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THERMODYNAMIC AND KINETIC STUDIES ON REVERSIBLE LIQUID-PHASE DIELS ALDER REACTION BETWEEN MALEIC ANHYDRIDE AND 2-METHYL FURAN

Dynamic modelling by thermal analysis

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Abstract

The liquid phase reaction between maleic anhydride and 1-methyl-furan leads to an exothermic cycloaddition. The reaction enthalpy, the rate constant and the equilibrium constant are evaluated with good precision by a method of analysis using thermal data and a dynamic model based on physical properties. The mathematical models that are presented here in a simple way (first-order system) represent the reaction accurately and are useful for studying other reactions and even industrial processes.

Keywords: Diels Alder reaction, kinetic studies, thermodynamic studies

Introduction

Dynamic modelling, which is widely used for the study of physical systems [1–5], is an original approach to the study of thermochemical systems. In our investigation of reversible reactions between a carboxylic acid and a Lewis base giving hydrogen bounded complexes [6, 7] for applications in thermochemical energy storage, we applied a global dynamic and phenomenological modelling [8]. The models constructed in this study concern instantaneous exothermic reactions and lead rapidly and correctly to the reaction heat (to within a difference of 2% from the value reported in the literature) [9–11]. The method presented here is used for non-instantaneous chemical reactions, obeying a known kinetic law. We have chosen a liquid phase Diels Alder reaction. The mathematical model is modified for the reaction phase, taking into account the second kinetic law, it is unchanged in the system's relaxation phase. The full analysis of the ex-

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perimental records permit calculation of the characteristic data of the reaction, such as the reaction enthalpy, the rate and the equilibrium constant.

Experimental procedure and modelling

Maleic anhydride (*A*) and 2-methyl-furan (*B*) and the solvent 1,4-dioxan, obtained from Prolabo and Merck with purities of 98 and 99% were used. The apparatus (100 cm^3 glass container) and experimental technique were described earlier [12, 13]. Solutions of *A* and *B* were prepared separately at the same concentration. It was necessary to wait until thermal equilibrium was reached (i.e. ambient temperature was the same as the solution temperature), before adding rapidly solution *B* to solution *A*.

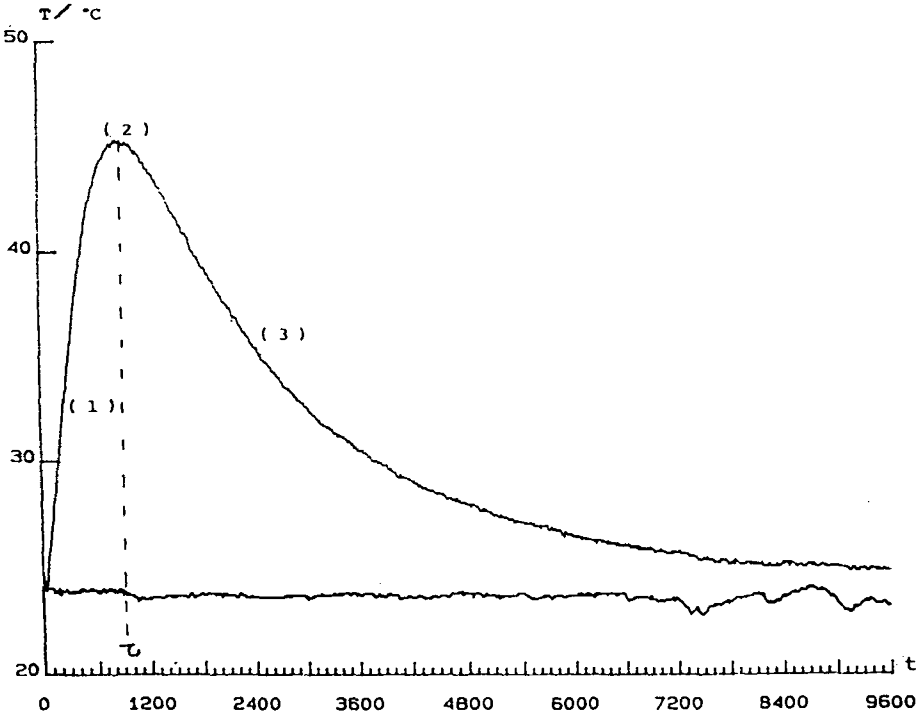
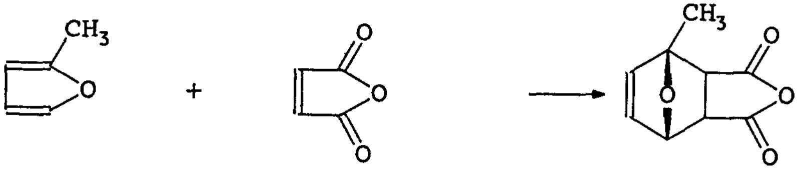


Fig. 1 Diagram of the experimental results

The diagram of the experimental results (Fig. 1) may be divided into three phases: reaction (1), equilibrium (2) and relaxation (3). To build a complete model, we used the chemical and kinetic reaction laws, and the global balance of thermal exchanges between the system and the surroundings. Some assumptions were made in order to get simple working model. These assumptions will be stated and clarified in each phase studied.



B 2-Methyl-furan *A* Maleic anhydride *C* Adduct

Kinetic law:

$$\frac{\mathrm{d}[C]}{\mathrm{d}t} = \frac{1}{V}\,\mathrm{d}\,\frac{N_C}{\mathrm{d}t} = k^*[A][B] = k^*[A]^2 = -\,\frac{\mathrm{d}[A]}{\mathrm{d}t}$$

$$[A] = \frac{1}{\frac{1}{[A_0]} + k^*t}$$

Chemical law: At time $t = \infty$, the amount of heat produced by the reaction is: $Q_\infty = \Delta H_r N_C$

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \Delta H_r \frac{\mathrm{d}N_C}{\mathrm{d}t}$$

Phase 1: Exothermic chemical cycloaddition produces a rise on the temperature of the reaction mixture. The global equation is:

$$Mc\,\frac{\mathrm{d}T}{\mathrm{d}t} = -k(T - T_a) + \frac{\mathrm{d}Q}{\mathrm{d}t}$$

The rate constant k^* is taken to be constant throughout the reaction: we discuss this assumption in the conclusion.

Phase 2: At time $t = \tau$, the system is in thermal equilibrium, represented by:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = 0$$

Phase 3: We assume that the reaction is nearly finished and that the amount of heat produced by the reaction is negligible.

We take $\theta = T - T_a$ and $\alpha = \frac{k}{Mc}$; $\frac{\mathrm{d}\theta}{\mathrm{d}t} = -\alpha\theta$.

The value of α is determined by logarithmic linearisation in this phase.

Results

Phase 1:

$$\frac{d\theta}{dt} = -\alpha\theta + (Mc)^{-1}\,\Delta H_r V k^* \left[\frac{1}{\frac{1}{[A_0]} + k^* t}\right]^2$$

Let $a = (Mc)^{-1}\,\Delta H_r V k^*\,[A_0]^2$ and $b = k^*[A_0]$

At time $t = 0$, $T_0 = T_a$ and $\theta = 0$, $\frac{d\theta}{dt}(t = 0) = a$

a is obtained by measuring the slope at the origin.

Phase 2: At time $t = \tau$, $\frac{d\theta}{dt} = 0 = -\alpha\theta(\tau) + \frac{a}{(1 + b\tau)^2}$

Phase 3: Mc can be determined by measuring the relaxation with different masses of reagents or water [14, 15].

The equilibrium constant can now be estimated. Since the initial concentrations of A and B are the same, their respective concentrations at any moment t are the same.

$$K = \frac{[C]}{[A][B]} = \frac{VN_C}{N_A N_B} = \frac{VN_C}{(N_{A_0} - N_C)^2}, \quad N_C = \frac{Q_\infty}{\Delta H_r}$$

Using the assumption made for phase 3, Q_∞ may be estimated from the expression:

$$\frac{d\theta}{dt} = \Delta H_r V k^* \left[\frac{1}{\frac{1}{[A_0]} + k^* t}\right]^2$$

by integrating over the interval of time $[0,\tau]$.

$$Q_\infty \approx Q_\tau = \int_0^\tau \Delta H_r V k^* \left[\frac{1}{\frac{1}{[A_0]} + k^* t}\right]^2 dt = \Delta H_r V [A_0]\left[1 - \frac{1}{1 + b_\tau}\right]$$

Results are given in the following table:

N_{A0}	V	τ	α	Mc	$\theta(\tau)$
0.175	0.05	944	$6.8\ 10^{-4}$	0.185	20.5
a	b	k^*	ΔH_r	Q_∞	K
0.0375	$6.78\ 10^{-4}$	$1.94\ 10^{-4}$	58.4	3.99	0.302

Conclusion

The analysis and modelling carried out here, with the prerequisite of simplicity, show clearly that several interesting values may be estimated with a high degree of accuracy. Taking into account the simplifying assumptions which were made, the results are very encouraging.

The most important assumption concerns the rate constant, which is taken to be constant throughout the process. In phase 1 the reaction obeys a second-order kinetic law, and the temperature of the reaction mixture is not constant, hence the rate constant varies during the experiment. However, the range of temperatures (between room temperature and the maximum) is 20.5°C. For a model to manage an industrial thermochemical system, it may be interesting to have this simple evaluation of the rate constant, considered as a mean value in this temperature range.

The time is estimated from the analysis of experimental readings and the assumption consists of considering the reaction being nearly finished between phase 2 and phase 3, i.e for $t = \tau$.

This preliminary work needs to be followed up. The model should be validated by resolving the differential equation obtained in phase 1 by the method of variation of the constant. This is the subject of research in progress.

Notation

t:	time /s
τ:	time of reaction /s
V:	total volume of the reagent mixture /l
N_A, N_B, N_C:	total number of moles of A, B, C /mol at time t
$[A]$, $[B]$, $[C]$:	concentrations of A, B, C /mol·l^{-1} at time t
N_{A0}, N_{B0}:	initial number of A and B /mol
$[A_0]$, $[B_0]$:	initial concentration of A and B /mol·l^{-1}
k^*:	average rate constant /l·mol^{-1}·s^{-1} in the reaction phase
T, T_a:	temperature of the reagent mixture and ambient temperature /K
Q_∞:	quantity of heat given of in the reaction /kJ
ΔH_r:	reaction enthalpy /kJ·mol^{-1}
k:	exchange coefficient of the system /kJ·s^{-1}·K^{-1}

M: water equivalent mass of the entire system /kg
c: thermal mass capacity of water /kJ·kg^{-1}·K^{-1}
$1/\alpha$: response time of the system /s

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Zusammenfassung — Die Flüssigphasenreaktion zwischen Maleinsäureanhydrid und 1-Methylfuran führt zu einer exothermen Cycloaddition. Reaktionsenthalpie, Geschwindigkeitkonstante und Gleichgewichtskonstante wurden mit guter Genauigkeit mittels einer Analysenmethode auf der Basis von thermischen Angaben und eines auf physikalischen Eigenschaften beruhenden dynamischen Modelles ermittelt. Die hier auf einfache Weise vorgestellten matematischen Modelle (Systeme erster Ordnung) repräsentieren die Reaktion recht genau und sind nutzbringend für die Untersuchung anderer Reaktionen und auch industrieller Prozesse.