STUDIES OF THE THERMOKINETICS
OF SECOND-ORDER REACTIONS *

YU DENG, XIANCHENG ZENG and YUANQING CHANG

Department of Chemistry, Sichuan University, Chengdu (P.R. China)

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ABSTRACT

A dimensionless parameter method used for studies of the thermokinetics of second-order reactions, with which the rate constant of reaction can be calculated from the thermogram's data without using the apparatus constants of the calorimeter, is proposed in this paper. The saponification of ethyl benzoate in aqueous alcohol and the nucleophilic substitution of benzyl chloride in aqueous DMSO solution have been studied. The rate constants calculated with this method are in fair agreement with that given in the literature.

INTRODUCTION

To study the rate of heat production of chemical reactions with a calorimeter is the object of thermokinetics. A dimensionless parameter method used to calculate the rate constant of a first-order and a second-order reaction with equal initial concentrations ($A_0 = B_0$) has already been reported [1]. The details of this method used for a second-order reaction under the condition $A_0 > B_0$ will be further discussed in this paper.

THEORY AND METHOD

Kinetic equations of a second-order reaction

The kinetic equations of a second-order reaction are

$$\frac{dx}{dt} = k_2(A_0 - x)(B_0 - x) \tag{1}$$

and

$$\frac{1}{(A_0 - B_0)} \ln\left[\frac{B_0(A_0 - x)}{A_0(B_0 - x)} \right] = k_2 t \tag{2}$$

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where A_0 and B_0 are the initial concentrations of the reactants, x is the extent of reaction, t is the time and k_2 is the rate constant of this second-order reaction.

If $A_0 > B_0$, we define

$$r = \frac{A_0}{B_0} \tag{3}$$

$$K_2^* = k_2(A_0 - B_0)$$

and eqn. (2) then becomes

$$\frac{B_0 - x}{B_0} = \frac{r - 1}{r\, e^{K_2^* t} - 1} \tag{4}$$

As $t \to \infty$, $x = x_\infty = B_0$ so we obtain

$$\frac{x_\infty - x}{x_\infty} = \frac{r - 1}{r\, e^{K_2^* t} - 1} \tag{5}$$

Theoretical model of the conduction calorimeter

When a chemical reaction is taking place in a conduction calorimeter, the thermogram recorded is as shown in Fig. 1.

According to Calvet and Prat [2], the rate of heat production (Ω) could be calculated using Tian's equation

$$\Omega = K\Delta + \Lambda\dot{\Delta} \tag{6}$$

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

On integration of eqn. (6) with respect to time, we obtain

$$Q = Ka + \Lambda\Delta \tag{7}$$

$$Q_\infty = KA \tag{8}$$

and

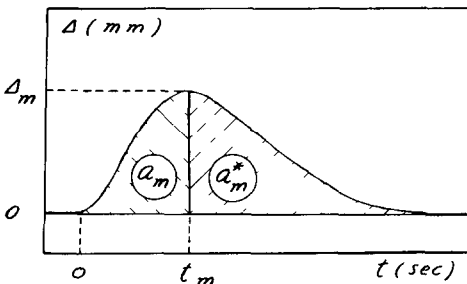$$\frac{Q_\infty - Q}{Q_\infty} = \frac{Ka^* - \Lambda\Delta}{KA} \tag{9}$$

Fig. 1. Thermogram of a chemical reaction.

where Q is the heat produced before time t, Q_∞ is the total heat effect, 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.

These quantities (Δ, a, a^*, and A) in the above equations are called the thermogram's data at time t. Especially, at $t = t_m$ and $\dot{\Delta} = 0$, the quantities Δ_m, a_m, a_m^*, A are called the characteristic data of a thermogram.

We now define $k = K/\Lambda$, which is called the cooling constant of the calorimeter. Multiplying both sides of Tian's equation, eqn. (6), by a factor e^{kt} and integrating between the limits 0 to t, we obtain

$$(K\Delta)\, e^{kt} = \int_0^t \Omega\, e^{kt}\, d(kt) \tag{10}$$

This is called the thermogram equation.

Thermokinetic equations of a second-order reaction

In the previous article [1], we proved that

$$\frac{Q_\infty - Q}{Q_\infty} = \frac{x_\infty - x}{x_\infty} \tag{11}$$

So, from eqns. (5) and (9), it is clear that

$$\frac{Ka^* - \Lambda\Delta}{KA} = \frac{r-1}{r\, e^{K_2^* t} - 1} \tag{12}$$

Differentiation with respect to time results in

$$\frac{K\Delta + \Lambda\dot{\Delta}}{KA} = \frac{r(r-1)K_2^*\, e^{K_2^* t}}{\left(r\, e^{K_2^* t} - 1\right)^2} \tag{13}$$

Equations (12) and (13) are called the thermokinetic equations of the second-order reaction. Inserting eqn. (13) into eqn. (10), we obtain

$$\Delta = e^{-kt} \int_0^t \frac{AK_2^* r(r-1)\, e^{K_2^* t}\, e^{kt}\, d(kt)}{\left(r\, e^{K_2^* t} - 1\right)^2} \tag{14}$$

This is the thermogram's equation of a second-order reaction.

Dimensionless parameter method

At $t = t_m$ and $\dot{\Delta} = 0$, the thermogram's data are $\Delta = \Delta_m$ and $a^* = a_m^*$. From eqns. (12) and (13), we obtain

$$\frac{Ka_m^* - \Lambda\Delta_m}{KA} = \frac{r-1}{r\, e^{K_2^* t_m} - 1} \tag{15}$$

and

$$\frac{\Delta_m}{A} = \frac{r(r-1)K_2^*\, e^{K_2^* t_m}}{\left(r\, e^{K_2^* t_m} - 1\right)^2} \tag{16}$$

We define

$$N = \frac{k}{K_2^*}$$

$$M = r\, e^{K_2^* t_m} \tag{17}$$

to be called the dimensionless parameter of a second-order reaction. Then, from eqns. (15) and (16), it can be shown that

$$K_2^* = \frac{\Delta_m}{a_m^*}\, f(N, M) \tag{18}$$

and

$$\frac{a_m^*}{A} = F(N, M, r) \tag{19}$$

in which

$$f(N, M) = 1 + \frac{1}{N} - \frac{1}{M} \tag{20}$$

and

$$F(N, M, r) = \frac{(r-1)M}{(M-1)^2}\left(1 + \frac{1}{N} - \frac{1}{M}\right) \tag{21}$$

From eqns. (14) and (16), it is clear that

$$\int_0^{t_m} \frac{r\, e^{K_2^* t}\, e^{kt}\, d(kt)}{\left(r\, e^{K_2^* t} - 1\right)^2} = \frac{r\, e^{K_2^* t_m}\, e^{kt_m}}{\left(r\, e^{K_2^* t_m} - 1\right)^2} \tag{22}$$

Writing

$$y = r\, e^{K_2^* t} \tag{23}$$

we obtain

$$y^N = r^N \cdot e^{kt}$$

and

$$N\, dy = r\, e^{K_2^* t}\, d(kt)$$

As $t = 0$, $y = r$; $t = t_m$, $y = M$, we obtain

$$\int_r^M \frac{y^N\, dy}{(y-1)^2} = \frac{M^{(N+1)}}{N(M-1)^2} \tag{24}$$

According to these formulas, if the ratio of the initial concentrations of reactants (r) is known, there is only one of these two dimensionless parameters to be independent. And so, the value of the function $f(N, M)$ can be calculated by computer from the thermogram's data without using the apparatus constants of the calorimeter.

TABLE 1

Correspondence of f(N, M) to F(N, M, r)
($r = A_0/B_0 = 7$)

N	M	F(N, M, 7)	f(N, M)	N	M	F(N, M, 7)	f(N, M)
4.400	10.447	0.795	1.132	9.500	8.938	0.845	0.993
4.820	10.220	0.800	1.110	10.250	8.830	0.850	0.984
5.150	10.064	0.805	1.095	11.000	8.735	0.855	0.976
5.600	9.879	0.810	1.077	11.750	8.652	0.860	0.969
6.000	9.734	0.815	1.064	12.750	8.553	0.865	0.962
6.500	9.575	0.820	1.049	13.750	8.467	0.870	0.955
7.000	9.436	0.825	1.037	15.000	8.370	0.875	0.948
7.500	9.314	0.830	1.026	16.250	8.293	0.880	0.941
8.100	9.184	0.835	1.015	17.500	8.222	0.885	0.936
8.750	9.061	0.840	1.004	19.000	8.148	0.890	0.930

For example, given $r = A_0/B_0 = 7$, the correspondence of f(N,M) to F(N, M, r) is shown in Table 1.

EXPERIMENTS

Reagents

The saponification of ethyl benzoate in aqueous alcohol and the nucleophilic substitution of benzyl chloride with HO^- in aqueous DMSO solution were studied to test the validity of this dimensionless parameter method.

50% $CH_3CH_2OH-H_2O$ was prepared by diluting 500 g analytical pure CH_3CH_2OH to 1 l with deionized water.

800/200 (v/v) $DMSO-H_2O$ was prepared by adding 200 ml deionized water to 800 ml DMSO which had been purified by distillation under reduced pressure. The benzyl chloride and sodium hydroxide used were analytical pure reagents, and the concentration of NaOH in solution was standardized with potassium hydrogen phthalate.

Apparatus

The experiments were carried out in a conduction calorimeter which has been described previously [3]. The heat effects of mixing, dilution, stirring and evaporation should be compensated with the same heat effects produced in the reference calorimeter.

TABLE 2

Saponification of ethyl benzoate
Solvent: 50% (v/v) $CH_3CH_2OH–H_2O$, $t = 25.0 \pm 0.1°C$, A_0(ethyl benzoate) = 0.350 M, B_0(NaOH) = 0.050 M.

Δ_m (mm)	$a_m^* \times 10^{-5}$ (mm s)	$A \times 10^{-5}$ (mm s)	$F(N, M, 7)$	$f(N, M)$	$k_2 \times 10^3$ (dm³ mol⁻¹ s⁻¹)
89.2	2.38	2.90	0.820	1.049	1.31
90.0	2.37	2.92	0.810	1.077	1.36
89.5	2.35	2.89	0.815	1.064	1.35
				Average value	1.34
				Literature value [4]	1.33

TABLE 3

Substitution of benzyl chloride
Solvent: 800/200 (v/v) $DMSO–H_2O$, $t = 25.0 \pm 0.1°C$, A_0(benzyl chloride) = 0.350 M, B_0(NaOH) = 0.050 M.

Δ_m (mm)	$a_m^* \times 10^{-4}$ (mm s)	$A \times 10^{-5}$ (mm s)	$F(N, M, 7)$	$f(N, M)$	$k_2 \times 10^3$ (dm³ mol⁻¹ s⁻¹)
65.0	9.38	1.10	0.855	0.976	2.25
65.7	9.79	1.14	0.860	0.968	2.17
68.2	9.82	1.16	0.850	0.984	2.28
				Average value	2.23
				Literature value [5]	2.26

RESULTS AND DISCUSSION

The saponification of ethyl benzoate in aqueous alcohol and the nucleophilic substitution of benzyl chloride with HO^- in aqueous DMSO solution have been studied under the condition of $r = A_0/B_0 = 7$. The thermogram's data and the rate constants calculated by the dimensionless parameter method are listed in Tables 2 and 3.

From these tables, it can be seen that the rate constants of these two reactions calculated using dimensionless parameter method in this paper are in fair agreement with the literature values and therefore the thermokinetic equations of the second-order reaction and the principles of the dimensionless parameter method are believed to be correct.

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