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Further study on thermokinetics of n-$C_{36}H_{74}$ oxidation(II) — the n-$C_{36}H_{74}$ oxidization at different temperatures

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Abstract

Calorimetric measurements had been carried out while n-hexatriacontane (n-$C_{36}H_{74}$) oxidized at different temperatures (403–443 K). Firstly the calorimetric data had been reconstructed, and then the thermogenesis had been matched with a two-step model. The activation energy (E_a) of n-$C_{36}H_{74}$ oxidization had been attained. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: n-Hexatriacontane; Thermokinetics

1. Introduction

One feature common to many thermal methods is that they allow a continuous record of the evolution of the system under study as a function of time or temperature. Thus, not only is information collected on equilibrium states of the system but also on the reversible or irreversible process of the transitions between equilibrium states. Therefore, thermal methods can be used for the kinetic study of chemical or physical process, as Gravelle [1] mentioned. He mentioned also that thermokinetic techniques are commonly used in some fields, biology and heterogeneous catalysis for instance. A Calvet-type calorimeter was used by them to study the thermokinetics of catalysis process [2,3]. In this field, we have reported a modified batch gas sampling-carrier gas flow (BGS-CGF) microcalorimetric method used to characterize heterogeneous catalyst [4].

The thermokinetic study of the oxidation of n-$C_{36}H_{74}$ at different oxygen partial pressure has been reported by us [5]. There we had given the results that the rate constant of the first step reaction of n-$C_{36}H_{74}$ oxidization and the reaction heats of each step increased while the oxygen partial pressure increased.

Because of the thermal lags in the heat-measuring device, *reconstruction* of the data is necessary [6,7]. After reconstruction of the data, the variations of thermal power with time, thermokinetics $W(t)$, expressed by $W(t)=dQ(t)/dt$, where Q is the amount of the evolved heat and t is the time, is proportional to the reaction rate. Therefore the rate equation of the reaction can be acquired by matching thermokinetic curve with an appropriate model. From the thermokinetic analysis some kinetic parameters can be acquired, and then the reaction mechanism can be probably investigated.

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As proposed by Zhang et al. [8], the results of oxidation thermokinetics of organic compounds can be used to study the general thermodynamics, and it is also of great importance for petroleum exploitation, chemical production and so on. So it is not only of great theoretical significance, but also of great practical importance to study the oxidation thermokinetics of organic compounds. We have done some researches about it [5,8,9].

In this paper, we propose the thermokinetic results of n-$C_{36}H_{74}$ oxidized at different temperatures.

2. Experimental

The SETARAM BT2.15 microcalorimeter was used to determine the heat flow rate of the oxidation of n-$C_{36}H_{74}$. The apparatus system (same as that of Yufeng Liu's [9]) is shown as in Fig. 1.

Mixed with quartz powder (70–130 mesh), heated up to 393 K (with the protection of the N_2), and then cooled down to the ambient temperature, the n-$C_{36}H_{74}$ was coated on the surface of the quartz. Then the sample was heated for 3 h at 873 K. As the n-$C_{36}H_{74}$ can be completely oxidized to form volatile productions, the weight loss during the heating, 11.4±0.2%, was determined, then the quantity of n-$C_{36}H_{74}$ in the sample was determined.

The specimen (3.0 g) was placed in the sample cell (Fig. 1, 13) of the calorimeter while the reference cell (Fig. 1, 14) contained 3.0 g pure quartz powder. Then turn the three-way valve (Fig. 1, 5) to add N_2 (with the flow rate of 15 ml/min) into the calorimeter vessels. After the temperature of the calorimeter vessels was raised to the predetermined temperature, begin to record the curve. While the baseline got smooth and steady, the N_2 was switched to O_2, and the n-$C_{36}H_{74}$ began to be oxidized. The oxygen pressure was 1.5 bar, with the flow rate of 6.4 ml/min.

The calorimetric measurement has been carried out at different temperatures (403, 413, 423, 433, and 443 K).

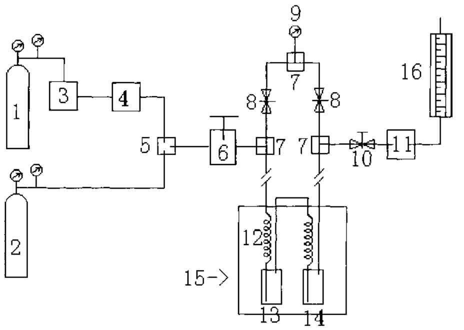

Fig. 1. Calorimetric system for thermokinetic investigation of oxidation of n-$C_{36}H_{74}$: 1, oxygen; 2, nitrogen; 3, absorption tube of CO_2; 4, absorption tube of H_2O; 5, three-way valve; 6, pressure stabilizer; 7, three-way connector; 8, cut-off valve; 9, pressure gauge; 10, regulating valve; 11, flow stabilizer; 12, pre-heating pipe; 13, sample cell; 14, reference cell; 15, calorimeter vessel; and 16, flowmeter.

3. Results and discussion

The data reconstruction method is same as Yufeng Liu [9]. After reconstruction of the calorimetric results, the thermokinetics *W(t)* during n-$C_{36}H_{74}$ oxidized at different temperatures are shown in Fig. 2.

From Fig. 2, it can be obviously seen that the oxidation of n-$C_{36}H_{74}$ seems to be two or more steps consecutive reaction. So presuming that it is two-step consecutive reaction, we have matched the *W(t)* curves of n-$C_{36}H_{74}$ oxidization with two empirical equations, which represent each step, respectively

$$\text{the first step}: \frac{A\,\mathrm{e}^{-Bt}}{1+C\,\mathrm{e}^{-Dt}} \tag{1}$$

$$\text{the second step}: M\,\mathrm{e}^{-k_1(t-t_1)} - N\,\mathrm{e}^{-k_2(t-t_2)} \tag{2}$$

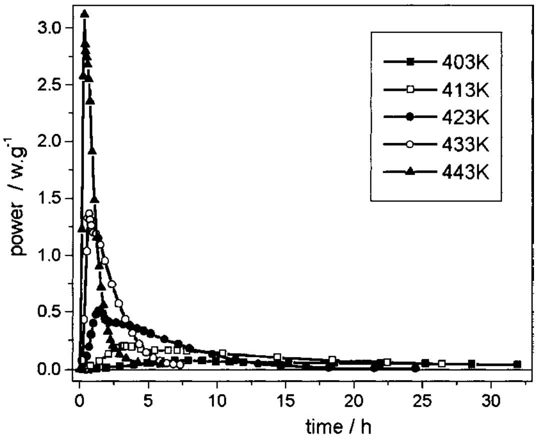

Fig. 2. Thermal power variations with time of n-$C_{36}H_{74}$ oxidized at different temperatures.

Table 1
The parameters of the first step ($\ln A = 56.83 - 2.104 \times 10^4/T$; $\ln C = 23.82 - 0.8157 \times 10^4/T$)

T (K)	A	B	C	D
403	128.47	0.00102	38.17	0.01378
413	326.16	0.00214	52.96	0.03282
423	1009.4	0.00710	77.28	0.07957
433	2955.0	0.01649	213.8	0.18662
443	15759	0.07586	186.2	0.37474

Table 2
The parameters of the second step ($\ln M = 61.98 - 2.338 \times 10^4/T$; $\ln N = 62.83 - 2.374 \times 10^4/T$)

T (K)	M	N	k_1	k_2	t_1 (min)	t_2 (min)
403	49.49	45.86	0.00033	0.00136	746.0	776.4
413	125.97	123.8	0.00106	0.00400	341.7	327.4
423	1855.1	1848.7	0.00486	0.00642	137.8	140.0
433	4105.6	4120.6	0.01267	0.01727	53.66	52.93
443	5854.8	5937.0	0.02713	0.06958	17.81	20.29

The results of matching are shown in Tables 1 and 2, and Figs. 3–7.

As the *W(t)* is proportional to the reaction rate, the two empirical equations can represent the rate equation. Then the parameter A, C, M, N can be seen as rate constant. With *Arrenius equation* the A's at different temperatures meet that $\ln A = \ln A_0 - E_a/RT$, where E_a represent activation energy. The same is done for the other three parameters C, M, and N. Linear regression

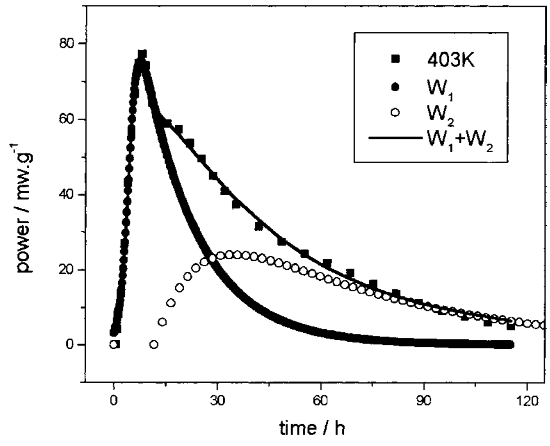

Fig. 3. Matching *W(t)* with a two-step model (403 K).

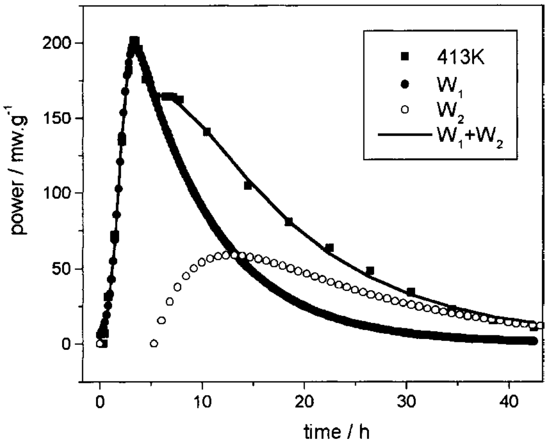

Fig. 4. Matching *W(t)* with a two-step model (413 K).

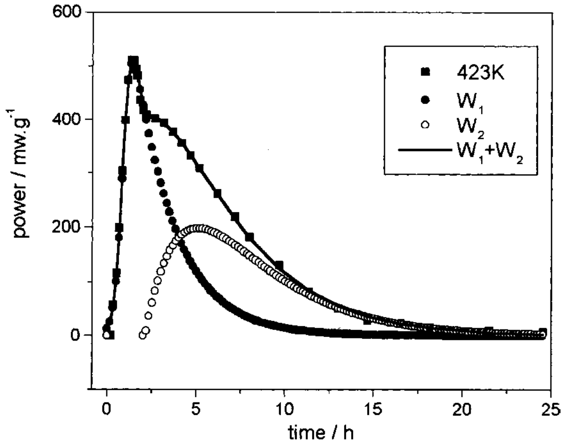

Fig. 5. Matching *W(t)* with a two-step model (423 K).

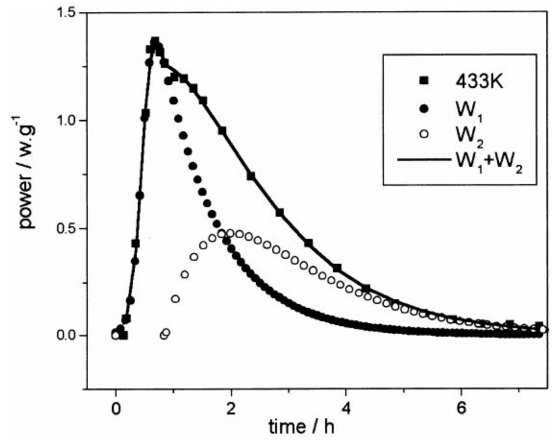

Fig. 6. Matching *W(t)* with a two-step model (433 K).

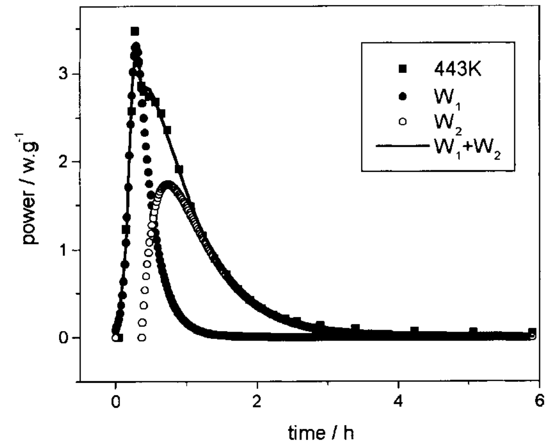

Fig. 7. Matching *W(t)* with a two-step model (443 K).

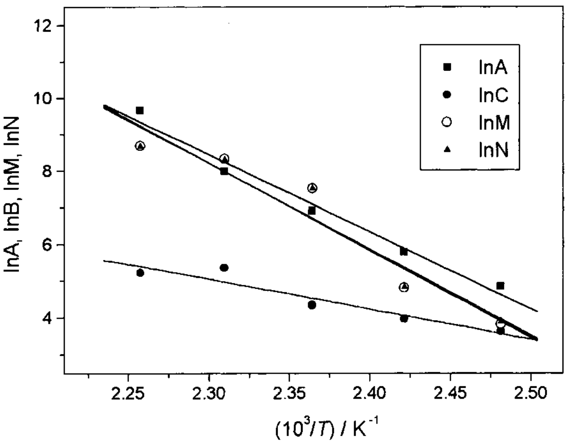

Fig. 8. Linear regression of ln *A*, ln *C*, ln *M*, ln *N* with 1/*T*.

of ln *A*, ln *C*, ln *M*, ln *N* with 1/*T* gives result which are shown in Fig. 8 and Table 3.

Integrating the thermokinetics over time gives the reaction heats of n-$C_{36}H_{74}$ oxidization at different temperatures as shown by Table 4 and Fig. 9. The average value is 5971.6 ± 139.6 kJ mol^{-1}. It is 4951.5 kJ mol^{-1} while the temperature is extrapolated to 298 K. Table 4 gives also the results of reaction heat of each step at different temperatures according to the model proposed by us. The reaction heats at different temperatures are almost same. The average values are 3046.3 ± 487.0 kJ mol^{-1} and 3058.4 ± 411.7 kJ mol^{-1}, respectively.

Table 3
The results of linear regression

	ln *A*	ln *C*	ln *M*	ln *N*
E_a ($\times 10^5$)	1.749	0.8157	1.944	1.974
ln A_0	56.83	23.82	61.98	62.83
R[a]	−0.991	−0.95	−0.96	−0.96

[a] Regression coefficient.

Table 4
The reaction heats of the overall reaction and each step at different temperatures

T (K)	ΔH (kJ mol^{-1})	ΔH_1 (kJ mol^{-1})	ΔH_2 (kJ mol^{-1})
403	5799.5	2936.4	3444.0
413	5955.8	3576.8	2696.2
423	5894.2	2959.4	2923.8
433	6046.5	3423.5	2681.8
443	6162.2	2335.5	3546.4

As mentioned above, after reconstruction of the calorimetric results, the thermogenesis *W(t)* during n-$C_{36}H_{74}$ oxidized at different temperatures were obtained here. The thermodynamic and kinetic parameters, such as the reaction heat and activation energy, were also obtained in this work by matching the thermokinetic results with a model proposed by us. With the technique in this work it is able to study a system, such as that of n-$C_{36}H_{74}$ oxidation, on equilibrium and at the same time on nonequilibrium thermodynamics if the experimental results under different conditions have been accumulated more enough.

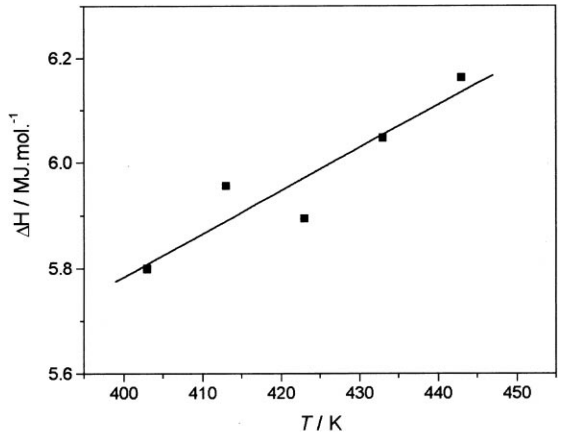

Fig. 9. The reaction heat change with temperature.

4. Conclusions

1. The thermokinetic results of n-$C_{36}H_{74}$ oxidation obtained from reconstruction of the calorimetric measurements can be matched very well with a two step mechanism proposed by us.
2. The calorimetric measurements can be used to study the apparent mechanism of a chemical reaction as to match the thermokinetic results of n-$C_{36}H_{74}$ oxidation with a two step mechanism proposed in this paper.
3. The reaction heats of n-$C_{36}H_{74}$ oxidation at 403, 413, 423, 433 and 443 K were obtained. The reaction heats of each step reaction of n-$C_{36}H_{74}$ oxidation according to the model proposed by us were obtained by matching thermokinetic results, respectively.
4. The kinetic parameter, such as the energy of activation and the frequency factor of each reaction, concerned were also obtained.
5. With the technique in this work it is able to study a system, such as that of n-$C_{36}H_{74}$ oxidation, on equilibrium and at the same time on nonequilibrium thermodynamics if the experimental results under different conditions have been accumulated more enough.

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