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TIME-PARAMETER METHOD FOR STUDYING KINETICS OF CONSECUTIVE FIRST-ORDER REACTIONS IN CALORIMETER

Y. Chen[1,2], *J. Li*[1], *Y. T. Li*[1] *and X.-C. Zeng*[1]*

[1]Department of Chemistry, Sichuan University, Chengdu 610064, P. R. China
[2]Department of Applied Oil Engineering, Logistical Engineering University, Chongqing 400016, P. R. China

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Abstract

In order to enrich the thermokinetic research methods and enlarge the applicable range of the thermokinetic time-parameter method, the integral and differential thermokinetic equations of consecutive first-order reaction have been deduced, and the mathematical models of the time-parameter method for consecutive first-order reactions have been proposed in this paper. The rate constants of two steps can be calculated from the same thermoanalytical curve measured in a batch conduction calorimeter simultaneously with this method. The thermokinetics of saponifications of diester in aqueous ethanol solvent has been studied. The experimental results indicate that the time-parameter method for the consecutive first-order reaction is correct.

Keywords: calorimetry, consecutive first-order reactions, thermokinetics, time-parameter method

Introduction

The study of chemical kinetics by calorimetry is a very interesting and significant technique. The thermoanalytical curve of a chemical reaction measured by a calorimeter implies the kinetic and thermodynamic information that the reaction has. It is an important purpose of thermokinetics to establish a research method for obtaining such valuable information. On the basis of the fundamental theory of thermokinetics, several thermokinetic research methods [1–5] have been proposed to determine rate constants of chemical reactions in a conduction calorimeter. In our previous article [6, 7], based on the fundamental theory of thermokinetics and regarding time as a known parameter, the time-parameter methods for simple order reactions and reversible reactions taking place in a batch conduction calorimeter had been suggested. The thermokinetics for several kinds of simple order reactions and reversible reactions had been studied successfully with these methods.

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* Author to whom all correspondence should be addressed.

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An irreversible consecutive reaction is an ideal model for describing the kinetic behavior of the reaction intermediate in physical organic chemistry and biochemistry. So, it is very significant to develop a thermokinetic research method for this kind of reaction. Owing to the complexity of the kinetic equations of consecutive reactions, it is very difficult to determine the two rate constants simultaneously by analyzing the thermoanalytical curve. For the consecutive first-order reactions taking place in a batch conduction calorimeter, the thermokinetic reduced parameter method had been proposed in literature [8]. However, the mathematical models of this method are much more complex and the thermoanalytical curve measured with a conduction calorimeter must be reconstructed into the adiabatic curve, which is inconvenient for users. In order to enrich the thermokinetic research method and enlarge the applicable range of the time-parameter method, the mathematical models of the time-parameter method for consecutive first-order reactions have been established in this paper. Needing only the characteristic time parameter t_m, $2t_m$ and $3t_m$ and corresponding thermoanalytical data from the same curve, the rate constants of two steps can be simultaneously determined. Additionally, a novel method to determine the values of $d\Delta/dt$ by using the time parameter t_m, the peak height Δ_m at time t_m and the total area of the curve, rather than by the use of slop from thermoanalytical curve at time t with differential method, is proposed. The thermokinetics of saponifications of two diesters in aqueous ethanol solvent have been studied and the validation of the theory and method of the time-parameter method for consecutive first-order reactions is verified by the experimental results.

Theory and method

Thermokinetic equation of consecutive first-order reactions

For an irreversible consecutive first-order reaction, if reactant S is transformed to product P via intermediate I, the behavior can be written as follows:

$$S \xrightarrow{k_1 \text{ and } \Delta H_1} I \xrightarrow{k_2 \text{ and } \Delta H_2} P$$

where k_1, k_2 and ΔH_1, ΔH_2 are the rate constants and molar enthalpies of the two steps, respectively.

According to the principle of chemical reaction kinetics, it can be proved that

$$\chi_1 = S_0 (1 - e^{-k_1 t}) \tag{1}$$

$$\chi_2 = S_0 \left(1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right) \tag{2}$$

$$\chi = S_0 \left(2 - \frac{2k_2 - k_1}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right) \tag{3}$$

where S_0 is the initial concentration of reactant S, χ_1 and χ_2 are the reaction extents of two steps at time t, χ is the total reaction extent.

When a consecutive first-order reaction takes place in a batch conduction calorimeter, the dynamic properties of calorimetric system are described by Tian's equation [9], and then we have

$$\Phi = K\Delta + \Lambda\frac{\mathrm{d}\Delta}{\mathrm{d}t} \tag{4}$$

where Δ is the peak height of thermoanalytical curve at time t, K and Λ are apparatus constants of the calorimeter.

Integrating Eq. (4) with respect to time t, we get

$$Q = Ka + \Lambda\Delta \tag{5}$$

$$Q_\infty = KA \tag{6}$$

Rearrangement of Eqs (4)–(6) leads to

$$\frac{Q_\infty - Q}{Q_\infty} = \frac{a^*}{A} - \frac{\Delta}{kA} \tag{7}$$

$$\frac{\Phi}{Q_\infty} = \frac{\Delta}{A} + \frac{\frac{\mathrm{d}\Delta}{\mathrm{d}t}}{kA} \tag{8}$$

where Q and Q_∞ are the heat evolved before time t and the total heat evolved by the reaction studied respectively, a and a^* are the peak areas before and after time t respectively, and $A=a+a^*$, which is the total area under the curve, $k(=K/\Lambda)$ is called the cooling constant of thermokinetic system.

In the previous article [10], we have proved that the thermokinetic transformation equation for consecutive first-order reaction can be described as

$$\frac{Q}{Q_\infty} = \frac{\chi_1 + \beta\chi_2}{S_0(1+\beta)} \tag{9}$$

$$\frac{\Phi}{Q_\infty} = \frac{\frac{\mathrm{d}\chi_1}{\mathrm{d}t} + \beta\frac{\mathrm{d}\chi_2}{\mathrm{d}t}}{S_0(1+\beta)} \tag{10}$$

where β is the ratio of molar enthalpy of the second step to the first step, i.e. $\beta = \Delta H_2/\Delta H_1$.

So, from Eqs (1)–(3) and Eqs (7)–(10), it turns to

$$\frac{a^*}{A} - \frac{\Delta}{kA} = (1-G)\mathrm{e}^{-k_1 t} + G\mathrm{e}^{-k_2 t} \tag{11}$$

$$\frac{\Delta}{A} + \frac{\frac{\mathrm{d}\Delta}{\mathrm{d}t}}{kA} = (1-G)k_1\mathrm{e}^{-k_1 t} + Gk_2\mathrm{e}^{-k_2 t} \tag{12}$$

where G is a constant. Equations (11) and (12) are the integral and differential thermokinetic equations of irreversible consecutive first-order reactions.

Mathematical models of time-parameter method for consecutive first-order reactions

Calculation of the rate constants k_1 and k_2

Defining $r=\phi/Q_\infty$, and from Eqs (8) and (12), we get

$$Ge^{-k_2t}=\frac{r-(1-G)k_1e^{-k_1t}}{k_2} \tag{13}$$

Inserting Eq. (13) into Eq. (11) and defining $R=(Q_\infty-Q)/Q_\infty$, it follows that

$$Rk_2-r=(1-G)\left(1+\frac{k_1}{k_2}\right)e^{-k_1t} \tag{14}$$

t_m is the time corresponding to the maximum peak height Δ_m of the curve, which is called as characteristic time parameter. When $t=t_m$, $t=2t_m$ and $t=3t_m$, we can get R_m, R_{2m}, R_{3m} and r_m, r_{2m}, r_{3m} using the corresponding thermoanalytical data from the curve, and therefore according to Eq. (14), we have

$$R_mk_2-r_m=(1-G)\left(1+\frac{k_1}{k_2}\right)e^{-k_1t_m} \tag{15}$$

$$R_{2m}k_2-r_{2m}=(1-G)\left(1+\frac{k_1}{k_2}\right)e^{-2k_1t_m} \tag{16}$$

$$R_{3m}k_2-r_{3m}=(1-G)\left(1+\frac{k_1}{k_2}\right)e^{-3k_1t_m} \tag{17}$$

So, from Eqs (15)–(17), it can be proved that

$$(R_{2m}k_2-r_{2m})^2=(R_mk_2-r_m)(R_{3m}k_2-r_{3m}) \tag{18}$$

$$k_1=\frac{1}{t_m}\ln\frac{k_2R_m-r_m}{k_2R_{2m}-r_{2m}}=\frac{1}{t_m}\ln\frac{k_2R_{2m}-r_{2m}}{k_2R_{3m}-r_{3m}} \tag{19}$$

Equations (18) and (19) are the mathematical models of the time-parameter method for consecutive first-order reactions. When the time parameter t_m, $2t_m$, $3t_m$ and corresponding thermoanalytical data are determined, the rate constant k_2 which is only unknown parameter in Eq. (18) can be easily calculated, and then the rate constant k_1 is determined with Eq. (19).

Determination of R and r

According to the definitions of R and r, we can get that

$$R=\frac{a^*}{A}-\frac{\Delta}{kA} \tag{20}$$

$$r=\frac{\Delta}{A}+\frac{\frac{\mathrm{d}\Delta}{\mathrm{d}t}}{kA} \tag{21}$$

In the previous article [11], we have established the characteristic equation for the thermoanalytical curve of the chemical reaction

$$\Delta=\Delta_{\mathrm{m}}\frac{t}{t_{\mathrm{m}}}\mathrm{e}^{1-(\mathrm{t}/\mathrm{t_m})} \tag{22}$$

Differentiating Eq. (22) with respect to time t, we obtain

$$\frac{\mathrm{d}\Delta}{\mathrm{d}t}=\frac{\Delta_{\mathrm{m}}}{t_{\mathrm{m}}}\left(1-\frac{t}{t_{\mathrm{m}}}\right)\mathrm{e}^{1-(\mathrm{t}/\mathrm{t_m})} \tag{23}$$

when $t=t_{\mathrm{m}}$, $t=2t_{\mathrm{m}}$ and $t=3t_{\mathrm{m}}$, from Eqs (20)–(23), it can be proved that

$$R_{\mathrm{m}}=\frac{a^*_{\mathrm{m}}}{A}-\frac{\Delta_{\mathrm{m}}}{kA},\ r_{\mathrm{m}}=\frac{\Delta_{\mathrm{m}}}{A} \tag{24}$$

$$R_{2\mathrm{m}}=\frac{a^*_{2\mathrm{m}}}{A}-\frac{2\Delta_{\mathrm{m}}}{\mathrm{e}kA},\ r_{2\mathrm{m}}=\frac{\Delta_{\mathrm{m}}}{\mathrm{e}A}\left(2-\frac{1}{kt_{\mathrm{m}}}\right) \tag{25}$$

$$R_{3\mathrm{m}}=\frac{a^*_{3\mathrm{m}}}{A}-\frac{3\Delta_{\mathrm{m}}}{\mathrm{e}^2kA},\ r_{3\mathrm{m}}=\frac{\Delta_{\mathrm{m}}}{\mathrm{e}^2A}\left(3-\frac{2}{kt_{\mathrm{m}}}\right) \tag{26}$$

where e is the base of natural logarithm. Equations (24)–(26) are the formulas to determine values of R and r at different time using the thermoanalytical data.

Experimental

Reaction system

In order to test the validity of the time-parameter method for consecutive first-order reactions, the thermokinetics of the reaction systems shown below have been studied:

- Saponification of diethyl phthalate in 60% (*v/v*) aqueous ethanol solvent at 35°C.
- Saponification of diethyl adipate in 80% (mass/mass) aqueous ethanol solvent at 20°C.

The saponification of the diesters in aqueous ethanol solvent was a consecutive second-order reaction. If C_0(KOH)>C_0(ester), the saponification may be treated as a consecutive first-order reaction, and then $k_1=k_{2.1}C_0$(KOH), $k_2=k_{2.2}C_0$(KOH), where $k_{2.1}$ and $k_{2.2}$ are the second-order rate constants of the first and second steps respectively.

Reactants

Chemical pure diethyl phthalate and diethyl adipate were further purified by distillation under reduced pressure. The other reactants were analytically pure. The solutions of reactants were prepared in deionized water by mass. The concentration of potassium hydroxide was standardized with potassium hydrogenphthalate.

Apparatus

All the thermoanalytical curves of the above-mentioned reactions were measured with a twin conduction calorimeter, which has been described in detail in the previous article [12]. The data for thermoanalytical curves were sampled, recorded, and analyzed by a computer.

Results and discussion

The cooling constants of reaction systems studied were determined by using electrical calibration. After the thermoanalytical curve has been measured in a batch conduction calorimeter, the values of R_m, R_{2m}, R_{3m} and r_m, r_{2m}, r_{3m} can be obtained from the thermoanalytical data at time t_m, $2t_m$ and $3t_m$ according to Eqs (24)–(26), respectively. Thus, the rate constants of two steps can be calculated via the mathematical models of the time-parameter method for consecutive first-order reactions. The experimental results and examples of thermoanalytical curve analysis are given in Tables 1–4.

From these tables, it can be seen that the rate constants calculated with this novel method are in agreement with those in literature. The results show that calculations are reproducible and self-consistent. Therefore, the time-parameter method for consecutive first-order reactions is believed to be correct.

Table 1 Experimental results of saponification of diethyl phthalate in 60%(v/v) aqueous ethanol solvent at 35°C

No.	C_0(KOH)/ mol l^{-1}	C_0(ester)/ mol l^{-1}	10^3k_1/s^{-1}	10^4k_2/s^{-1}	$10^3k_{2,1}$/ l mol^{-1} s^{-1}	$10^4k_{2,2}$/ l mol^{-1} s^{-1}
1	0.4185	0.01925	1.95	3.64	4.66	8.70
2	0.4586	0.02116	2.21	4.12	4.82	8.98
3	0.4586	0.02308	2.18	3.95	4.75	8.61
4	0.5645	0.02570	2.67	4.97	4.73	8.80
5	0.5645	0.02710	2.77	4.99	4.91	8.84
				average	4.77	8.79
				[13]	4.62	8.72

The thermokinetic equations of consecutive first-order reactions (Eqs (11) and (12)) are the non-linear function with respect to time *t*. It is much more difficult to determine the two rate constants directly. The mathematical models of the reduced parameter method [8] for consecutive first-order reaction taking place in a batch conduction calorimeter were more complex and it took a great deal of work to analyze the thermoanalytical curve with this method. Meanwhile, with this method, we must determine which step of the consecutive reaction was faster by means of other physical and chemical technique before kinetic evaluation, which is not convenient for users. The same as the time-parameter methods for simple order reactions and reversible reactions, the mathematical models to calculate the kinetic parameter of our novel method are concise and the kinetic analyzing procedure needs a little computing effort and work. Taking only the thermoanalytical data of the characteristic time parameters t_m $2t_m$ and $3t_m$ from the one thermoanalytical curve, the kinetic parameters can be simultaneously obtained.

Table 2 The thermoanalytical data of saponification of diethyl phthalate

No.	t_m/s	R_m	R_{2m}	R_{3m}	$10^4 r_m$/s^{-1}	$10^4 r_{2m}$/s^{-1}	$10^4 r_{3m}$/s^{-1}
1	642	0.640	0.418	0.216	4.95	2.27	1.00
2	630	0.633	0.409	0.208	5.08	2.30	1.01
3	625	0.627	0.421	0.215	5.24	2.37	1.03
4	610	0.610	0.390	0.189	5.39	2.40	1.03
5	608	0.599	0.397	0.193	5.52	2.45	1.05

Table 3 Experimental results of saponification of diethyl adipate in 80%(mass/mass) aqueous ethanol solvent at 20°C

No.	C_0(KOH)/ mol l^{-1}	C_0(ester)/ mol l^{-1}	$10^3 k_1$/s^{-1}	$10^4 k_2$/s^{-1}	$10^3 k_{2,1}$/ l mol^{-1} s^{-1}	$10^4 k_{2,2}$/ l mol^{-1} s^{-1}
1	0.3695	0.01746	2.08	1.55	5.63	4.19
2	0.4128	0.02254	2.16	1.54	5.23	3.73
3	0.4128	0.02650	2.20	1.49	5.33	3.61
4	0.4650	0.03014	2.61	1.97	5.61	4.24
5	0.4650	0.03562	2.59	1.91	5.57	4.11
				average	5.47	3.98
				[14]	5.62	3.62

Table 4 The thermoanalytical data of saponification of diethyl adipate

No.	t_m/s	R_m	R_{2m}	R_{3m}	$10^4 r_m$/s^{-1}	$10^4 r_{2m}$/s^{-1}	$10^5 r_{3m}$/s^{-1}
1	533	0.558	0.387	0.204	6.10	2.33	8.88
2	512	0.539	0.352	0.179	6.15	2.26	8.30
3	520	0.545	0.369	0.189	6.12	2.25	8.37
4	498	0.525	0.399	0.200	5.99	2.14	7.62
5	490	0.530	0.371	0.180	6.06	2.13	7.44

The values of $d\Delta/dt$ should be determined in advance in calculation of r, which is generally obtained by the use of the slope of the thermoanalytical curve $\Delta(t)$ at time t with the differential method [15]. However, such values may not possess as high enough accuracy as required and would lead to an experimental error in kinetic evaluation. In this paper, a novel method to calculate the values of $d\Delta/dt$ has been proposed. With this method, the values of r at t_m $2t_m$ and $3t_m$ can be directly calculated using the thermoanalytical data with a higher accuracy degree. The experimental results indicate that this method to determine the value of r at time t is reasonable.

The characteristic time t_m is an important parameter in our novel method. The precision in evaluating kinetic parameters of our method depends on the accurate determination of t_m. If the t_m were determined inaccurately from the curve, the experimental error would increase. In general, t_m is obtained from the measured thermoanalytical curve directly. So, the distortion degree of the measured curve owing to thermal inertia will lead to an experimental error in kinetic evaluation. For a slower reaction, the thermal delay will decrease, and the influence of distortion can be neglected. But for a faster consecutive reaction, the distortion degree of the measured curve will obviously increase. In this case, the measured curve must be modified by the method proposed in the previous paper [16] before kinetic evaluation.

As stated above, the time-parameter method for consecutive first-order reactions further enriches and perfects the kinetic research method. The theoretical basis of this method is the thermokinetic equation of the consecutive first-order reaction. It is universal in the thermokinetic investigations of consecutive first-order reactions in the batch conduction calorimeter at isothermal condition. It can be extensively applied to studies on chemical kinetics of the saponification of diester, the consecutive quaternization and the enzyme-catalyzed reaction, and the other reaction, the kinetic behaviour of which can be described as a consecutive first-order reaction.

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