Mechanism and Kinetics of Polychlorination of Long Chain n-Alkanes by Photo-Initiation

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Abstract Based on the mechanism analysis of the polychlorination of long chain n-alkanes by photo-initiation, a kinetic model was developed. The model parameters were obtained by the method of non-linear fitting. The influences of luminous intensity and concentration of molecular chlorine on the rate of polychlorination are demonstrated by the model. If the luminous intensity is adequate, the polychlorination rate of n-alkane is only controlled by the flow rate of molecular chlorine in a wide range of temperature, and the changes of temperature and luminous intensity have less effect on the reaction rate. In addition, the predictions of chlorine content of polychlorinated n-alkane calculated with the model agree very well with experimental results.
Keywords photochlorination, polychlorination, photo-initiation, chlorination, long chain n-alkanes, mechanism, kinetics

1 INTRODUCTION

Radical chlorination of hydrocarbons with molecular chlorine is a common industrial process, which can be initiated by thermal, chemical, or photo methods. Among them, the photo-initiation is much less common than other methods on an industrial scale, but it is the most efficient one[1]. Photochlorination reactions of alkanes have attracted wide interest due to the characteristics of high selectivity and low operating temperature of the photo-initiated chain reactions[2−4]. There were many researches[1−12] on mechanism and kinetics of photochlorination of alkanes in bulk or in solution. However, most researches were limited in mono- or di-chlorination, or focused on the low-chain alkanes, such as methane, ethane, propane or n-butane, 2,3-dimethylbutane, etc. The kinetic model or chlorination rate equation of polychlorination of long chain n-alkanes under solvent free condition was little explored.

The intrinsic kinetics of liquid phase chlorination are quite complex [5], especially in a polychlorination process. On one hand, monochloro-isomers can be formed with varying selectivity; on the other hand, the substitution of a second hydrogen atom by a chlorine atom is possible as soon as the monochlorinated derivative has been formed[1]. This paper presents the mechanism and kinetics study on the liquid phase polychlorination of long chain n-alkanes by photo-initiation. A kinetic model was developed to describe the characteristics of polychlorination, and to predict the degree of chlorination of long chain n-alkanes by using photo-process.

2 EXPERIMENTAL

Normal alkane (C_{14-15}) and liquid molecular chlo-

rine were industrial materials. n-Alkane was purified by passing through columns of activated carbon and 0.3 A molecular sieve. Liquid molecular chlorine was used directly after vaporization.

The experimental apparatus used in this study, as shown in Fig. 1, was a semi-batch photochlorination system. The liquid phase polychlorination was performed in an annular quartz reactor, equipped with a reflecting shield layer outside and a high mercury arc lamp inside which was cooled by an air pump. n-Alkane was added batchwise while the gaseous molecular chlorine was bubbled continuously. In order to maintain the same temperature in the reactor, the mixture was circulated rapidly by means of a peristaltic pump.
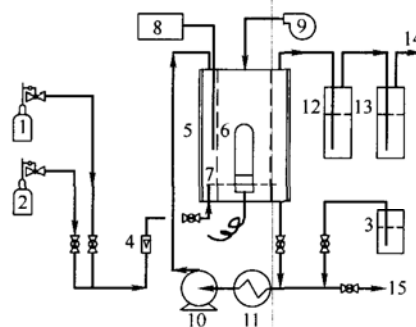

Figure 1 Experimental apparatus
1—N$_2$ tank; 2—Cl$_2$ tank;
3—n-alkane container; 4—rotameter;
5—reactor; 6—high mercury arc lamp;
7—gas distributor; 8—temperature controller;
9—air pump; 10—peristaltic pump;
11—heat exchanger; 12—water bottle;
13—NaOH water solution bottle;
14—waste gas out; 15—products out

The chlorine content of polychlorinated n-alkane was determined by the Volhard method[13] after burn-

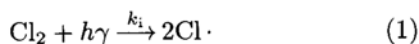ing the sample in a flask fulfilled with oxygen.

3 MECHANISM AND KINETIC MODEL DEVELOPMENT
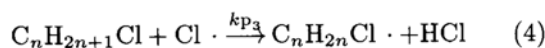
3.1 Analysis of reaction mechanism

Photochlorination is radical chain reactions for which the quantum yields are high, often higher than unity[1]. The reaction is initiated by homolysis of chlorine molecule by ultraviolet irradiation, and then chlorine atoms take part in the chain reaction propagation. Termination can occur by the recombination of any two radicals and wall reactions.

Based on previous descriptions[1,2] of mechanism for radical substitution of radical chlorine species to n-alkane, the mechanism of polychlorination reaction for a long chain n-alkane by photo-initiation is summarized below.
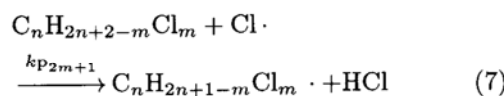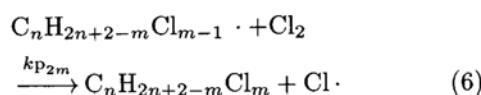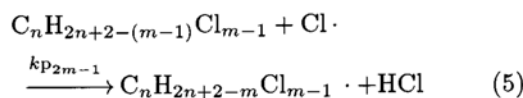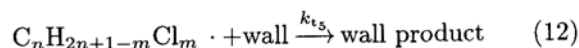
Initiation

$$Cl_2 + h\gamma \xrightarrow{k_i} 2Cl \cdot \qquad (1)$$

Propagation

$$C_nH_{2n+2} + Cl \cdot \xrightarrow{k_{P_1}} C_nH_{2n+1} \cdot + HCl \qquad (2)$$

$$C_nH_{2n+1} \cdot + Cl_2 \xrightarrow{k_{P_2}} C_nH_{2n+1}Cl + Cl \cdot \qquad (3)$$

$$C_nH_{2n+1}Cl + Cl \cdot \xrightarrow{k_{P_3}} C_nH_{2n}Cl \cdot + HCl \qquad (4)$$

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$$C_nH_{2n+2-(m-1)}Cl_{m-1} + Cl \cdot$$
$$\xrightarrow{k_{P_{2m-1}}} C_nH_{2n+2-m}Cl_{m-1} \cdot + HCl \qquad (5)$$

$$C_nH_{2n+2-m}Cl_{m-1} \cdot + Cl_2$$
$$\xrightarrow{k_{P_{2m}}} C_nH_{2n+2-m}Cl_m + Cl \cdot \qquad (6)$$

$$C_nH_{2n+2-m}Cl_m + Cl \cdot$$
$$\xrightarrow{k_{P_{2m+1}}} C_nH_{2n+1-m}Cl_m \cdot + HCl \qquad (7)$$

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Termination

$$2Cl \cdot \xrightarrow{k_{t_1}} Cl_2 \qquad (8)$$

$$C_nH_{2n+1-m}Cl_m \cdot + Cl \cdot \xrightarrow{k_{t_2}} C_nH_{2n+1-m}Cl_{m+1} \qquad (9)$$

$$C_nH_{2n+1-m}Cl_m \cdot + C_nH_{2n+1-m}Cl_m \cdot$$
$$\xrightarrow{k_{t_3}} C_{2n}H_{4n+2-2m}Cl_{2m} \qquad (10)$$

$$C_nH_{2n+1-m}Cl_m \cdot + C_nH_{2n'+1-m'}Cl_{m'} \cdot$$
$$\xrightarrow{k_{t_4}} C_nH_{2n+1-m}Cl_m + C_{n'}H_{2n'+1-m'}Cl_{m'} \qquad (11)$$

$$C_nH_{2n+1-m}Cl_m \cdot + wall \xrightarrow{k_{t_5}} wall\ product \qquad (12)$$

The overall reaction path is

$$C_nH_{2n+2} + mCl_2 \longrightarrow C_nH_{2n+2-m}Cl_m + mHCl \qquad (13)$$
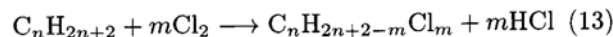
where m is zero or integer greater than zero, n is an integer greater than 10.

3.2 Kinetic model development

The description of polychlorination reaction mechanism for a long chain n-alkane seems very complex. Some simplifications[2,14] are necessary to develop the kinetics of polychlorination. (1) It is considered as perfect mixing so that chlorination process is reaction controlled. (2) Compared with termination reactions between chain radical and chlorine atom, termination reactions of chain radical coupling and disproportionation are negligible for a long chain radical substitution. (3) These wall termination reactions are negligible due to the high density of the liquid-phase system. (4) Effect of wavelength of the ultraviolet light is negligible, that is, the light is monochromatic.

Furthermore, it is assumed that the reactions follow: (1) the quasi-steady-state hypothesis, (2) the principle of equal chemical reactivity of free radicals. That means

$$\frac{d[C_nH_{2n+1-m}Cl_m \cdot]}{dt} = 0 \qquad (14)$$

$$\frac{d[Cl \cdot]}{dt} = 0 \qquad (15)$$

$$k_{P_1} = k_{P_3} = k_{P_5} = \cdots = k_{P_{11}} \qquad (16)$$

$$k_{P_2} = k_{P_4} = k_{P_6} = \cdots = k_{P_{12}} \qquad (17)$$

For simplicity, we assume

$$RCl_m = C_nH_{2n+2-m}Cl, RCl_m \cdot = C_nH_{2n+1-m}Cl \cdot$$

$$[PCA \cdot] = \sum\{[RCl_1 \cdot] + [RCl_2 \cdot] + \cdots + [RCl_m \cdot] + \cdots\}$$

$$[PCA] = \sum\{[RCl_1] + [RCl_2] + \cdots + [RCl_m] + \cdots\}$$

According to the steady state hypothesis, we have

$$2k_{t_2}[PCA \cdot][Cl \cdot] = v_i - k_{t_1}[Cl \cdot]^2 \qquad (18)$$

The rate of photo-initiation can be given by the Beer-Lambert Law[1]

$$v_i = 2\phi I_0(1 - e^{-\varepsilon r[Cl_2]}) \qquad (19)$$

Under steady-state conditions, the net rate of homolysis of chlorine molecules can be approximately expressed by applying Beer-Lambert Law with a modified formula

$$v_i - k_{t_1}[Cl \cdot]^2 = 2\phi' I_0(1 - e^{-\varepsilon' r[Cl_2]}) \qquad (20)$$

where ε' is molar absorption coefficient of polychlorination, ϕ' is quantum yield of polychlorination. Eq. (18) may be written as

$$k_{t_2}[\text{PCA}\cdot][\text{Cl}\cdot] = \phi'I_0(1 - e^{-\varepsilon'r[\text{Cl}_2]}) \qquad (21)$$

The rate of formation of the polychlorinated n-alkanes by photo-initiation is expressed as

$$\frac{d[\text{PCA}]}{dt} = k_{p_2}[\text{R}_1\cdot][\text{Cl}_2] + k_{p_4}[\text{R}_2\text{Cl}\cdot][\text{Cl}_2]+$$
$$k_{p_6}[\text{R}_3\text{Cl}_2\cdot][\text{Cl}_2] + k_{p_8}[\text{R}_4\text{Cl}_3\cdot][\text{Cl}_2]+$$
$$k_{p_{10}}[\text{R}_5\text{Cl}_4\cdot][\text{Cl}_2] + k_{p_{12}}[\text{R}_6\text{Cl}_5\cdot][\text{Cl}_2]+$$
$$k_{t_2}[\text{PCA}\cdot][\text{Cl}\cdot] \qquad (22)$$

Thus

$$\frac{d[\text{PCA}]}{dt} = k_{p_2}[\text{Cl}_2][\text{PCA}\cdot] + \phi'I_0(1 - e^{-\varepsilon'r[\text{Cl}_2]}) \quad (23)$$

For a batch process, neglecting the change of volume of reaction mixture during the photochlorination, the molar concentration of feedstock of n-alkanes [F] is

$$[\text{F}] = [\text{PCA}\cdot] + [\text{PCA}] \qquad (24)$$

Substituting Eq. (24) into Eq. (23) gives

$$\frac{d[\text{PCA}]}{dt} + k_{p_2}[\text{Cl}_2][\text{PCA}]$$
$$= k_{p_2}[\text{F}][\text{Cl}_2] + \phi'I_0(1 - e^{-\varepsilon'r[\text{Cl}_2]}) \qquad (25)$$

Integrating Eq. (25) yields

$$[\text{PCA}] = \left\{[\text{F}] + \frac{\phi'I_0(1 - e^{-\varepsilon'r[\text{Cl}_2]})}{k_{p_2}[\text{Cl}_2]}\right\}\left\{1 - e^{-k_{p_2}[\text{Cl}_2]t}\right\}$$
$$\qquad (26)$$

Equations (25) and (26) show that the polychlorination rate is a function of the concentration of molecular chlorine and the luminous intensity. However, if the rate of initiation is much less than that of propagation, that is

$$\phi'I_0(1 - e^{-\varepsilon'r[\text{Cl}_2]}) \ll k_{p_2}[\text{F}][\text{Cl}_2]$$

the luminous intensity will have less effect on the polychlorination rate of n-alkanes.

4 RESULTS AND DISCUSSION
4.1 Effects of experimental conditions on the rate of polychlorination

Experiments were made under different reaction conditions in detail. The influences of reaction temperature, volumetric flow rate of Cl_2 and luminous density on the rate of polychlorination are shown in Figs. 2—4. It can be summarized that:

(1) At the temperature range studied (50—80℃), the reaction temperature has almost no effect on the

chlorination rate of n-alkane under conditions of the same flow rate of molecular chlorine and the same luminous density.

(2) If the luminous intensity is adequate, the change of luminous intensity has little effect on the chlorination rate of n-alkane in the same flow rate of gaseous molecular chlorine.

(3) The chlorination rate of n-alkane is only related to the gas flow rate of molecular chlorine when the luminous intensity is adequate.
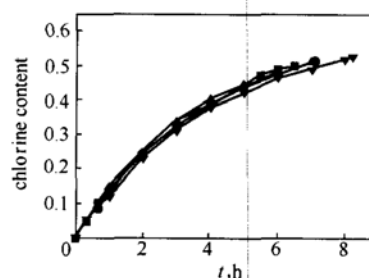
Figure 2 Influence of reaction temperature on the polychlorination rate of long chain n-alkanes
($I_0 = 0.24\,\text{J·s}^{-1}\text{·L}^{-1}$, $Q_{\text{Cl}_2} = 100\,\text{L·min}^{-1}$)
T, ℃: ■ 50; ● 60; ▲ 70; ▼ 80

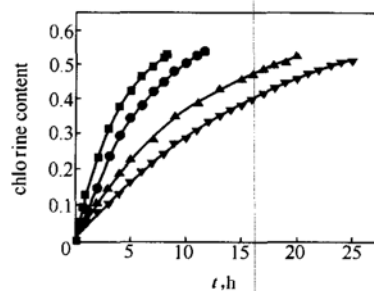**Figure 3** Influence of Q_{Cl_2} on the polychlorination rate of long chain n-alkanes
($I_0 = 0.24\,\text{J·s}^{-1}\text{·L}^{-1}$, $T = 80$℃)
Q_{Cl_2}, L·min^{-1}: ■ 100; ● 60; ▲ 30; ▼ 20

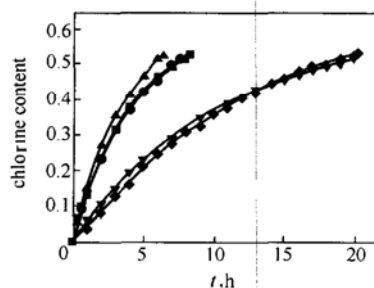**Figure 4** Influence of luminous intensity and Q_{Cl_2} on the polychlorination rate of long chain n-alkanes
($T = 80$℃)
I_0, J·s^{-1}·L^{-1}: ■ 0.24; ● 1.2; ▲ 56; ▼0.24; ◆ 1.2
Q_{Cl_2}, L·min^{-1}: ■ 100; ● 100; ▲ 100; ▼ 30; ◆ 30

4.2 Determination of model parameters

The experimental results show that the influence of reaction temperature is less important and can be ignored. That is, the parameters in Eq. (26) can be considered as constants. Moreover, for the chlorinated

reaction of n-alkane in bulk, the value of [F] is about $3.84\,\mathrm{mol \cdot L^{-1}}$ in this experiment.

To determine the model parameters and the kinetic equation of polychlorination of long chain n-alkane by photo-initiation, two approximations are further made. The first is that the molar concentration of Cl_2 in chlorinated n-alkane could be regarded as being proportional to its chlorine content. If the chlorine content of chlorinated n-alkane is written as c_{Cl} ($0 \leqslant c_{Cl} < 1$), we define

$$c_{Cl} = \beta[PCA] \qquad (27)$$

where β is a coefficient. Hence, Eq. (26) becomes

$$c_{Cl} = \beta \left\{ [F] + \frac{\phi' I_0 (1 - e^{-\varepsilon' r[Cl_2]})}{k_{p2}[Cl_2]} \right\} \left\{ 1 - e^{-k_{p2}[Cl_2]t} \right\} \qquad (28)$$

Another approximation would be that the concentration of molecular chlorine in reaction mixture was proportional to the volumetric flow rate of gaseous molecular chlorine due to the difficulty of measurement.

Then Eq. (28) becomes

$$c_{Cl} = \left[3.84a + \frac{bI_0 (1 - e^{-cQ_{Cl_2}})}{dQ_{Cl_2}} \right] \left(1 - e^{-dQ_{Cl_2}t} \right) \qquad (29)$$

in which a, b, c, d are model parameters, and $a = \beta$, $b = \phi'$, $c = \varepsilon' r$, $d = k_{p2}$.

That is, the chlorine content of polychlorinated n-alkane can be predicted with Eq. (29). By using the experimental data and the method of non-linear fitting, the model parameters were obtained. The results are shown in Table 1.

Table 1   Values of model parameters obtained

Parameter	Value
$a = \beta$	1.625×10^{-1}
$b = \phi'$	6.527×10^{-5}
$c = \varepsilon' r$	1.124×10^{2}
$d = k_{p2}$	2.706×10^{-3}

Thus we obtain the model equation

$$c_{Cl} = \left[0.624 + \frac{I_0 (1 - e^{-112.4Q_{Cl_2}})}{41.46Q_{Cl_2}} \right] \cdot \left(1 - e^{-2.706 \times 10^{-3} Q_{Cl_2} t} \right) \qquad (30)$$

The significance test of regression equation: $F = 1708.1$ [As $F_{0.05}(3, 129) = 2.60$].

Equation (30) can be simplified to

$$c_{Cl} = \left(0.624 + \frac{I_0}{41.46Q_{Cl_2}} \right) \left(1 - e^{-2.706 \times 10^{-3} Q_{Cl_2} t} \right) \qquad (31)$$

Equations (30) and (31) show the influences of the volumetric flow rate of gaseous Cl_2 and luminous density on the polychlorination rate of long chain n-alkane directly. It is demonstrated that the polychlorination rate is more sensitive to the volumetric flow rate of gaseous Cl_2.

It can be considered that the significance of two factors is different in different steps of reactions. In the step of initiation, the stronger luminous intensity could increase the rate of homolysis of chlorine molecule, and generate more chlorine radicals. So, all factors are important in this step. Since the chlorine atoms take part in the chain reaction propagation immediately after formation, the time of initiation step is short, which also has been tested by the experiment.

In the step of propagation, the homolysis of Cl_2 by photo-initiation is in competition with the reaction of propagation. The photo-homolysis of Cl_2 only acts as a supplementation of chlorine radicals terminated by reactions. If the luminous intensity was already high enough in this step, increasing of luminous intensity has almost no effect on the rate of polychlorination. The experimental results are shown in Fig. 5. That is, the polychlorination rate is controlled by the flow rate of Cl_2 during the propagation step of radical chain reaction.
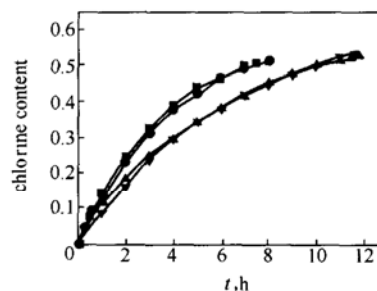

Figure 5   Influence of luminous intensity and initiation time on the polychlorination rate of long chain n-alkanes ($T = 80°C$)
Q_{Cl_2}, L·min^{-1}: ■ 100; ● 100; ▲ 60; ▼ 60
I_0, J·s^{-1}·L^{-1}: ■ 56; ● 0.24; ▲ 56; ▼ 0.24
t_j, h: ■ 1; ● continuous; ▲ 1; ▼ continuous

4.3 Validation of the model equation

The comparison of experimental results with predictions of polychlorination rate under different reaction conditions is shown in Fig. 6. It can be observed that the calculated data of chlorine content agree very well with experimental results with average deviation less than 10%(shown in Fig. 7). So the model equation based on the mechanism analysis can be used as a satisfactory kinetic model for polychlorination of long chain n-alkanes by photo-initiation.

5 CONCLUSIONS

Based on the mechanism analysis of photo-chlorination of long chain n-alkanes, a kinetic model
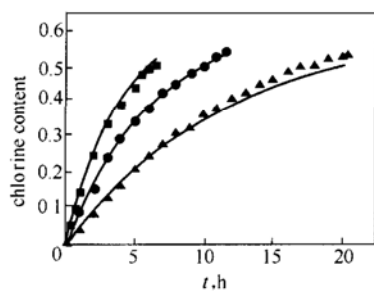
Figure 6 Comparison of experimental results of polychlorination rate with predictions
Q_{Cl_2}, L·min^{-1}: ■ 100; ● 60; ▲ 30
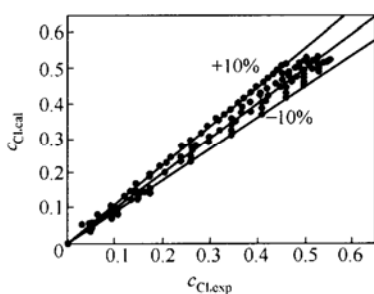■, ●, ▲ experimental data; —— model cal.

Figure 7 Comparison of experimental results of chlorine content with calculated data from model

was developed. By using experimental data and the method of non-linear fit, model parameters were obtained. The model equation demonstrates the influences of volumetric flow rate of gaseous Cl_2 and luminous density on the polychlorination rate of long chain n-alkane directly. It shows that the polychlorination rate is more sensitive to the volumetric flow rate of gaseous Cl_2. If the luminous intensity is already adequate in the step of propagation, increasing of luminous intensity has less effect on the polychlorination rate. That is, the polychlorination rate is controlled by the flow rate of Cl_2 during the propagation step. Additionally, the predictions of chlorine content of polychlorinated n-alkane by model calculated agree well with experimental results. It can be used as a model for the polychlorination of long-chain n-alkanes by photo-initiation.

NOMENCLATURE

a, b, c, d	model parameters
c_{Cl}	chlorine content of polychlorinated n-alkane
I_0	luminous intensity, J·s^{-1}·L^{-1}
k_i	kinetic constants for initiation
k_p	kinetic constants for propagation
k_t	kinetic constants for termination
Q_{Cl_2}	volumetric flow rate of Cl_2, L·h^{-1}
r	radial thickness of liquid traversed by light, m
T	reaction temperature, °C
t	reaction time, h
t_i	initiation time, h
v_i	rate of initiation
v_p	rate of propagation
β	proportional coefficient
$\varepsilon, \varepsilon'$	molar absorption coefficient, mol^{-1}·L·s^{-1}
ϕ, ϕ'	quantum yield
[ ]	concentration, mol·L^{-1}

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