STUDIES ON THERMOKINETICS OF CONSECUTIVE FIRST-ORDER REACTIONS

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Abstract

The transformation equation for the thermokinetics of consecutive first-order reactions has been deduced, and a thermokinetic research method of irreversible consecutive first-order reactions, which can be used to determine the rate constants of two steps simultaneously, is proposed. The method was validated and its theoretical basis was verified by the experimental results.

Introduction

The study of chemical kinetics by calorimetry is a very interesting and significant technique. A number of simple reaction systems have been investigated [1–6] and the feasibility of the method has been tested. A thermokinetic method for studies on composite reactions, which usually have two or more kinetic constants, is still a debated subject. Consecutive reactions are one kind of significant composite reactions. Some studies [7] have been made on the thermokinetics of consecutive reactions, but certain problems remain to be solved, owing to the complexity of the kinetic equations and the difficulty of determination of two rate constants simultaneously.

An irreversible consecutive first-order reaction is an ideal model for describing the kinetic behaviour of the reaction intermediate in physical organic chemistry and biochemistry. A thermokinetic research method for this kind of consecutive reaction, with which the rate constants of two steps can be determined simultaneously, is proposed in this paper. The thermokinetics of saponification of two diesters in aqueous solution have been studied with a conduction calorimeter, and the validation of this method in this paper has been verified by the experimental results.

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Theory and method

Relationship between the rate of generation of heat in a chemical reaction and the rates of formation of its constituents

Let us consider a homogeneous closed system within a volume V in which a chemical reaction is taking place. The chemical reaction includes m elementary reaction steps and can be described by a set of stoichiometric equations involving n constituents (A_1, A_2, ..., A_n). These equations will be written in the form [8]:

$$0 = \sum_{j=1}^{n} v_{ij}A_j \quad (i=1, 2, ..., m)$$ (1)

where v_{ij} is the stoichiometric number of constituent A_j in elementary reaction i, which is positive for a product and negative for a reactant.

At constant temperature and pressure, the rate of generation of heat in the chemical reaction, Ω, can be written as

$$\Omega = V \sum_{i=1}^{m} r_i \Delta H_i$$ (2)

where $r_i = (dn_i/dt)/(v_iV)$ is the rate of elementary reaction i, and ΔH_i is its molar enthalpy.

ΔH_i can be expressed as a function of the molar formation enthalpies, h_j, of the constituents A_j by the relationship

$$\Delta H_i = \sum_{j=1}^{n} v_{ij}h_j$$ (3)

By combining Eqs (2) and (3), we obtain

$$\Omega = V \sum_{i=1}^{m} r_i \sum_{j=1}^{n} v_{ij}h_j$$ (4)

or

$$\Omega = V \sum_{j=1}^{n} \left(\sum_{i=1}^{m} v_{ij}r_i \right) h_j$$ (5)

we define

$$R_j = \sum_{i=1}^{m} v_{ij} r_i \tag{6}$$

where R_j is called the total rate (algebraic rate) of production of constituent A_j. Consequently, Eq. (5) becomes

$$\Omega = V \sum_{j=1}^{n} R_j h_j \tag{7}$$

From Eq. (7), it results that the rate of generation of heat Ω in a reaction is, in fact, the sum of the products of the total rates of formation of the constituents and their molar formation enthalpies.

According to the quasi-stationary-state approximation, for very reactive and short-lived intermediates, the overall production rates R_j are equal to zero, and do not appear in the calculation of Ω.

Transformation equation for thermokinetics of irreversible consecutive first-order reactions

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

$$S \xrightarrow[\Delta H_1]{r_1} I \xrightarrow[\Delta H_2]{r_2} P \tag{8}$$

where r_1, r_2 and ΔH_1, ΔH_2 are the rates and molar enthalpies of the two steps, respectively.

The rate of generation of heat Ω in this reaction is related not only to reactant S and product P, but also to intermediate I. According to Eq. (7), we have

$$\Omega = V(R_S h_S + R_I h_I + R_P h_P) \tag{9}$$

In this reaction system:

$$R_S = -r_1; \quad R_I = r_1 - r_2; \quad \text{and} \quad R_P = r_2$$

It follows that

$$\Omega = -r_1 h_S V + (r_1 - r_2) h_I V + r_2 h_P V \tag{10}$$

or

$$\Omega = r_1(h_I - h_S)V + r_2(h_P - h_I)V \tag{11}$$

Since

$$\Delta H_1 = h_I - h_S; \quad \Delta H_2 = h_P - h_I$$

Equation (11) becomes

$$\Omega = r_1 \Delta H_1 V + r_2 \Delta H_2 V \tag{12}$$

If we define the derivative of the extent of reaction x, dx/dt, as the rate of reaction, i.e. $r = dx/dt$, we have

$$\Omega = \frac{dx_1}{dt} \Delta H_1 V + \frac{dx_2}{dt} \Delta H_2 V \tag{13}$$

where x_1 and x_2 are the extents of reaction of the two steps. On integration, we obtain

$$Q = (x_1 \Delta H_1 + x_2 \Delta H_2) V \tag{14}$$

and

$$Q_\infty = (x_{1,\infty} \Delta H_1 + x_{2,\infty} \Delta H_2) V \tag{15}$$

For an irreversible consecutive first-order reaction, it is clear that

$$x_{1,\infty} = x_{2,\infty}$$

Then, from Eqs (13), (14) and (15), it can be proved that

$$\frac{\Omega}{Q_\infty} = \frac{\dfrac{dx_1}{dt} + \beta \dfrac{dx_2}{dt}}{(1 + \beta) x_{1,\infty}} \tag{16}$$

and

$$\frac{Q}{Q_\infty} = \frac{x_1 + \beta x_2}{(1 + \beta) x_{1,\infty}} \tag{17}$$

where

$$\beta = \frac{\Delta H_2}{\Delta H_1}$$

Equations (16) and (17) are the transformation equations for the thermokinetics of consecutive first-order reactions.

Mathematical model for thermokinetics of irreversible consecutive first-order reactions

Thermokinetic reduced extent equation

Let the initial concentration of reactant S be S_o, let the initial concentrations of intermediate I and product P be equal to zero, let the concentrations of reactant, intermediate and product at time t be S, I and P, respectively, and let the rate constants of the two steps be k_1 and k'_1, respectively. We then define

$$\rho = \frac{k'_1}{k_1} \quad \text{and} \quad \theta = k_1 t$$

According to the kinetic equations of consecutive first-order reactions [9], it can be proved that

$$S = S_o \exp(-\theta) \tag{18}$$

$$I = \frac{S_o}{\rho - 1} [\exp(-\theta) - \exp(-\rho\theta)] \tag{19}$$

$$P = S_o \left[1 - \frac{\rho}{\rho - 1} \exp(-\theta) + \frac{1}{\rho - 1}\exp(-\rho\theta) \right] \tag{20}$$

We then obtain that

$$x_1 = S_o - S = S_o[1 - \exp(-\theta)] \tag{21}$$

$$x_2 = P = S_o \left[1 - \frac{\rho}{1 - \rho} \exp(-\theta) + \frac{1}{\rho - 1} \exp(-\rho\theta) \right] \tag{22}$$

and

$$x_{1, \infty} = x_{2, \infty} = S_o \tag{23}$$

Inserting Eqs (21–23) into Eq. (17) and defining

$$\Phi = \frac{Q}{Q_\infty}; \quad \alpha = 1 - \Phi \quad \text{and} \quad G = \frac{\beta}{(1 + \beta)(1 - \rho)}$$

we can prove that

$$\alpha = (1 - G) \exp(-\theta) + G \exp(-\rho\theta) \tag{24}$$

where Φ and α are called the thermokinetic reduced extent and the reduced remains, respectively.

Equations (24) is known as the thermokinetic reduced extent equation of an irreversible consecutive first-order reaction.

Calculation of rate constants

If the reduced remains α_i of a reaction under investigation at any time t_i can be determined, four data (α_1, α_2, α_3, α_4) can be obtained for a fixed time interval, i.e. $\Delta t = t_4 - t_3 = t_3 - t_2 = t_2 - t_1$.

According to Eq. (24), it can be proved that, when $k_1 > k'_1$:

$$k_1 = \frac{1}{\Delta t} \ln (b + \sqrt{b^2 - c}) \tag{25}$$

$$k'_1 = \frac{1}{\Delta t} \ln (b - \sqrt{b^2 - c}) \tag{26}$$

and when $k_1 < k'_1$:

$$k_1 = \frac{1}{\Delta t} \ln (b - \sqrt{b^2 - c}) \tag{27}$$

$$k'_1 = \frac{1}{\Delta t} \ln (b + \sqrt{b^2 - c}) \tag{28}$$

where

$$b = \frac{\alpha_1\alpha_4 - \alpha_2\alpha_3}{2(\alpha_2\alpha_4 - \alpha_3^2)}; \quad c = \frac{\alpha_1\alpha_3 - \alpha_2^2}{\alpha_2\alpha_4 - \alpha_3^2}$$

Which step is faster can be judged according to the characteristics of the investigated reaction or by means of other physical and chemical techniques.

Experimental

Reagents

The saponifications of diethyl succinate and diethyl adipate were studied to test the validation of the mathematical model in this paper. Chemically pure diethyl succinate and adipate were purified by distillation under reduced pressure. The mixed solvent was prepared from analytically pure ethanol and deionized water. The potassium hydroxide was of guaranteed grade and its concentration in solution was standardized with potassium hydrogenphthalate.
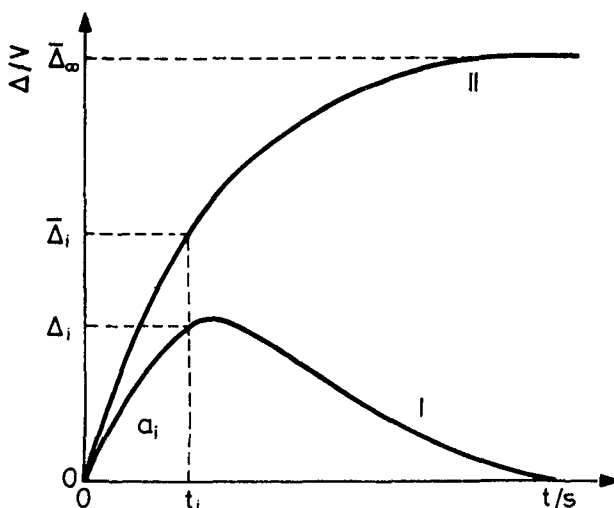
Fig. 1 Thermoanalytical curve reconstruction for an irreversible consecutive first-order reaction; curve I: measured with a conduction calorimeter; curve II: ideal adiabatic curve reconstructed

Apparatus

A batch conduction calorimeter, whose construction details have been reported previously [10], was applied to measure the thermoanalytical curves of these reactions. The effects of mixing, dilution, stirring and evaporation in the working cell should be compensated for by the same effects produced in the reference cell. Thermoanalytical curves were recorded as shown in Fig. 1.

Table 1 Experimental conditions and results of saponification of diethyl succinate (solvent: 50 mol% EtOH–H$_2$O; temperature: 15.0°C)

No.	C$_0$(KOH) /	C$_0$(ester) /	10^3·k_1 /	10^3·k'_1 /	10^2·k_2 /	10^3·k'_2 /
	mol·l^{-1}		s^{-1}		l·mol^{-1}·s^{-1}	
1	0.4025	0.01685	5.63	0.805	1.40	2.00
2	0.4439	0.01685	6.04	1.03	1.36	2.32
3	0.4439	0.02184	7.73	0.817	1.74	1.84
4	0.4914	0.02184	8.84	1.14	1.80	2.33
5	0.5563	0.02608	8.73	1.21	1.57	2.19
				Average:	1.57	2.13
				Ref. [13]:	1.33	2.27

Table 2 Example of data analysis (No. 1 in Table 1)

α_1	α_2	α_3	α_4	Δt / s	$10^3 \cdot k_1$	$10^4 \cdot k_1$	$10^2 \cdot k_2$	$10^3 \cdot k_2$
					s^{-1}	s^{-1}	$l \cdot mol^{-1} \cdot s^{-1}$	
0.7354	0.5037	0.3811	0.2982	300	4.95	7.73	1.23	1.92
0.6419	0.4587	0.3511	0.2730	300	5.96	8.25	1.48	2.05
0.7354	0.4587	0.3233	0.2328	400	5.43	8.09	1.35	2.01
0.6419	0.4191	0.2982	0.2142	400	6.48	8.25	1.61	2.05
0.7354	0.4191	0.2730	0.1822	500	4.43	8.01	1.10	1.99
0.6419	0.3813	0.2537	0.1700	500	6.48	8.01	1.61	1.99
0.7354	0.3813	0.2328	0.1430	600	6.44	8.09	1.60	2.02
0.6419	0.3511	0.2142	0.1321	600	4.79	8.05	1.19	2.00
				Average:	5.63	8.05	1.40	2.00

Results and discussion

If $C_o(KOH) > C_o(ester)$, the saponifications of the diesters may be treated as irreversible consecutive first-order reactions [12–14], and $S_o = C_o(diester)$, $k_1 = k_2 \cdot C_o(KOH)$ and $k'_1 = k'_2 \cdot C_o(KOH)$. According to the thermoanalytical curve reconstruction method proposed previously [11], a recorded thermoanalytical curve (curve I, Δ vs. t) can be reconstructed to an ideal adiabatic thermoanalytical curve (curve II, $\overline{\Delta}$ vs. t), as shown in Fig. 1, and the thermokinetic reduced extent Φ_i at any time t_i can be obtained:

$$\Phi_i = \frac{\overline{\Delta}_i}{\overline{\Delta}_\infty} = \frac{ka_i + \Delta_i}{kA}$$

where Δ_i is the peak height at time t in curve I, a_i is the peak area before time t, A is the total area under the thermoanalytical curve and k is the cooling constant.

For the saponification of diesters, according to their reaction mechanism, the first step is faster than the second step, which has been verified in many previous studies. Thus, the rate constants can be calculated via the mathematical model in this paper. Experimental results are listed in Tables 1–4.

Table 3 Experimental conditions and results of saponification of diethyl adipate (solvent:80%) by weight (EtOH–H$_2$O; temperature: 20.0°C)

No.	$C_o(KOH)$ /	$C_o(ester)$ /	$10^3 \cdot k_1$ /	$10^4 \cdot k'_1$ /	$10^3 \cdot k_2$ /	$10^4 \cdot k'_2$ /
	mol·l^{-1}		s^{-1}		l·mol^{-1}·s^{-1}	
1	0.9746	0.04720	4.93	4.16	5.06	4.27
2	0.9746	0.04720	5.01	4.36	5.14	4.47
3	0.8684	0.04198	4.64	4.45	5.34	5.13
4	0.9631	0.04512	5.28	4.43	5.49	4.60
5	0.9631	0.04512	5.15	4.76	5.35	4.92
				Average:	5.28	4.68
				Ref. [14]:	5.62	3.62

From these Tables, it can be seen that the rate constants calculated in this paper are in agreement with those reported in the literature [13, 14]. The mathematical model and its theoretical basis are therefore believed to be correct.

Conclusions

In this article, a transformation equation for the thermokinetics of consecutive first-order reactions has been derived according to the relationship between

Table 4 Example of data analysis (No. 1 in Table 3)

α_1	α_2	α_3	α_4	Δt / s	$10^3 \cdot k_1$	$10^4 \cdot k_1'$	$10^3 \cdot k_2$	$10^4 \cdot k_2'$
					s^{-1}		l·mol^{-1}·s^{-1}	
0.6725	0.5277	0.4518	0.4023	200	5.21	4.47	5.35	4.59
0.5870	0.4841	0.4250	0.3826	200	5.50	4.50	5.65	4.62
0.7885	0.5277	0.4250	0.3666	300	4.56	3.92	4.68	4.02
0.6725	0.4841	0.4023	0.3510	300	4.61	3.87	4.73	3.97
0.7885	0.4841	0.3826	0.3219	400	4.51	3.93	4.53	4.03
0.6725	0.4518	0.3666	0.3074	400	5.18	4.26	5.32	4.37
				Average:	4.93	4.16	5.06	4.27

the rate of generation of heat in a chemical reaction and the rates of formation of its constituents. In the same way, transformation equations for thermokinetics of other reactions can be derived. This kind of transformation equation, as a bridge linking thermochemistry and chemical kinetics, is the theoretical basis for thermokinetic studies of chemical reactions.

With the mathematical model suggested in this paper, the rate constants of two steps of an irreversible consecutive first-order reaction can be calculated simultaneously. Thus, it can be widely applied to studies on chemical kinetics in physical organic chemistry and biochemistry.

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Zusammenfassung — Die Transformationsgleichung für die Thermokinetik konsekutiver Reaktionen erster Ordnung wurde abgeleitet und es wurde eine thermokinetische Untersuchungsmethode für irreversible konsekutive Reaktionen erster Ordnung vorgeschlagen, bei der die Geschwindigkeitskonstante zweier Schritte simultan bestimmt werden kann. Die Methode wurde bestätigt und die theoretischen Grundlagen durch experimentelle Ergebnisse überprüft.