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Thermochimica Acta 273 (1996) 53–60

thermochimica
acta

Development and applications of a method for kinetic analysis of consecutive reactions under isothermal conditions

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Received 23 March 1995; accepted 27 May 1995

Abstract

The kinetic method for analysing consecutive reactions under isothermal conditions has been developed further. An approach to assessing the correspondence of the calculated values of the rate constants to the exact steps is suggested. As an example of application of this method, the consecutive quaternizations between *N,N,N′,N′*-tetramethyl-1,3-propylenediamine and bromobutane, which is a model reaction to elucidate the formation of the ionene polymers, were investigated with a conduction calorimeter in different solvents and at different temperatures. The characteristics of the described method and the influence of the solvent and temperature on the kinetic parameters of the two steps are discussed.

Keywords: Calorimetry; Consecutive reaction; Kinetics; Quaternizations

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1. Introduction

The study of the kinetics of consecutive reactions has a special place in physico-organic chemistry, biochemistry and chemical engineering. In particular, the two-stage consecutive process can be applied to describe the kinetic behaviour of the formation of organic intermediates [1,2], the decompositions of proteins [3,4] and many other solid-state processes [5,6]. Thermal analysis and calorimetry have been regarded as feasible approaches to the study of the macrokinetics of chemical reactions. To date, many non-isothermal methods for consecutive kinetic analysis have been proposed [7–11]; most of these are on the basis of computer simulations and have been used for solid-state processes. However, they are not sufficiently developed.

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SSDI 0040-6031(95)02546-4

While the validity of non-isothermal kinetic analysis is being discussed [12], isothermal approaches, especially isothermal microcalorimetry, are versatile techniques, particularly for solution reactions in organic chemistry, biochemistry, pharmacology, etc. For consecutive reactions, Vaganova et al. [9] proposed a method for determination of the kinetic parameters from thermoanalytical data under isothermal conditions. However, its accuracy and reliability are still questionable in practical measurements of chemical reactions, particularly when the value of the derivative of the heat flux (d^2Q/dt^2) is used for the evaluations.

In our previous work, isothermal methods for kinetic analysis of simple-order reactions [13], reversible reactions [14], and enzymatic reactions [15] have been suggested. One or more rate constants can be determined simultaneously from a single calorimetric measurement, and the analysis is less sensitive to noise owing to the integrated character of the data used. Likewise, a kinetic method for consecutive first-order reactions has been suggested [16], which can be used to determine the rate constants of the two steps simultaneously. The shortcoming of this method is the lack of correspondence of the values obtained for the two rate constants to the exact steps. One must determine these steps through other techniques, or from the characteristics of the reaction under investigation.

However, the consecutive quaternization between *N,N,N′,N′*-tetramethyl-1,3-propylenediamine (TPD) and bromobutane can be used as a model reaction for elucidating the formation of the so-called ionene polymer [17] which is the backbone of our desired biopolymer [18]. The influences of temperature and solvent on this consecutive reaction are of interest to us in choosing the best conditions for the formation of this polymer. In this paper, the kinetic method for consecutive reactions has been developed further. An approach for determining the correspondence of the rate constants to the exact steps is suggested, and the thermokinetics of the consecutive quaternization between TPD and bromobutane was investigated under different experimental conditions. The characteristics of this method and the experimental results are discussed in detail.

2. Method

2.1. Kinetic equation of a consecutive reaction

For a consecutive first-order reaction, the general scheme of its kinetics can be described as

$$S \xrightarrow[\Delta H_1]{k_1} I \xrightarrow[\Delta H_2]{k'_1} P \tag{1}$$

where k_1, k'_1 and ΔH_1, ΔH_2 are the rate constants and the molar enthalpies of the two steps, respectively. According to the kinetic equations and the transformation equation for kinetics of consecutive reactions in a calorimeter [16], the following equation can be derived

$$\alpha = (1-G)\cdot\exp(-\theta) + G\cdot\exp(-\rho\theta) \tag{2}$$

where $\alpha = 1 - \phi$; $\phi = Q/Q_\infty$; $\theta = k_1 t$; $\rho = k'_1/k_1$; $G = \beta/[(1+\beta)(1-\rho)]$, $\beta = \Delta H_2/\Delta H_1$; ϕ is called the reduced-extent [13], its value at time t being determined by thermoanalytical data, the heat amount Q generated before time t, and the total heat effect of the reaction Q_∞; α is called the reduced-remains.

2.2. *Calculation of the rate constants of the two steps*

One set of thermoanalytical data $(\alpha_1, \alpha_2, \alpha_3, \alpha_4)$ can be selected at fixed time intervals, i.e. $t = t_4 - t_3 = t_3 - t_2 = t_2 - t_1$. According to Eq. (2), it can be proved that

$$k_1 \quad \text{or} \quad k'_1 = (1/\Delta t)\cdot\ln(X_i) = (1/\Delta t)\cdot\ln(b \pm \sqrt{b^2 - c}) \tag{3}$$

where $b = (\alpha_1\alpha_4 - \alpha_2\alpha_3)/[2(\alpha_2\alpha_4 - \alpha_3^2)]$ and $c = (\alpha_1\alpha_3 - \alpha_2^2)/(\alpha_2\alpha_4 - \alpha_3^2)$.

In terms of Eq. (3), the rate constants of the steps of a consecutive reaction can be calculated simultaneously from the thermoanalytical data of a single calorimetric experiment. From Eq. (3), the dimensionless parameters (X_1, X_2), which characterize the kinetics of a consecutive reaction, are the two positive real roots of the same algebraic equation. This is an interesting characteristic of consecutive processes, which will be discussed below.

However, the two calculated values could not be distinguished for the two steps, owing to the symmetry of Eq. (2) and the lack of values for the molar enthalpies of the two steps.

The validity of Eq. (3) was verified by studying the kinetics of the saponifications of diethyl succinate and diethyl adipate in a mixed solvent of ethanol and water [16]. However, in that work, the correspondence of the calculated rate constants to the exact steps of the saponifications was determined through other approaches.

The remaining problem is how to determine which of the k values calculated via Eq. (3) relates to the first step and which to the second.

2.3. *Correspondence of the rate constants to the individual steps*

For consecutive first-order reactions, the characteristic time t_m, when the concentration of the intermediate I is a maximum, is generally helpful in kinetic analysis, because t_m is only dependent on the values of the two rate constants, and is symmetrical for both of them: $t_m = \ln(k'_1/k_1)/(k'_1 - k_1)$. So the value of t_m can be calculated with k_1 and k'_1, irrespective of their correspondence to the steps.

When $t = t_m$ and $\alpha = \alpha_m$, from Eq. (1) one obtains

$$\alpha_m = [\rho^{1/1-\rho} + \rho^{\rho/1-\rho}] - [1/(1+\beta)]\cdot\rho^{\rho/1-\rho} \tag{4}$$

Writing

$$\varepsilon_m = [\rho^{1/1-\rho} + \rho^{\rho/1-\rho}] - \alpha_m \tag{5}$$

it follows that

$$\varepsilon_m = [1/(1+\beta)]\cdot\rho^{\rho/1-\rho} \tag{6}$$

For the first term on the right-hand side of Eq. (5), $[\rho^{1/1-\rho}+\rho^{\rho/1-\rho}]$, can also be calculated irrespective of the correspondence of k_1 and k'_1; and the second term can be obtained from the thermoanalytical data at t_m. Then the value of ε_m can be determined.

At the same time, according to the derivative expression of Eq. (2), it can be proved that

$$\dot{\alpha} = -\dot{Q}(t_m)/Q_\infty = (-k'_1)\cdot\rho^{\rho/1-\rho} \tag{7}$$

where $\dot{Q}(t_m)$ is the heat flux at time t_m, and so $\dot{\alpha}_m$ can be determined easily from one thermoanalytical curve. From Eqs. (6) and (7)

$$M = \dot{\alpha}_m/\varepsilon_m = -(1+\beta)k'_1 \tag{8}$$

Eq. (8) shows that the characteristic parameter M at time t_m is proportional to the rate constant of the second step, with a coefficient $[-(1+\beta)]$.

Thus, if two experiments are performed at different temperatures T_1 and T_2, the values $M(T_1)$ and $M(T_2)$ corresponding to the special time t_m can be obtained, and then we have

$$M(T_2)/M(T_1) = k'_1(T_2)/k'_1(T_1) \tag{9}$$

Accordingly, the values of the rate constants calculated according to Eq. (3), whose ratio at temperatures T_1 and T_2 is equal to $M(T_2)/M(T_1)$, should correspond to the second step.

Consequently, after the individual values of the rate constants of the two steps have been determined at two or more temperatures, the kinetic parameters, the activation energy E and the pre-exponential factor A, can be calculated using the Arrhenius equation. Furthermore, in principle, if the correspondence of the rate constants to the steps is determined, the values of β can be calculated on the basis of Eq. (4), and then the molar enthalpies of the two steps can be determined from thermoanalytical data [19]. It should be noted that the accuracy of the values of ΔH_1 and ΔH_2 is sensitive to the ratio of the rate constants of the two steps, ρ.

3. Applications

3.1. Reacting systems under investigation

The kinetic method described above was used to study the quaternization between TPD and bromobutane. This reaction is a consecutive second-order reaction, whose scheme can be described as

$$(\mathrm{CH_3})_2\mathrm{N}(\mathrm{CH_2})_3\mathrm{N}(\mathrm{CH_3})_2 + n\text{-}\mathrm{C_4H_9Br} \xrightarrow{k_2} \mathrm{Br^-}(\mathrm{CH_3})_2\overset{+}{\mathrm{N}}(\mathrm{C_4H_9})(\mathrm{CH_2})_3\mathrm{N}(\mathrm{CH_3})_2$$

$$\xrightarrow[n\text{-}\mathrm{C_4H_9Br}]{k'_2} \mathrm{Br^-}(\mathrm{CH_3})_2\overset{+}{\mathrm{N}}(\mathrm{C_4H_9})(\mathrm{CH_2})_3\overset{+}{\mathrm{N}}(\mathrm{C_4H_9})(\mathrm{CH_3})_2\mathrm{Br^-}$$

This reaction was studied with the initial concentration of bromobutane in large excess of that of TPD, so it may be treated as a consecutive pseudo-first-order reaction.

The experiments were performed at 25.0, 35.0 and 45.0°C in the solvents dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO).

3.2. Reagents

TPD was synthesized and purified according to the method in Ref. [20]. Chemically pure bromobutane was purified further under reduced pressure. The solvents, DMF and DMSO, were of analytically pure grade. The solutions of reactants were prepared by mass.

3.3. Calorimeter

The calorimeter used for measurements of the thermoanalytical curve of the reactions under investigation was an isothermal conduction calorimeter with twin vessels, whose construction was described in detail in Ref. [21]. The extraneous heat effects, except for the reaction heat generated in the reaction vessel, such as the heat effects of mixing, dilution, stirring and evaporation, can be compensated by the same effects in the reference vessel.

4. Results and discussion

4.1. On the method

From the formula for calculating rate constants, i.e. Eq. (3), the values of the parameters (X_i), which characterize a consecutive reaction, are the two positive real roots of the same algebraic equation of the second degree in one unknown. In our previous work on the kinetics of a first-order reaction in a heat conduction calorimeter [22], we found that the values of the parameters to determine the rate constant k_1 and the cooling constant of the calorimeter k are also the two positive real roots of an algebraic equation. As pointed out by Bell and Clunie [23], the whole process consisting of heat generation from the first-order reaction and the heat transfer from the vessel to the surroundings can be considered as a consecutive process. In our work on the theoretical modelling of the conduction calorimeter [24], it was found again that the values of the parameters to determine the cooling constants of the calorimeter and the sensor are in the same situation; in fact, the heat transfer process from the heat source to the external boundary of the vessel, and then to the sensor, is also a consecutive process. Vaganova et al. [9] found similar phenomena when they studied consecutive reactions. So it could be an interesting common characteristic of two-stage consecutive processes.

Vaganova et al. [9] reported a thermoanalytical method for determining the kinetics of two-stage reactions. However, the data used for the determination include the heat amount Q, the heat flux $\dot{Q}$ and the derivative of the heat flux with respect to time t, $\ddot{Q}$. For kinetic investigations of practical reacting systems, the lack of sufficient accuracy of $\ddot{Q}$ will be a limitation to its application. By comparison, for the method in this paper, all

Table 1

Experimental conditions and results of consecutive quaternizations between *N*, *N*, *N'*, *N'*-tetramethyl-1,3-propylenediamine and bromobutane

Solvent	Temp./°C	$k_2 \times 10^3$ $\mathrm{l\,mol^{-1}\,s^{-1}}$	$k'_2 \times 10^4$ $\mathrm{l\,mol^{-1}\,s^{-1}}$	(k_2/k'_2)	E_a/ $\mathrm{kJ\,mol^{-1}}$	E'_a/ $\mathrm{kJ\,mol^{-1}}$	A/ $\mathrm{l\,mol^{-1}\,s^{-1}}$	A'/ $\mathrm{l\,mol^{-1}\,s^{-1}}$
DMF	25.0	0.370(± 0.07)	0.774(± 0.23)	4.83	51.8(± 3.6)	46.0(± 0.3)	$4.49(\pm 0.12) \times 10^5$	$8.92(\pm 0.05) \times 10^3$
	35.0	0.764(± 0.05)	1.42(± 0.20)	5.38				
	45.0	1.38(± 0.04)	2.49(± 0.18)	5.56				
DMSO	25.0	1.38(± 0.05)	1.01(± 0.18)	13.7	50.6(± 0.3)	45.4(± 0.8)	$1.01(\pm 0.01) \times 10^6$	$9.16(\pm 0.08) \times 10^4$
	35.0	2.67(± 0.03)	1.85(± 0.18)	14.4				
	45.0	4.99(± 0.03)	3.20(± 0.15)	15.6				

the data used for calculation are of sufficient accuracy, owing to the integrated expression. Moreover, the method suggested to determine the correspondence of the calculated k values to the exact steps is also simple.

4.2. On the experimental results

According to the method of thermogram reconstruction proposed in Ref. [13], the thermogram measured with the conduction calorimeter can be reconstructed into an ideal adiabatic thermogram, and the reduced-extent ϕ or reduced-remains α at any time t_i can be easily obtained.

Under the experimental conditions in this work, C_0(bromobutane)$\gg C_0$(TPD), so this reaction can be treated as a consecutive first-order reaction and $k_1 = k_2 C_0$ (bromobutane) and $k'_1 = k'_2 C_0$ (bromobutane). Then we can evaluate the measured curves of the reactions using the method suggested in this paper.

Through kinetic evaluations, we found that the calculated results from a single curve are consistent, and those from different experimental curves under the same conditions of temperature and solvent are reproducible. For discussion, the rate constants and activation energies of the reactions under different experimental conditions are summarized in Table 1.

From Table 1, the rate constants at the same temperature of the two steps are remarkably dependent on the solvents. Both DMF and DMSO are polar non-proton solvents. An enhancement of the polarity will decelerate the activation free-energy of the individual step reactions, and so the rate constants in DMSO are larger than in DMF, as the polarity of DMSO is larger than DMF. This result is similar to that of the general quaternization [25]. At the same time, one of the reactants of the second step is a positive ion, while the reactants of the first step are neutral molecules, so the influence of the solvents on the second step is not as remarkable as that on the first step. Murai and Kimura [26] also reported activation energies of the reaction in propylene carbonate (PC): $E_a = 50.6$ kJ mol^{-1}, $E'_a = 44.7$ kJ mol^{-1}. These values are very close to those in Table 1.

Although increasing both the polarity of the solvent and temperature will accelerate the rate constants of the two steps, the ratio of the rate constants of the two steps (k_1/k'_1) will also increase; and the influence of the solvents is much more remarkable than that of temperature. This is an important result in this work, which will help us to choose the conditions of synthesis of desired ionene polymers. The large reaction rate will reduce the time necessary for the formation of the polymer, but it is unfavorable to the formation of polymers with high molecular mass. Therefore, the influences of the solvent and the temperature should be considered comprehensively while choosing the best conditions for the synthesis of ionene polymers.

5. Conclusion

A method for kinetic analysis of consecutive reactions under isothermal conditions has been developed further and an approach to assessing the correspondence of the calculated values of the rate constants to the exact steps has been proposed in this paper. This method was applied to investigate a consecutive quaternization. The experimental results are considered to be important for the choice of the conditions for the synthesis of ionene polymers.

Acknowledgement

The support for this project from the National Natural Science Foundation of China is gratefully acknowledged.

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