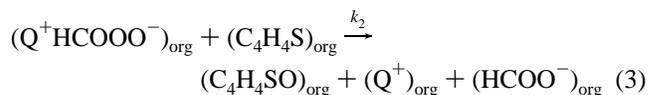
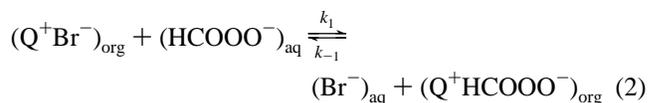
1.3. Dissociate Reaction of the Complexation in the Organic Phase. The dissociation of the complexation is needed for reaction with the substrate of thiophene in the organic phase. With the same anions of [HCOOO⁻] and [Br⁻], the energy of delocalization is determined by the available radius of phase-transfer cation [Q⁺] (Table 3). It can be seen that $r(\text{TBAB}) > r(\text{TPAB}) > r(\text{TEAB}) > r(\text{TMAB})$. As a consequence, TBAB is a good phase-transfer catalyst, which is consistent with the experiment.

After oxidation, with different retention times, the GC-FPD chromatographic analysis showed that some sulfur products were left in the organic phase. In the examination of the components with FIR, the specific infrared absorptions of 1358.13, 1122.28, and 1040.15 cm⁻¹ illustrated the formation of thiophene sulfone and sulfoxide. Further examination of GC-MS also confirmed the formation of thiophene sulfone. Besides thiophene sulfone and sulfoxide, thiophene was also oxidized to sulfuric acid, which was identified by depositing BaSO₄.

2. Mechanism Aspects of Oxidation of Thiophene in the Liquid-Liquid Phase. There are two steps in the process of the liquid-liquid phase system of oxidation of thiophene by quaternary ammonium salts, containing the extractive equilibrium and the oxidative reaction.¹⁵⁻¹⁶ In the first step, the oxidant [HCOOO⁻] is transported from the aqueous phase to the organic phase. In the transfer process, there is a complexation [HCOOO⁻-Q-X] formed, and this plays two roles. First, the complexation can enhance the transfer rate.¹²⁻¹³ Primarily, the negative charge is concentrated on the anion of oxidant [HCOOO⁻], but in the presence of complexation [HCOOO⁻-Q-X], the negative charge

is dispersed. As a result, a decrease in the polarity of the oxidant (HCOOO⁻) may enable the oxidant (HCOOO⁻) to transport to the organic phase more easily. Second, in the experiment of Otsuki et al.,¹⁷ the sulfur compounds reacted with formic acid/H₂O₂ directly but the oxidant could not support enough energy to overcome the E_a needed in the oxidation of thiophene. So, thiophene was not oxidized by hydrogen peroxide and formic acid at 50 °C. Whereas, in the presence of quaternary ammonium salts as phase-transfer catalysts, the mechanism may be changed and the apparent activation energy is decreased, so thiophene shows higher a reactivity ratio and readily oxidized to the corresponding sulfone. The second step is oxidation of thiophene. In this step, thiophene is removed and the other product is (HCOO⁻)_{org} together with the phase-transfer catalyst (Q⁺Br⁻)_{org} which are subsequently redistributed with (Q⁺HCOOO⁻)_{aq} by repeating the first step. On the basis of this, the cycling model of oxidation of thiophene by quaternary ammonium salts is developed (see Scheme 1).

3. Kinetics of Oxidation of Thiophene. A dynamic model is developed to investigate the mass transfer and reactive activity for the oxidant [HCOOO⁻] on the conversion of thiophene in the liquid-liquid phase system.¹⁸⁻²⁰ There are two steps in this process essentially. The first step describes the extraction between the aqueous phase and the organic phase. Q⁺ is the phase-transfer cation, HCOOO⁻ is the oxidant, and the subscripts aq and org represent the aqueous and the organic phase, respectively. This step has been described by two rate constants (k_1 and k_{-1}) in order to address the effect of mass transfer across the interfacial region of the reaction system. The mass transfer rate constants k_1 and k_{-1} are each functions of the interfacial area. The second step k_2 describes an irreversible oxidative reaction taking place within the organic phase.



The rate of formation of product is

$$\frac{d[\text{C}_4\text{H}_4\text{SO}]_{\text{org}}}{dt} = k_2[\text{Q}^+\text{HCOOO}^-]_{\text{org}}[\text{C}_4\text{H}_4\text{S}]_{\text{org}} \quad (4)$$

(17) Yadav, G. D.; Lande, S. V. *Adv. Synth. Catal.* **2005**, *347*, 1235-1241.

(18) Otsuki, S.; Nonaka, T.; Takashima, N.; Qian, W.; Ishihara, A.; Tamotsu, T. K. *Energy Fuels* **2000**, *14*, 1232-1239.

(19) Dehmlow, E. V.; Pehmlow, S. S. *Phase-transfer Catalysts*; Chem. Ind. Press: Beijing, 1988; pp 33-35.

(20) Maw-Ling, W.; Chang, S.-W. *Ind. Eng. Chem. Res.* **1994**, *33*, 1606-1611.

(15) Starks, C. M.; Liotta, C. L.; Halpern, M. E. *Textbook of Phase-transfer Catalysts: Fundamentals, application and industrial perspectives*; New York: Chapman & Hall, 1994; pp 306-307.

(16) Karmakar, R.; Samanta, A. *J. Am. Chem. Soc.* **2001**, *123*, 3809-3817.

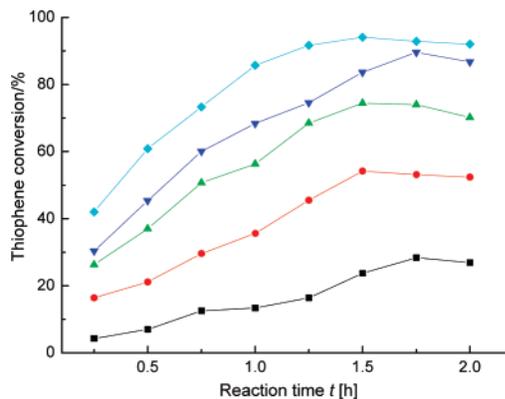


Figure 4. Changing of thiophene conversion during the reaction as a function of reaction time: (reaction condition) 323 K, (amount of catalyst) 0.0116 mol L⁻¹; (◆) TBAB, (▼) TPAB, (▲) TEAB, (●) TMAB, (■) no PTC.

Where, $[C_4H_4SO]_{org}$ is the concentration of product at a particular time during the course of the reaction. The different rate expression describing the formation of $(Q^+HCOOO^-)_{org}$ is

$$\frac{d[Q^+HCOOO^-]_{org}}{dt} = k_1[Q^+Br^-]_{org}[HCOOO^-]_{aq} - k_{-1}[Q^+HCOOO^-]_{org}[Br^-]_{aq} - k_2[Q^+HCOOO^-]_{org}[C_4H_4S]_{org} \quad (5)$$

To simplify, a postulation is proposed that quaternary ammonium salts and oxidant are excessively used, so there is no change in the individual concentration of $[Q^+HCOOO^-]_{org}$; therefore, the steady-state approximation may be made for $[Q^+HCOOO^-]$, and eq 5 may be set equal to zero,

$$\frac{d[Q^+HCOOO^-]_{org}}{dt} = 0 \quad (6)$$

Then,

$$k_1[Q^+Br^-]_{org}[HCOOO^-]_{aq} = k_{-1}[Q^+HCOOO^-]_{org}[Br^-]_{aq} + k_2[Q^+HCOOO^-]_{org}[C_4H_4S]_{org} \quad (7)$$

The total concentration of the phase-transfer anion in the organic phase $(Q^+)_{org}$ is

$$(Q^+)_{org} = [Q^+Br^-]_{org} + [Q^+HCOOO^-]_{org} \quad (8)$$

Then, applying the steady-state approximation eqs 7 and 8 for $[Q^+HCOOO^-]_{org}$ gives

$$[Q^+HCOOO^-]_{org} = \frac{k_1[Q^+]_{org}[HCOOO^-]_{aq}}{k_1[HCOOO^-]_{aq} + k_{-1}[Br^-]_{aq} + k_2[C_4H_4S]_{org}} \quad (9)$$

Substitution into eq 4 gives the following differential rate expression describing the rate of formation of product,

$$\frac{d[C_4H_4SO]_{org}}{dt} = \frac{k_1k_2[Q^+]_{org}[HCOOO^-]_{aq}[C_4H_4S]_{org}}{k_1[HCOOO^-]_{aq} + k_{-1}[Br^-]_{aq} + k_2[C_4H_4S]_{org}} \quad (10)$$

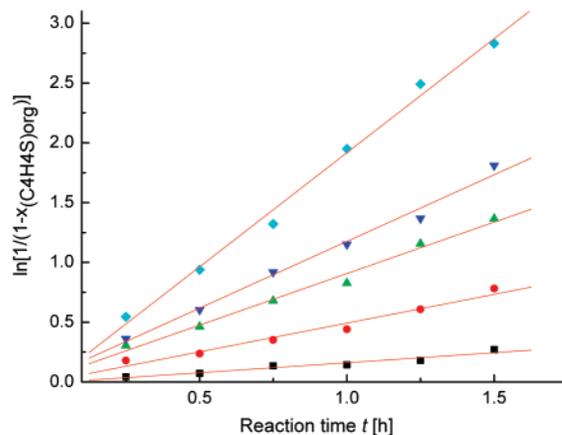


Figure 5. Pseudo-first-order rate constants for different kinds of phase-transfer catalysts at 323 K: (amount of catalyst) 0.0116 mol L⁻¹; (◆) TBAB, (▼) TPAB, (▲) TEAB, (●) TMAB, (■) no PTC.

In this process, the rate of mass transfer of $(HCOOO^-)_{aq}$ is fast, so $(HCOOO^-)_{org}$ and $(Q^+)_{org}$ rapidly accumulate in the organic phase and maintain a steady-state concentration,

$$k_1[HCOOO^-]_{aq} \gg k_{-1}[Br^-]_{aq} + k_2[C_4H_4S]_{org} \quad (11)$$

and

$$\frac{d[C_4H_4S]_{org}}{dt} = k_2[Q^+]_{org}[C_4H_4S]_{org} \quad (12)$$

Kinetic study usually involves the disappearance of $[C_4H_4S]_{org}$ and the related rate of appearance of oxidative product.

$$-\frac{d[C_4H_4S]_{org}}{dt} = \frac{d[C_4H_4SO]_{org}}{dt} \quad (13)$$

Then

$$\frac{d[C_4H_4S]_{org}}{dt} = -k_2[Q^+]_{org}[C_4H_4S]_{org} \quad (14)$$

Define $k_2[Q^+]_{org} = k_3$

$$\frac{d[C_4H_4S]_{org}}{dt} = -k_3[C_4H_4S]_{org} \quad (15)$$

Make the integral transformation, and define the constant as k ($[C_4H_4S]_{org0}$ represents the fractions in the organic phase at time zero)

$$\ln \frac{1}{1 - \chi_{[C_4H_4S]_{org}}} = kt \quad (16)$$

$$\chi_{[C_4H_4S]_{org}} = \frac{[C_4H_4S]_{org0} - [C_4H_4S]_{org}}{[C_4H_4S]_{org0}} \quad (17)$$

So, with excessive quaternary ammonium salts and oxidant used for oxidation of thiophene, the reaction order may be pseudo-first-order in theory.

Experiments to obtain kinetics parameters for oxidation of thiophene were carried out in the phase-transfer catalytic system. The effect of reaction time on the oxidation of thio-

Table 4. Fitted Linear Line of $\ln[1/(1 - x_{(C_4H_4S)_{org}})]$ vs t

PTC	fitted linear line	correlation factor R^2
no PTC	$y = 0.167x - 0.09$	0.9440
TMAB	$y = 0.481x + 0.08$	0.9694
TEAB	$y = 0.861x + 0.41$	0.9872
TPAB	$y = 1.116x + 0.06$	0.9890
TBAB	$y = 1.910x + 0.01$	0.9925

phene by different kinds of phase-transfer catalysts is shown in Figure 4, where the conversion of thiophene versus time is plotted.

With an excessive amount of $HCOOOH$, consistent linear reaction kinetics were demonstrated in the plot of $\ln[1/(1 - \chi_{(C_4H_4S)_{org}})]$ as a function of reaction time (Figure 5). The oxidation reaction order is pseudo-first-order, and experimental results are consistent with the simulation results in the dynamic model.

With the method of least-squares, the fitted linear line of $\ln[1/(1 - \chi_{(C_4H_4S)_{org}})]$ vs t can be observed (Table 4).

As shown in Table 4, it can be observed that the values of the reaction rate rise substantially as phase-transfer catalyst is added to the liquid–liquid-phase system. It is also found that k shows a maximum value when TBAB was used as the phase-transfer catalyst and the conversion of thiophene was up to 94.67%.

Conclusions

When quaternary ammonium salts, which are frequently used as phase-transfer catalysts, are employed in the liquid–liquid phase system of thiophene oxidation, their characteristics of solubility not only in the organic phase but also in the aqueous phase are advantageous. The complexation $[HCOOO-Q-X]$ formed in the transfer process is playing a key role in the oxidation of thiophene. It can decrease the polarity of the oxidant ($HCOOO^-$), thereby availing the oxidant ($HCOOO^-$) to transport to the organic phase easily. It can also change the mechanism and decrease the apparent activation energy, thus enhancing the reaction rate. A dynamic model is developed concerning mass transfer and reaction for oxidation of thiophene by phase-transfer catalysts. Using this model, simulation results are consistent with the experimental data. From the study of kinetics, it can be shown that the reaction order is pseudo-first-order.

Acknowledgment. We acknowledge financial support from the National Natural Science Foundation of China (Grant Nos. 20276015, 20576026).

EF070152G