Journal of Thermal Analysis and Calorimetry, Vol. 83 (2006) 1, 41–44

THERMAL PHENOMENA STUDIES FOR DICUMYL PEROXIDE AT VARIOUS CONCENTRATIONS BY DSC

K. W. Wu[1], *H. Y. Hou*[1] *and C. M. Shu*[2*]

[1]Doctoral Program of Engineering Science and Technology, National Yunlin University of Science and Technology (NYUST),
123, University Rd., Sec. 3, Touliu, Yunlin, Taiwan 64002, ROC
[2]Process Safety and Disaster Prevention Laboratory, Department of Safety, Health, and Environmental Engineering, NYUST,
123, University Rd., Sec. 3, Touliu, Yunlin, Taiwan 64002, ROC

Information about the kinetics and thermal decomposition of dicumyl peroxide (DCPO) is required for safety concerns, due to its wide applications and accident cases. To understand the inherent hazards during DCPO manufacturing, we selected various concentrations in different stages and analyzed them by differential scanning calorimetry (DSC). We evaluated thermokinetic parameters to set up a simple, but comprehensive kinetic model, with various tests conducted at heating rates of 2, 4, 6 and 10°C min^{-1}. Subsequently, we established a more efficient, resource-effective, and cost-effective model of safety evaluation for DCPO with different concentrations, according to thermokinetic parameters, such as activation energy E_a is 125.35 kJ mol^{-1}, frequency factor k_0 is $3.124\cdot10^{12}$ s^{-1}, reaction order n is 0.9 and heat of decomposition ΔH is 750.52 J g^{-1} for DCPO 99 mass%.

Keywords: *dicumyl peroxide, DSC, safety evaluation, thermokinetic parameters*

Introduction

Dicumyl peroxide (DCPO, $C_6H_5C(CH_3)_2OOC(CH_3)_2C_6H_5$) is widely used as a cross-linking agent for polyethylene (PE), ethylene vinyl acetate (EVA) copolymer, ethylene-propylene terpolymer (EPT), and also as a curing agent for unsaturated polystyrene (PS). In addition, DCPO is applied to various resins to improve physical properties in architectural materials, decorations, electronics, electric insulators, plastic foams, composite parts, footware, and so on [1]. If cured by DCPO, the materials above will have better heat resistance and persistent dimension stability.

Practically speaking, the most common monofunctional di-tertiary alkyl peroxide is DCPO [1]. Since it has highly commercial applications, but with different accident cases, its inherent hazards have drawn concern and its safety properties at various concentrations in each step need evaluating.

In 2003, a thermal explosion caused by DCPO, in Taiwan, damaged a reactor and its accessories. During manufacturing, either strong acid or sulfur dioxide (SO_2) is used as the potential catalyst. Under these conditions, cumyl alcohol (CA, $C_6H_5C(CH_3)_2OH$) combines with cumene hydroperoxide (CHP, $C_6H_5C(CH_3)_2OOH$) to produce DCPO. This step may incur thermal runaway incidents because the proxy group reacts with incompatible substances. Through a dehydration process, the concentration of DCPO is increased about 50 mass%. During alkalization, crystallization, and purification, the concentrations of DCPO are enhanced to 70, 94, and 99.3 mass%, respectively. As a potent screening tool, differential scanning calorimetry (DSC) has been used to evaluate thermokinetic parameters, such as activation energy E_a, frequency factor k_0, heat of decomposition ΔH, and decomposition kinetics, for reactive chemicals. By the ForK software, the kinetic model and parameters related to various DCPO concentrations can be calculated and, in turn, used to provide some information concerning DCPO plants and to establish emergency relief systems under upset conditions. It is possible to obtain the E_a by using the methods of Kissinger [2], from the dependence between heating rates and peak temperature. In this paper, we discussed the essential hazards of finished products DCPO of 99 mass% and the intermediate products from the chemical process.

Experimental

Samples

DCPO of 99 mass%, white crystal, was stored at room temperature, below 35°C. DCPO of 50, 70, and 94 mass% are intermediate products in the manufacturing process. All of them were from the Coin Akzo Nobel Chemical Industrial Co. in Taiwan.

---

[*] Author for correspondence: shucm@yuntech.edu.tw

1388–6150/$20.00

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

Methods

DSC was used to measure the difference between the heat flows to a sample and a reference pan, performed on a Mettler TA8000 system coupled with a DSC821^e measuring cell that could withstand relatively high pressure. STAR^e software was used for acquiring curve traces. A high–pressure sealed pan was adopted to avoid the evaporation of the DCPO during scanning. The evaporation phenomenon is an endothermic process that can distort the experimental signal of decomposition kinetics of peroxide. To approach thermal equilibrium, the scanning rate for the temperature-programmed ramp was set at 4°C min^{-1}. Other heating rates of 2, 6 and 10°C min^{-1}, were selected for comparison. To build up the numerical simulations for the kinetic model, ForK software (Formal Kinetic Models), developed by ChemInform Saint Petersburg (CISP) Ltd., was used in this study [3].

Results and discussion

Thermal analysis

We focused on the thermal analysis of DCPO of 50–99 mass%. Figure 1 displays the heat evolution *vs.* temperature for the thermal decomposition of different DCPO finished and intermediate products by comparing experimental data with the simulated one. In practice, the onset temperature T_0 of DCPO 99 mass% decomposition was estimated at 123.47°C by DSC at heating rate of 4°C min^{-1}. In accordance with the experimental results, the reaction model was identified as the *n*-order reaction. Therefore, the temperature dependency of the reaction rate follows the Arrhenius law as expressed in Eq. (1) [4]:

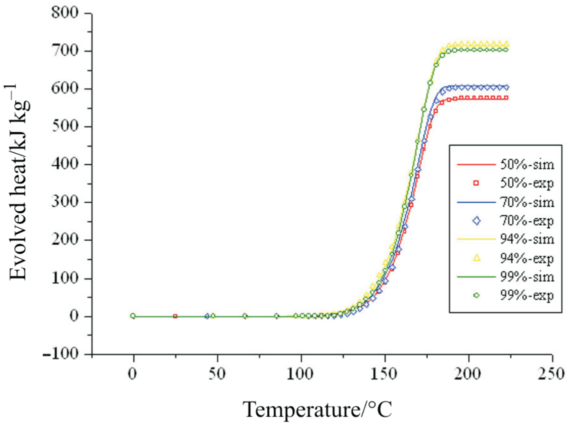

Fig. 1 Evolved heat (ΔH) *vs.* temperature (T) of DCPO between numerical simulations (sim.) and experimental data (exp.) of heating rate 4°C min^{-1}

$$k(T)=k_0 e^{\left[\frac{-E_a}{RT}\right]} \qquad (1)$$

The thermal decomposition hazards at various DCPO concentrations were characterized by using the dynamic screening experiment and comparing with the thermal analysis software (ForK). By DSC data, Fig. 1 depicts the simulated *n*-order model based by ForK. In Table 1, the ΔH and the temperature parameters for DCPO [5] were compared with the values in literature. The decomposition products of DCPO 94 and 99 mass% were carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), CA, phenol (C_6H_5OH), and acetophenone ($C_6H_5COCH_3$). The impurity composition of DCPO 50 and 70 mass% was cumene hydroperoxide (CHP), cumyl alcohol (CA), benzoic acid, acetone, and phenol.

Here, we merely compared the exothermic heat for different concentrations of DCPO. Discussion of the effects of impurities will be conducted in the future.

The exothermic heat for DCPO of 99 mass% was 750.52 J g^{-1}; a material is usually judged as an inherent hazardous one when its heat of reaction exceeds 250 J g^{-1} [6]. In addition, the DCPO of 50 mass% was 574 J g^{-1}, was lower than 99 mass%, but it had high heat of reaction impurities, such as CA and CHP [7]. Accordingly, we could not ignore the inherent hazards of the DCPO of 50 mass%. The other 50 mass% of DCPO are about 1~10 mass% CHP, and 30~40 mass% CA.

The stoichiometric reaction could be expressed as follows:

$$C_6H_5C(CH_3)_2OOH+C_6H_5C(CH_3)_2OH\xrightarrow{\text{strong acid}}$$
$$C_6H_5C(CH_3)_2OOC(CH_3)_2C_6H_5+H_2O+\text{heat}$$

The heat of decomposition of CHP was determined as 1200 J g^{-1}, indicating intermediate product

Table 1 Heat and the temperature parameters of decomposition of the DCPO by DSC and compared with values in literature

Mass%	T_0/°C	T_p/°C	ΔH/J g^{-1}	ΔH (99 mass%)[5]
50	122.86	168.58	574.00	x
70	123.21	168.95	607.40	x
94	124.08	169.21	715.80	x
99	123.47	169.78	750.52	631

x: not detectable

Table 2 Thermokinetic parameters of DCPO of 99 mass% by DSC and compared with values from other methods

Sourses	$\ln k_0$/s^{-1}	n	ΔH/J g^{-1}	E_a/kJ mol^{-1}
DSC-STAR^e	28.75	0.86	741.15	125.39
ForK	28.77	0.90	750.52	125.35
Kissinger's method				118.03
Coin Chem. Ind.	x	x	781.00	134.50

x: not detectable

could result in an unexpected reaction if triggered by the abnormal process variations.

Kinetic analysis

The typical DSC curves of DCPO at heating rates of 2, 4, 6, and 10°C min^{-1} are shown in Fig. 2. Tables 2 and 3 illustrate the kinetic parameters estimated by ForK, based on the four experimental curves. Obviously, they all fit well, as can be seen in Fig. 2. From Fig. 2, the DSC data could be corrected and improved to be the reliable ones, which were based on Fig. 2, Eqs (1) and (2). We could simulate DSC heating rate 8, and 12°C min^{-1} without experiments by Fig. 2.

To determine E_a, the Kissinger plot is used by many authors and demonstrated in Fig. 3. The results of the DSC heating curves can be analyzed by Eq. (2): Since $T=T_r+\beta t$; $dT=\beta dt$

$$\theta=\frac{d\alpha}{dt}=\beta\frac{d\alpha}{dT}=k_0 e^{\left[\frac{-E_a}{RT}\right]}(1-\alpha)^n \qquad (2)$$

where T is the temperature, T_r the reference temperature, t the time, α the conversion, β the heating rate, θ the reaction rate, and R the universal gas constant. Since the maximum rate takes place when dr/dt is zero, differential of the above equation gives Eq. (3):

$$\beta\frac{E_a}{RT_p^2}=k_0 n(1-\alpha)^{n-1}e^{\left[\frac{-E_a}{RT}\right]} \qquad (3)$$

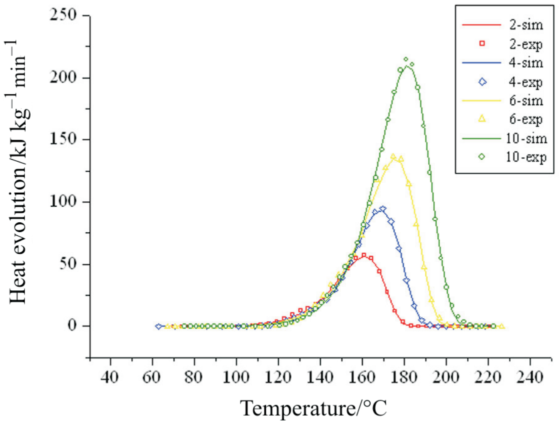

Fig. 2 Thermal decomposition of DCPO 99 mass% by various DSC heating rates, ranging from 2 to 10°C min^{-1}

The relationship of the conversion and the temperature is obtained by integrating the heat flow *vs.* time. Equation (3) can be expressed in the natural logarithm form, as revealed in Eq. (4):

$$\ln\left(\frac{\beta}{T_p^2}\right)=-\ln\left(\frac{E_a}{R}\right)\ln(k_0 n)+(n-1)\ln(1-\alpha_p)-\frac{E_a}{RT_p} \qquad (4)$$

where T_p is the peak temperature in the DSC exothermic curve while the maximum reaction rate occurs. The plot of $\ln(\beta/T_p^2)$ *vs.* $(1/T_p)$ is disclosed in Fig. 3.

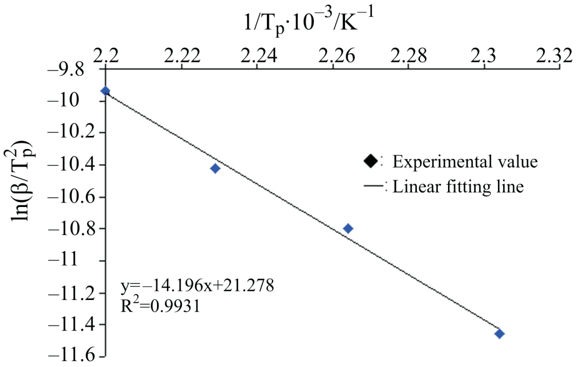

Fig. 3 Estimated E_a for DCPO 99 mass% by Kissinger's method

These methods show a linear dependence of the $1/T_p$ on the $\ln\beta$ and $\ln(\beta/T_p^2)$. E_a was calculated from the slope of the straight line obtained by linear regression. By comparing Eqs (2)–(4), we listed E_a values and other thermokinetic parameters by DSC and ForK in Tables 2 and 3. The $\ln(k_0)$ of DCPO 94 and 99 mass% was lower than 50 and 70 mass% due to its physical property as the solid. E_a has been equated with minimum energy that must be possessed by reacting molecules before the reaction occurs. Generally speaking, there are quite a few theories used to estimate E_a, as displayed in Table 2, and compared values with other methods. We ascertained that the reaction of DCPO is n-order by DSC experiments. If we simulated n=1 by ForK, the DSC data could not be fit the simulated line. However, so far we could not decide if the reaction order of DCPO is 1.

Table 3 Thermokinetic parameters of DCPO of 50–94 mass% by DSC and compared values by ForK

Mass%	Software	$\ln k_0$/s^{-1}	n	ΔH/J g^{-1}	E_a/kJ mol^{-1}
50	STAR^e	32.15	0.92	597.38	137.05
	ForK	32.27	0.94	574.00	137.38
70	STAR^e	34.16	1.01	622.06	144.43
	ForK	32.71	0.95	607.40	139.19
94	STAR^e	25.24	0.71	710.83	112.84
	ForK	27.46	0.83	715.80	120.00

Conclusions

If the finished DCPO product, a white crystalline solid, was properly kept at low temperature during transportation and storage stage, it would not initiate any runaway reaction, unless it went through the melting stage under high temperature. However, it is likely to incur accidents in chemical processes under higher temperature, incompatible substances, improper temperature control, human error, fire exposure, and so on. Future studies might also focus on reaction hazards at various DCPO concentrations of 50, 70 and 94 mass% during different stages, such as oxidation, condensation, synthesis, crystallization and purification. In this process, CHP will play a key role in loss prevention from runaway reactions for DCPO to a deeper extent so that a proactive accident prevention program can be adequately established.

Acknowledgements

The authors are indebted to Dr. Y. S. Duh of Jen-Teh Junior College of Medicine, Nursing and Management of ROC and Mr. T. S. Liao of NYUST for their constant support for this study. Finally, the authors appreciate the financial support of NSC 94-2211-E-224-008 and NSC 94-2622-E-224-005-CC3.

References

1 Organic Peroxides Product Bulletin, France, Atofina Chemical, Inc., USA 2000, p. 1.
2 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
3 A. A. Kossoy and E. Koludarova, J. Loss Prev. Process Ind., 8 (1995) 229.
4 H. S. Fogler, Elements of Chemical Reaction Engineering, 3rd Ed., New Jersey, USA 1999, p. 69.
5 J. Peng and K. Hasegawa, J. Loss Prev. Process Ind., 1 (1995) 287.
6 Guidelines for Chemical Reactivity Evaluation and Application to Process Design, CCPS, AIChE, New York, USA 1995, p. 13.
7 H. Y. Hou, C. M. Shu and Y. S. Duh, AIChE J., 47 (2001) 1893.

DOI: 10.1007/s10973-005-6983-2