



Short communication

Chemical kinetics on thermal decompositions of cumene hydroperoxide in cumene studied by calorimetry: An overview

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ABSTRACT

Study on chemical kinetics related to the thermal decomposition of cumene hydroperoxide (CHP) in cumene is summarized in this work. It is of great importance to gather and compare the differences between these kinetic parameters for further substantial applications in the chemical industry and process safety. CHP has been verified to possess an autocatalytic behavior by using microcalorimetry (such as TAM and C-80) operated at isothermal mode in the temperature range from 70 °C to 120 °C. However, it exhibits a reaction of n-th order detected by non-isothermal DSC scanning and adiabatic calorimetry. By the isothermal aging tests, activation energy and frequency factor in $\log A(s^{-1})$ were averaged to be $(117.3 \pm 5.9) \text{ kJ mol}^{-1}$ and (11.4 ± 0.3) , respectively. Kinetic parameters acquired from data of inter-laboratories by using heat-flow calorimetry, the averaged activation energy and frequency factor in $\log A(s^{-1})$ were $(119.3 \pm 11.3) \text{ kJ mol}^{-1}$ and (12.0 ± 0.2) , respectively. On the analogy of results from adiabatic calorimetry, the activation energy and frequency factor in $\log A(s^{-1})$ were respectively averaged to be $(122.4 \pm 9.2) \text{ kJ mol}^{-1}$ and (11.8 ± 0.8) . Five sets of kinetic models in relation to autocatalytic reactions are collected and discussed as well.

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1. Introduction

Cumene hydroperoxide (CHP) is generally made from the cumene oxidation process using air or pure oxygen as the oxidant in a batch reactor. Two CHP molecules can further dimerize by the condensation reaction to produce a dicumyl peroxide (DCPO) and to give off a water molecule. In the phenol process, CHP is an intermediate used for producing phenol and acetone by acidic cleavage. Besides, CHP is also widely used as an initiator for making the acrylonitrile-butadiene-styrene (ABS) copolymer in a ABS plant. Fires and Explosions occurred in cumene oxidation reactor, CHP condensation reactor or CHP storage tank were the common types of incidents which were caused by the violent decomposition of CHP [1,2]. CHP 80 mass% has been classified to the class III (Fire hazards) by the NFPA, however, runaway incidents related to the reactive hazard of CHP in the lower concentration such as 35 mass% have been reported [3,4].

In 1951, Kharasch et al. studied the chemistry of thermal decomposition of CHP by analyzing products and establishing the

possible mechanisms in various solvents [5]. In these early years, researchers seldom devoted to the kinetic parameters related to thermal decompositions of CHP due to the chemical analysis of transient intermediates being difficult and time consuming. In 1970, Hattori et al. reported that the reaction order on the thermal decomposition of CHP in bubble column was determined to be near 1.0 by using iodometry [6]. However, in these twenty years, some major incidents caused by the thermal runaway in the process vessels containing CHP had ever been reported [1,2]. These incidents recalled and emphasized the noticeable relationships between the phenomena of thermal runaway on CHP associated with chemical kinetics. Duh et al. highlighted this viewpoint and these incidents occurred in Taiwan [1,2]. Hou et al. first proposed the autocatalytic behavior on thermal decomposition of CHP 80 mass% at temperature below 90 °C detected by the Thermal Activity Monitor (TAM) [7]. Miyake et al. and Di Somma et al. reported the autocatalytic exothermic reactions of CHP in the concentration range of 30 mass% to 80 mass% by spectroscopy, calorimetry, chromatography, equations of material balance and thermal balance [8–10]. Thereafter, five models related to the characteristics of autocatalytic decomposition on CHP were consequentially propounded by four laboratories [8,9,11–14].

The ASTM International Committee E27 on Hazard Potential of Chemicals had performed the search of calorimetric reference

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Nomenclature

A, A_{01}, A_{02}	Frequency factor [$\text{sec}^{-1}\text{M}^{1-n}$]
dT/dt	Self-heat rate [K min^{-1}]
E_a, E_{a1}, E_{a2}	Activation energy [kJ mol^{-1}]
k, k_1, k_2	Rate constant [$\text{s}^{-1}\text{M}^{1-n}$]
k^*	Pseudo zero-order rate constant [$\text{s}^{-1}\text{M}^{1-n}$]
$n, n_1, n_2, n_{11}, n_{21}, n_{22}$	Order of reaction
R	Gas constant [$8.314\text{ J g}^{-1}\text{K}^{-1}$]
α	Degree of conversion

materials and issued the E2781 [15]. Blaine had examined six candidate materials, including di-tertiary-butyl peroxide (DTBP), trityl azide, azobenzene, azobisisobutyronitrile (AIBN), cumene hydroperoxide (CHP), and phenyltetrazolthiol to identify possible calorimetric reference materials for evaluating kinetic parameters, CHP was one of the chosen compounds that ever been discussed [16]. Phenomena of macroscopic kinetics in relation to thermal decompositions of CHP/cumene solutions performed by DSC, RSST and ARC were published [3,4,17]. Nevertheless, the reported activation energies (E_a) and frequency factor ($\log A$, A in $\text{s}^{-1}\text{M}^{1-n}$) displayed the quite broad distinction, E_a varied from 100.0 to 176 kJ mol^{-1} and $\log A(\text{s}^{-1}\text{M}^{1-n})$ distributed from 11.25 to 14.89, respectively [16]. In recent years, some few astonishing $\log A$ (sec^{-1}) around 20 and E_a as high as 196 kJ mol^{-1} were successively reported [11,18,19]. Besides, several similar studies on the thermal decomposition of dicumyl peroxide (DCPO) which possessing the same cumyloxy radical and dissipating mechanism have been reported [20–23]. Though calorimetry offers a very high efficient approach to determine the chemical kinetics of a typical reaction with one-step global kinetic mechanism, the kinetic triplets differ between interlaboratory tests and sometimes the between-laboratory uncertainty larger than 20%. However, being existed significant discrepancy among these frequency factors and activation energies, the microscopic pinpoints or evidences have not been exaggerated to resolve the existing paradox. Obviously, the biased quantities of these activation energies and frequency factors in the published literature are too huge to be convincing so far forth. The relative standard deviation between laboratories recommended by the ASTM E2041 for activation energy, frequency factor, and reaction order have to be less than 9.8, 9.8 and 22%, respectively [24]. For this reason, the International Conference on Thermal analysis and Calorimetry (ICTAC) had taken a mathematical model to verify kinetic methods selected in worldwide laboratories. By using the thermal decomposition of calcium carbonate as a model compound, the inter-method reliability should be less than the simulated standard deviation a 39% for reaction order, a 16% for E_a , and a 25% for \log (frequency factor) [25].

Based on emphasizing the mentioned reasons and to solve the disputes for long views, an objective for declaring the gigantic differences in activation energy and frequency factor is ardently desired to be executed now. Especially, the accurate kinetic parameters are of great importance in the following aspects:

- (1) Optimization for the cumene oxidation process with controllable CHP concentrations (rate constant of oxidation versus thermal decomposition).
- (2) Emergency relief system design of cumene oxidation reactor such as vent sizing and mass flow rate (analytical equation for vent sizing versus rate constant).
- (3) Evaluation of a safe reaction region for cumene oxidation reactor (reactor parameters versus rate constant).

- (4) Emergency response base on the temperature with respect to time curve such as emergency cooling and bottom dumping (self-heat rate versus rate constant).
- (5) Linkage between lumped kinetics and stepwise kinetics of elementary reactions.
- (6) Relationship between n -th order reaction and autocatalytic reaction.
- (7) A possible candidate of kinetic reference materials for thermal analysis and adiabatic calorimetry.

In order to make better uses of the kinetic parameters in the above mentioned applications, it is cardinal to have the kinetic triplets within acceptable uncertainty. Consequently, a summary work on searching precise kinetic parameters is imperative for the safety engineering to avoid oversizing or underestimating designs.

2. Experimental

2.1. Chemicals

Cumene hydroperoxide (CHP) with a purity of about 82 mass% was provided from local company in Taiwan. Cumene with the purity higher than 99.9% was purchased from Merck Company and used as a compatible diluent. CHP was stored in a refrigerator at the 4 °C environment for maintaining the purity. Samples of CHP in diluted concentrations were made of cumene and CHP in 82 mass%. Both chemicals were commercially available and were used without further purification.

2.2. Differential scanning calorimeter (DSC)

Dynamic scanning tests were performed by a Mettler TA-4000 system coupled with a DSC822^e measuring cell [26]. CHP samples were sealed in the disposable crucibles (ME-26732) which were used for highly exothermic reactions or decomposition reactions. The data acquisition system recorded the thermal curves and stored for further analysis. Scanning rates were selected to be 2, 4, and 10 °C min^{-1} in programmatic ramps from 30 to 350 °C.

2.3. Accelerating rate calorimeter (ARC)

An accelerating rate calorimeter (ARC), manufactured by Columbia Scientific Industries in Austin, Texas [27], was used to conduct the unrestrained CHP runaway experiments. Three types of test bomb made of titanium, Hastloy C, and stainless 316 with a volume of 10 ml were utilized. The thermal inertia were about from 1.2 to 4. The detailed performance and theory of the ARC instrument was proposed by Townsend or by ASTM E1981 [28,29]. Once the ARC system detected the temperature rate exceeding the sensitivity of 0.02 °C min^{-1} , then turned off the radiating heater and switched on the guard heaters for tracing the accelerating reactions. The temperature and pressure behaviors related to the violent thermal runaway of CHP samples can thus be explored by using an accelerating rate calorimeter.

2.4. VSPII(vent sizing packageII)

For conducting the highly exothermic reaction in the ARC, mass of sample was generally less than 3 g, the thermal inertia thus had a value larger than 2. For a larger phi-factor transcends a value of 2, the collected data will be distorted by the thermal inertia. This is the so-called phi effect. Even by using Townsend's methods for deconvoluting the effects of high phi-factor, data of the adiabatic temperature rise can be corrected accurately. However, the kinetics-related data such as self-heat rate and adiabatic time-to-maximum-rate cannot be recovered as precise as the real ones

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