Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 1, 127–133

UTILIZATION OF MICROCALORIMETRY FOR AN ASSESSMENT OF THE POTENTIAL FOR A RUNAWAY DECOMPOSITION OF CUMENE HYDROPEROXIDE AT LOW TEMPERATURES

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The exothermic decomposition of cumene hydroperoxide (CHP) in cumene liquid was characterized by isothermal microcalorimetry, involving the thermal activity monitor (TAM). Unlike the exothermic behaviors previously determined from an adiabatic calorimeter, such as the vent sizing package 2 (VSP2), or differential scanning calorimetry (DSC), thermal curves revealed that CHP undergoes an autocatalytic decomposition detectable between 75 and 90°C. Previous studies have shown that the CHP in a temperature range higher than 100°C conformed to an n^{th} order reaction rate model. CHP heat of decomposition and autocatalytic kinetics behavior were measured and compared with previous reports, and the methodology and the advantages of using the TAM to obtain an autocatalytic model by curve fitting are reported. With various autocatalytic models, such as the Prout–Tompkins equation and the Avrami–Erofeev rate law, the best curve fit among models was also investigated and proposed.

Keywords: *autocatalytic model, cumene hydroperoxide (CHP), curve fitting, isothermal microcalorimetry, thermal activity monitor (TAM)*

Introduction

As a pivotal intermediate, cumene hydroperoxide (CHP) has been widely employed in Taiwan to produce dicumyl hydroperoxide (DCPO) and phenol. In the polymer industry, it is also used as an initiator for polymerization, such as acrylonitrile-butadiene-styrene (ABS) copolymer, which plays a dominant role in terms of world production. Since the 1980s, several fire and explosion incidents have occurred due to CHP and other materials' inherent instability or reactive incompatibility, as shown in Table 1. Runaway incidents have occurred in oxidation reactors, vacuum condensation reactors and storage tanks. CHP is given a hazard classification as a flammable type or class by the National Fire Protection Association (NFPA) [1].

In recent years, many studies have investigated the runaway hazards and decomposition kinetics of CHP for various process conditions [2]. This research showed the incompatibilities of CHP and contaminants, e.g., HCl, H_2SO_4 or $FeCl_3$, with which it might inadvertently mix, and revealed various degrees of hazard [3]. However, the CHP reactive characteristics for storage and transportation conditions were not clearly identified, especially for an ambient temperature environment.

Previous studies have indicated that the exothermic onset temperature (T_0) is 109°C for 80 mass% CHP conducted by differential scanning calorimetry (DSC) tests [4] and 140°C for 35 mass% CHP by vent sizing package 2 (VSP2) tests [3, 5]. The T_0 for a runaway reaction, as generally recognized, is that at which the reaction is initially detected by a specific instrument [6]. A summary of CHP onset temperatures obtained by using different types of calorimeters is listed in Table 2. In this study, a microcalorimeter, thermal activity monitor (TAM), was used to detect and record the exothermic activity of CHP under isothermal conditions in the temperature range from 75 to 90°C [7]. At these temperatures, conventional calorimeters, such as the DSC, or adiabatic calorimeters, such as the VSP2, cannot detect the extremely weak heat-release from CHP [8, 9].

The aim of this research was to verify the thermal kinetics and to establish a simplified autocatalytic model to illustrate the exothermic decomposition of CHP, by using an isothermal microcalorimeter to obtain the required data. The simulation results were compared by different known models presented in the open literature with the experimental data. The value of a model is that it may be used in a simulation to predict conceptual consequences without the need for conducting further

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1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 Selected thermal explosion accidents caused by CHP and other hazardous materials since 1974 [26–31]

Date	Chemical	Injuries/fatalities	Hazard	Cause
1974	CHP	4/0	explosion (human error)	thermal decomposition
1977	CHP	1/0	explosion (distillation tower)	thermal decomposition
1981	CHP	3/1	explosion (condensation)	thermal decomposition
1986	CHP	0/0	explosion (reactor)	thermal decomposition
1996	MEKPO	47/10	explosion (reactor)	thermal decomposition
1999	DCPO	0/0	explosion (reactor)	thermal decomposition
2001	MEKPO	1/0	explosion (reactor)	thermal decomposition
2003	MEKPO	3/5	explosion (reactor)	thermal decomposition
2003	CHP/DCPO	2/0	explosion (reactor)	thermal decomposition

Table 2 Thermal analysis data acquired from various calorimeters [2, 4–6]

Calorimeter	CHP concentr./mass%	T_0/°C	ΔH_d/J g^{-1}	Kinetics
DSC	80	109	1.382	n^{th}
VSP2	35	140.9	–	n^{th}
TAM	80	75	1.163±80	autocatalytic

experiments. By the TAM, the obtained thermal runaway data, such as exothermic onset temperature (T_0), heat flow (Q), time to maximum rate (TMR), self-acceleration decomposition temperature (SADT), temperature of no return (T_{NR}), etc., can be fully exploited for thermal hazard evaluation and emergency planning, as well as for designing an emergency relief system with the methodology of Design Institute for Emergency Relief System (DIERS) sponsored by the American Institute of Chemical Engineers (AIChE).

Experimental

CHP sample

80 mass% CHP in 20 mass% cumene purchased directly from the supplier (Fluka Chemical Co.) was analyzed for both density and concentration. The sample was then stored at 4°C in a refrigerator.

Thermal decomposition analysis by DSC

As one of the most popular instruments for establishing kinetic equations of thermal decomposition, a Mettler TA8000 system coupled with a DSC 821$^{e®}$ measuring cell that can withstand relatively high-pressure (ca. 100 bar) was used for performing dynamic screening experiments. STAR^e software [10] was used for acquiring thermal curves and isothermal traces. To better approach thermal equilibrium, the scanning rate for the temperature-programmed ramp was chosen to be 4°C min^{-1} [7, 11–15].

Thermal runaway hazards analysis by TAM

A heat conduction calorimeter is designed to monitor a wide range of reaction types, such as pharmaceutical, chemical, biochemical reactions, iron, and other heavy metal corrosion rates, for the construction business, shipping, and biological industries. In practice, reactions can be investigated between 10 and 90°C, the working temperature range of this calorimeter. Constant temperature is maintained within $\pm 2\cdot 10^{-4}$°C day^{-1}, which allows heat flow in fractions of a μW to be measured routinely. However, the TAM is capable of detecting quite small heat flow, ±50 nW produced or absorbed by a sample system [16]. The 80 mass% CHP was dispensed into the glass or stainless containers, capped, and then the cell was placed in the measuring and reference chambers. For an isothermal decomposition reaction, experiments were conducted isothermally over the temperature range from 75 to 90°C and held for enough time to assure the CHP decomposed completely.

Results and discussion

Thermal analysis

The experimental data for the thermal runaway of CHP are not constrained by heat transfer control, due to the maintenance of an excellent isothermal

Table 3 TAM experimental data from the autocatalytic reaction of 80 mass% CHP

Temperature/ °C	Sample mass/ g	Cell	Maximum heat flow/ mW	Time to main peak/ day	ΔH_d of main peak/ J g^{-1}
90	0.495	glass	2.850	5.5	1.241
88	0.504	glass	2.115	6.6	1.243
85	0.634	glass	1.795	9.0	1.091
80	0.500	glass	1.248	11.8	1.229
75	0.505	glass	0.661	20.7	1.083

environment. Many reactions, such as polymerization, decomposition, oxygenation, and change of physical behaviors, can be predicted by either isothermal models or adiabatic models [17]. In principle, isothermal methods have the advantage of greater simplicity of data interpretation, which provides more reliable kinetics data and broader applicability. The isothermal method introduces fewer experimental variables into a single measurement, which significantly reduces, or even avoids, ambiguity in the interpretation of data [18, 19].

Experimental data for the autocatalytic reaction of CHP are summarized in Table 3. The slow reactions for each isothermal measurement reported here had time histories between 16 and 43 days. Peak power of these exothermic curves ranged from 0.6 to 2.8 mW, which could not be detected by using DSC or an adiabatic calorimeter such as VSP2. Heat of reaction was determined to be about 1.163±80 J g^{-1} (80 mass% CHP at 88°C isothermal condition). Around 20% of heat of reaction was not accounted for in the 88°C isothermal test, compared to the 1.500 J g^{-1} (80 mass% CHP) heat of decomposition as determined by DSC [20].

Thermal curves of 80 mass% CHP thermostatted at various temperatures in the TAM are demonstrated in Fig. 1. After an induction period, the rate of the reaction began to accelerate, and the time for the overall reaction increased as temperature decreased. Meanwhile, the maximum rate of the reaction (heat flow) and enthalpy change (ΔH_d) decreased as the temperature decreased [21].

The mass and ampoule material effects on both overall time increase and heat release rate are clearly illustrated in Fig. 2. It shows that the exothermic traces were independent of a mass effect, in that the three curves almost overlap despite representing different masses. Furthermore, the ampoules, either made of glass or stainless steel, validated that the thermal curves and heat of reaction changed for 80 mass% CHP were not conspicuously different.

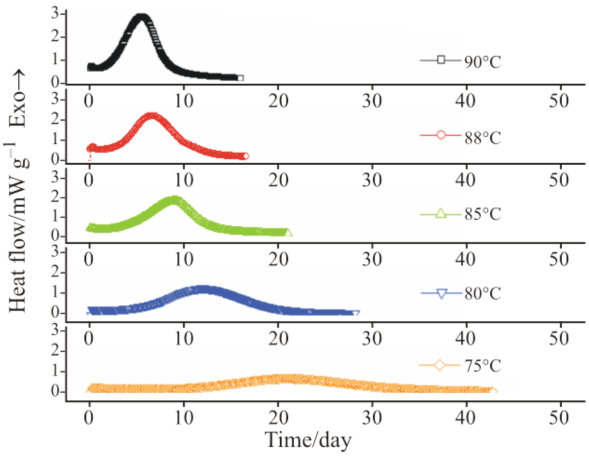

Fig. 1 Heat flow *vs.* time for the thermal decomposition of 80 mass% CHP at constant temperature

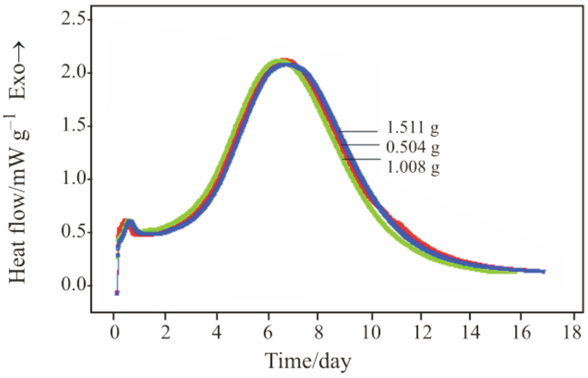

Fig. 2 Heat flow *vs.* time for the thermal decomposition of 80 mass% CHP at 88°C with three different sample masses

Autocatalytic behavior

Although it was difficult in practice to maintain the calorimeter absolutely isothermally due to all reactions dissipating or absorbing various quantities of heat, the TAM was effectively used to minimize these adverse effects by accurate thermostatting. Theoretically, isothermal calorimeters can be utilized to investigate whether a reaction is autocatalytic or displays n^{th} order kinetics. In this study, the results of the different isothermal runs demonstrate that CHP behaves autocatalytically. This is significant for hazard analysis purposes because an autocatalytic decomposition can result in a runaway even under isothermal storage conditions due to accumulation of the catalyst. Autocatalytic reactions were verified in the isothermal curve by a maximum rate of heat release at about 40–60% conversion of the reactant [7].

The location of the maximum heat release with respect to conversion of CHP was indicative of autocatalytic behavior, similar to that for 2,4,6-trinitrotoluene (TNT) which was verified to be autocatalytic in the temperature range from 245 to 269°C, and was shown to have a temperature dependent induction period prior to its exothermic decomposition, resulting from a small concentration of a catalytic substance being formed during the induction stage [22]. Distinguishing the three periods – ‘induction period’, ‘acceleration period’, and ‘decay period’ – is critically important for loss prevention considerations [22].

Previous studies at this laboratory had shown that the exothermic decomposition of CHP under higher temperature conditions followed an n^{th} order reaction [7]. This study was to employ an isothermal microcalorimeter to investigate the thermal runaway phenomenon of CHP in a low temperature range from 75 to 90°C. The results reproducibly confirmed that CHP has an autocatalytic nature at lower temperature, but the transition between n^{th} order behavior and autocatalytic behavior was not defined and required further investigations. This new finding showed that CHP may behave differently in different temperature regions. With regard to thermal reaction hazards, realizing the behavior of this material is crucial since autocatalytic behavior can lead to a delayed thermal runaway or explosion from isothermal conditions once enough catalyst has accumulated.

Thermal decomposition kinetics

As mentioned earlier, numerous reactions, such as hydrogenation, oxygenation, hydrolysis, and nitration, can be observed from either isothermal or adiabatic perspectives. Isothermal analysis does eliminate the thermal lag effect. Usually, an isotherm can be readily maintained, revealing in the thermal curves that an autocatalytic model can appropriately be applied [23, 24].

According to the reaction kinetics, the rate equation for various CHP and catalytic product concentrations can be expressed as Eq. (1):

$$-\frac{\mathrm{d(CHP)}}{\mathrm{d}t}=k(\mathrm{CHP})^{\mathrm{m}}\,(\mathrm{P})^{\mathrm{n}} \qquad (1)$$

where (CHP): concentration of CHP, M; (P): concentration of reactant, M; k: rate constant, min^{-1}; m: reaction order of reactant, dimensionless; n: reaction order of product, dimensionless.

As a typical example, this study conducted an isothermal run of 80 mass% CHP at 90°C and determined the reaction order for both the reactant and product to be 0.5. Experimental results reveal the autocatalytic behavior of CHP was detectable in isothermal runs as low as 75°C. After an induced period, the autocatalytic product of CHP resulting from the decomposition then catalyzed the isothermal reaction, which further significantly accelerated the reaction rate, even in an isothermal environment. The important feature of autocatalytic decomposition is that it requires the presence of a certain initial catalyst concentration to trigger the reaction. Once autocatalytic kinetics for thermal decomposition of CHP are established, they can be readily utilized to simulate the production, transportation and even storage periods in a real scale facility subject to different upset conditions. The runaway autocatalytic reaction is a self-accelerating reaction [20]. One way to represent the reaction is by the following reaction model [18]:

$$\text{Initiation reaction: } \mathrm{A} \rightarrow \mathrm{B} + \mathrm{C} + \ldots \qquad (2)$$

$$\text{Autocatalytic reaction: } \mathrm{A} + \mathrm{B} \rightarrow 2\mathrm{B} + \mathrm{C} + \ldots \qquad (3)$$

By two reactions, given by Eqs (2) and (3), no initial catalyst B is required. The second equation shows that the rate of the autocatalytic reaction is proportional not only to the reactant concentration, but also to the product concentration. Hence the rate function for Eq. (4) can be expressed as follows:

$$-\frac{\mathrm{d(A)}}{\mathrm{d}t}=k(\mathrm{A})^{\mathrm{m}}\,(\mathrm{B})^{\mathrm{n}} \qquad (4)$$

where (A): concentration of reactant, M; (B): concentration of product (catalyst), M.

Measured rate of heat flow, dQ/dt, is directly proportional to the rate at which A is expended, with the proportionality constant being the expenditure of the mass and the enthalpy of reaction per mole of A:

$$\dot{Q}=\frac{\mathrm{d}Q}{\mathrm{d}t}=\Delta H_{\mathrm{d}}V\rho\frac{\mathrm{d(A)}}{\mathrm{d}t} \qquad (5)$$

where ΔH_{d}: heat of decomposition, kJ mol^{-1}; V: the total volume of the reaction material, L; ρ: the density of sample, g L^{-1}.

By running experiments, the sample CHP, the catalyst product, and the α are the reactant A, product B and degree of conversion, respectively. It was assumed that ΔH_{d} is independent of temperature changes. Combining the rate constant with Eq. (5), it can be expressed as follows:

Table 4 Comparison of experimental and simulation results for the time to maximum rate at various temperatures for 80 mass% CHP

TMR/day	Temperature/°C				
	75	80	85	88	90
Time to max. rate by experiment	21.2	13.8	10.1	7.0	5.0
Time to max. rate by simulation	21.2	13.6	10.3	8.6	5.3

$$\dot{Q}=\frac{\mathrm{d}Q}{\mathrm{d}t}=\Delta H_{\mathrm{d}}\rho VZ\mathrm{e}^{-E_{\mathrm{a}}/RT}(\mathrm{CHP})_0^{\mathrm{m+n}}(1-\alpha)^{\mathrm{m}}\alpha^{\mathrm{n}} \qquad (6)$$

where E_a: activation energy, J mol^{-1}; R: universal gas constant, J mol^{-1}; T: absolute temperature, K; Z: frequency factor, (mol^{-1})$^{m+n-1}$ s^{-1}; α: conversion, dimensionless.

Considering that not all of the products for reaction had a catalytic effect, a proposed constant factor β, ranging from 0 to 1, which is fixed as 0.38 as the best value in this study, was added to modify the amount of catalyst. Equation (6) can be expressed as follows:

$$\dot{Q}=\frac{\mathrm{d}Q}{\mathrm{d}t}=\Delta H\rho VZ\mathrm{e}^{-E_{\mathrm{a}}/RT}(\mathrm{CHP})_0^{\mathrm{m+n}}(1-\alpha)(\beta\alpha)^{\mathrm{n}} \qquad (7)$$

According to the Prout–Tompkins rationale for autocatalytic reactions, the reaction order of autocatalytic reactions is based on the rate-determining step rather than the overall reaction order, despite the complex reactions of the follow-up reactions [20]. The Avrami–Erofeev rate law [25] was also considered in the modeling investigation of the autocatalytic reaction. Based on that work and the observations that the experimental curve appeared completely symmetrical, a reaction order of 0.5 was selected [4]: $m=n=0.5$. By inserting these kinetic parameters into the model, new model constants were fit, and the simulated data using this model are shown in Fig. 4. Although Fig. 3 reveals good agreement with the experimental data during part of the acceleration period, for the overall fit of this model attention should be paid to the first peak. The cause of the first peak was determined to have relatively little influence on the overall kinetics. According to the observation mentioned above, it might come from radicals decomposing, an oxidation reaction or vapor phase decomposition of CHP.

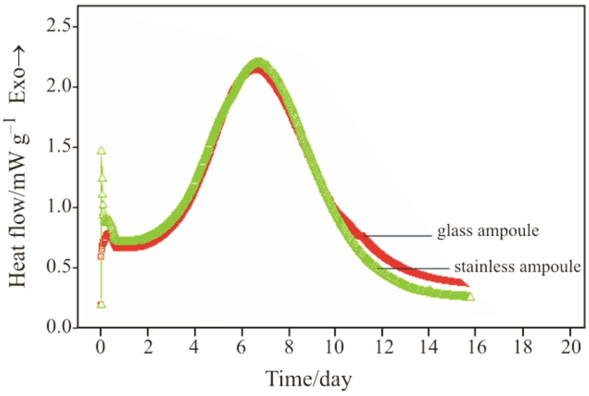

Fig. 3 Sample container material effect on the heat flow *vs.* time for the thermal decomposition in isothermal situation

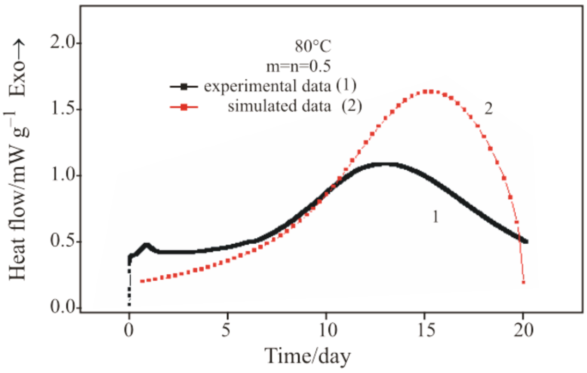

Fig. 4 Comparison of experimental and simulated data for 80 mass% CHP thermostatted at 80°C

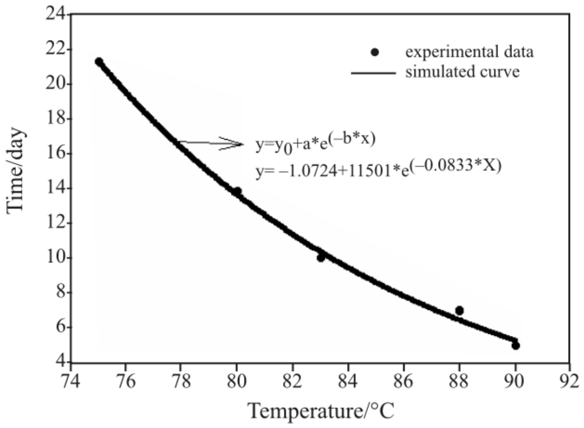

Fig. 5 Estimates of the isothermal time to maximum rate for 80 mass% CHP as a function of temperature

The experimental time to maximum rate data from Table 2 were used to predict expected isothermal time to maximum rate for temperatures other than those tested. Considering the experimental curves were symmetrical, the following was assumed: the reaction time under various temperatures can be regarded as twice time to maximum rate, and at a lower temperature more reaction time must be spent.

Based upon the observation, an exponential decay model with three parameters was simulated to predict the length of time required to finish the experiments at various temperatures, and the simulated equation was expressed in Eq. (8) as depicted in Fig. 5:

$$Y = -1.0724 + 11.501\exp(-0.0883X) \qquad (8)$$

The above constants represent the parameters y_0, *a* and *b*, as demonstrated in Fig. 5. Accordingly, the equation could be used to predict the time required to complete an experiment. For instance, if the experimental temperature was set at 95°C, about 6.2 days would be required to finish the experiment according to the equation. The comparison of the experimental and predicted time to maximum rate at experimental temperatures for 80 mass% CHP is presented in Table 4. The simulated results were very close to the experimental data.

Conclusions

Under isothermal conditions, CHP appeared to behave conspicuously differently in various temperature regions: at higher temperatures, exothermic decomposition appears to conform well to an n^{th} order Arrhenius model; and at lower temperatures, the decomposition can be better fit to an autocatalytic one. This phenomenon indicates that the dominant thermokinetic parameters shift with temperature conditions, and draws attention to cautiously applying decomposition models to transportation, storage, processing and disposal scenarios.

Thermokinetics determined by the autocatalytic thermal curve employed to optimize the simulation models showed that the experimental heat flow *vs.* time data reasonably agreed with the proposed model that had the reaction orders set to 0.5. Application of the Avrami–Erofeev rate law with attention paid to the first exothermic peak, the modifications made the simulations predict better. However, the thermokinetic parameters would be useful to assess the thermal explosion hazard of reactive substances, such as peroxides, and to determine other useful parameters, such as exothermic onset temperature (T_0), self-accelerating decomposition temperature (SADT), temperature of no return (T_{NR}), adiabatic time to maximum rate ($\mathrm{TMR}_{\mathrm{ad}}$), and adiabatic temperature rise (ΔT_{ad}).

A systematic research was applied to carry out the thermal decomposition modes at temperatures below those where a reaction can be thermally detected with adiabatic calorimetry. In summary, DSC and TAM methodologies are promising techniques for generating data on the study of decomposition kinetics for reactive chemicals, especially for an autocatalytic reaction.

Acknowledgements

The authors are indebted to the donors of the National Science Council (NSC) in Taiwan under the contract No. NSC-96-2625-Z-224-001 for financial support. The authors also gratefully acknowledge Mr. Anthony M. Janeshek of the Dow Chemical Co., Freeport, Texas, USA, for his valuable suggestions.

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DOI: 10.1007/s10973-007-8834-9