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REACTION HAZARD ANALYSIS FOR CUMENE HYDROPEROXIDE WITH SODIUM HYDROXIDE OR SULFURIC ACID

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Organic peroxides (OPs) are very susceptible to thermal sources, chemical pollutants or even mechanical shock. Over the years, they have caused many serious explosions. Cumene hydroperoxide (CHP) is widely employed to produce phenol and dicumyl peroxide (DCPO) in the manufacturing process. Differential scanning calorimetry (DSC) and thermal activity monitor (TAM) were employed to determine the potential thermal hazards and thermokinetic parameters (such as exothermic onset temperature (T_0), maximum temperature ($T_{\max}$), and enthalpy (ΔH)) of CHP mixed with sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4). High performance liquid chromatography (HPLC) was used to analyze the concentration *vs.* time of CHP. When CHP is mixed with NaOH, the T_0 is induced earlier and reactions become more intricate than the pure CHP solution. CHP added to NaOH or H_2SO_4 is more dangerous than pure CHP alone. Depending on the operating conditions, NaOH and H_2SO_4 are the incompatible chemicals for CHP.

Keywords: *cumene hydroperoxide (CHP), differential scanning calorimetry (DSC), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), thermal activity monitor (TAM)*

Introduction

Organic peroxides (OPs) are very sensitive to thermal sources, chemical pollutants or even mechanical shock, causing many serious explosions worldwide. The characteristics of OPs are very complex. In essence, various thermal runaway accidents have been caused by OPs with other incompatible materials, such as acids, bases, metals, and ions, owing to the peroxy functional group (–O–O–) which is intrinsically unstable and reactive.

The threshold temperatures of many exothermic OPs are below 120°C and sometimes even as low as ambient temperature [1]. The United Nations (UN) suggested OPs must make a precise test of the self-accelerating decomposition temperature (SADT) in any specific commercial package [2]. SADT is the minimum ambient room temperature at which a reactive material of specified stability decomposes in a specified commercial package in a period of seven days or less. Values for SADT are determined to decide whether a substance should be subject to temperature control during transportation [3].

Cumene hydroperoxide (CHP) is widely employed to produce the phenol and the dicumyl peroxide (DCPO), and treated as an initiator in polymerization, especially for acrylonitrile-butadiene-styrene (ABS) copolymer in a manufacturing process [4]. In Kirk–Othmer, the hazard classification of CHP was recognized to be a flammable type or class III (fire hazard) by the National Fire Protection Association (NFPA) [5]. Thermal explosions or runaway reaction accidents caused by OPs, including CHP have been important issues in the past four decades. Consequently, CHP materials must be controlled and stored with caution, as any accidental mixing of industrial chemicals possesses a potential energy hazard during transport, storage, or processing [6].

This study investigated the thermal hazard of CHP with sodium hydroxide (NaOH) by DSC, HPLC and TAM, analyzing the potential thermal hazards of CHP mixed with NaOH or H_2SO_4.

Experimental

Materials

Fifteen and 80 mass% CHP purity were obtained from Fluka Co., DCPO of 80 mass% was produced by Unity Chemical Co., NaOH of 99 mass% was from Sigma-Aldrich Laborchemikallen, and H_2SO_4 of 96 mass% were purchased directly from the supplier (Mallinckrodt Baker), and then stored in a 4°C environment.

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Equipments

Glass tube tests

In glass tube tests with magnetic stirrer, CHP, CHP with NaOH (aq.) or CHP with H_2SO_4 were heated to reach the exothermic onset temperature (T_0), followed by terminating the heating step to observe the whole runaway excursion.

Differential scanning calorimetry (DSC)

Calorimetry was measured with a Mettler TA8000 DSC 821^e system which can acquire the heat flux for CHP and the composition products of heat flow. In the beginning of reaction, the thermal decomposition phenomenon was determined. The heating rate was set at 4°C min^{-1} with a range of 30–300°C. The test cell (Mettler ME-26732) could withstand high pressure until about 100 bar [7]. About 3 to 8 mg of the test samples was used for acquiring the experimental data. The test cell was sealed manually by a special tool equipped with Mettler's DSC, and the dynamic scanning was studied by programmed setting of the DSC equipment.

Thermal activity monitor (TAM)

Reactions can be investigated between 12 and 90°C, which is the working temperature range of this calorimeter. The thermal stability is maintained at a fixed temperature, constant to within $\pm 2\cdot 10^{-4}$°C, which allows fractions of a microwatt to be measured effectively [8].

Eighty mass% CHP was dispensed into disposable calorimetric glass and stainless containers, which were capped and then placed in the measuring and reference chambers, respectively. Samples were dispensed into the disposable calorimetric glass and stainless containers, capped and then respectively placed in the measuring and reference chambers. Measurements were conducted isothermally in the temperatures from 70, 80 and 90°C.

High performance liquid chromatograph (HPLC)

The HPLC instrument consists of a reservoir of mobile phase, a pump, an injector, a separation column, and a detector. Compounds are separated by injecting a plug of the sample mixture into the column. The different components in the mixture pass through the column at different rates due to differences in their partitioning behavior between the mobile liquid phase and the stationary phase. The presence of analytics in the column effluent is recorded by detecting a change in refractive index, UV-VIS absorption at a set wavelength, fluorescence after excitation with a suitable wavelength, or electrochemical response. Mass spectrometers can also be interfaced with liquid chromatography to provide structural information and help identify the separated analytics. Column XDB-C18, 4.6×250 mm (5 μm), and UV detection at 254 nm were used in the whole study.

Results and dicussion

Glass tube tests

Identification of the incompatible reaction of OPs is crucial since these materials mixed with catalysts could lower the exothermic onset temperature and trigger a thermal runaway or explosion [9]. Through experiments, NaOH and H_2SO_4 were incompatible material for CHP. CHP was heated to the runaway temperature, followed by mixing NaOH (solid) and finally terminated heating step. In Table 1, we could realize that CHP mixed with NaOH will induce the runaway reaction to occur earlier.

Table 1 Relationship between time and temperature by glass tube tests for CHP and CHP with NaOH

Time/min	Temperature/°C	
	15 mass% CHP	15 mass% CHP+ 99 mass% 3 N NaOH
0:0	170.0	170.0
0:20	174.2	184.4
0:40	178.5	200.0
1:00	182.9	–
1:20	188.5	–
1:40	194.7	–
2:00	200.0	–

Differential scanning calorimetry (DSC)

A simple approach for both evaluating runaway reaction and emergency relief condition was suggested. Thermal curves detectability by DSC combined with physical properties, pressure behaviors and mathematical methods offered an alternative course to assess the runaway hazard and to determine the basic data for the emergency relief system [10]. The basic thermokinetic data such as the heat of reaction, onset temperature, and the maximum temperature were evaluated for CHP mixed with NaOH or H_2SO_4. Figure 1 depicts the thermal runaway decomposition scanning with 80 mass% CHP. The T_0 was determined at about 80°C, the heat of reaction was about 1.152 J g^{-1} and the maximum temperature was 183°C. For a semi-manufactured product of DCPO

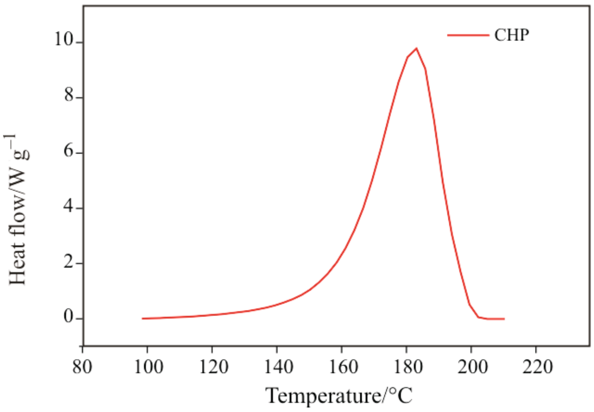

Fig. 1 Exothermic reaction of 80 mass% CHP by DSC test

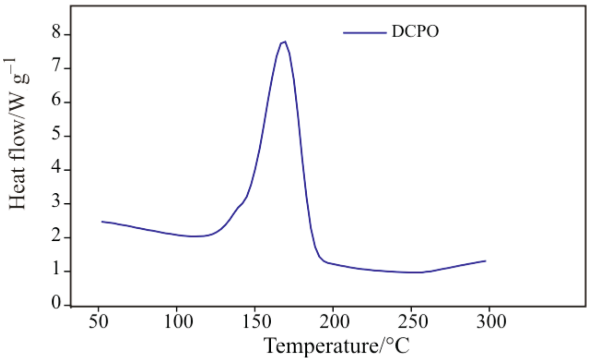

Fig. 2 Exothermic reaction of 80 mass% DCPO by DSC test

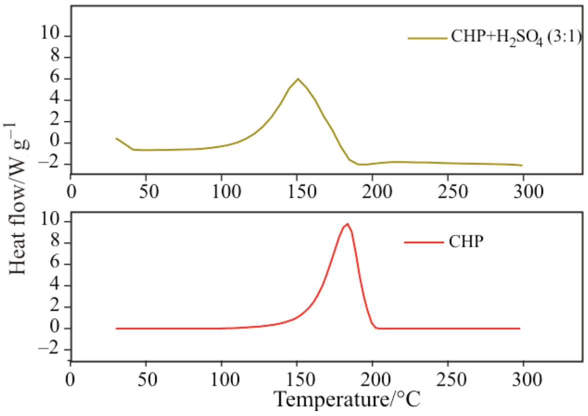

Fig. 3 Thermal curves for 80 mass% CHP and 3N H_2SO_4 by DSC tests

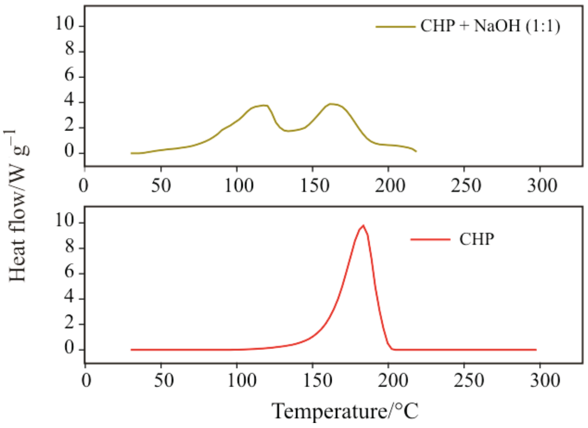

Fig. 4 Thermal runaway scanning with 80 mass% CHP and NaOH by DSC tests

Table 2 Scanning data of the thermal runaway decomposition for four samples by DSC

Sample	T_0/ °C	T_{max}/ °C	ΔH/ J g^{-1}
80 mass% CHP	80.00	163.60	1152.75
80 mass% DCPO	143.35	168.94	697.91
80 mass% CHP+ 3 N NaOH	40.00	98.25	826.37
80 mass% CHP+ 3 N H_2SO_4	53.00	150.00	1346.45

(Fig. 2), its T_0 and the heat of reaction were about 143°C and 698 J g^{-1}, respectively. In addition, thermal curves for 80 mass% CHP with 3 N H_2SO_4 or NaOH by DSC tests are shown in Figs 3 and 4. The 80 mass% CHP mixed with NaOH was the most dangerous reaction, as displayed in Table 2. When CHP is mixed with NaOH, the onset temperature will be lowered from 80 to 40°C. DSC was used to test the exothermic behavior of the mixture (CHP comparing with NaOH). We operated three tests (CHP mixed with NaOH) for reproducibility by DSC. CHP ($C_6H_5C(CH_3)_2OOH$) mixed with NaOH (strong base) had two peaks that included the first peak of the hydroxide ion (OH^-) dissociation and the second profile of peroxide (–O–O–) decomposition.

Thermal activity monitor (TAM)

Isothermal aging tests offer the advantage of thermal equilibrium within the reactant, which can generate more precise kinetics and simple interpretation [11]. Through experiments, we employed NaOH or H_2SO_4

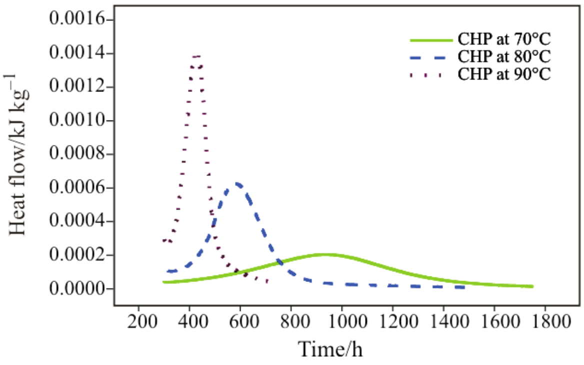

Fig. 5 Thermal curves for 80 mass% CHP by TAM at 70, 80 and 90°C

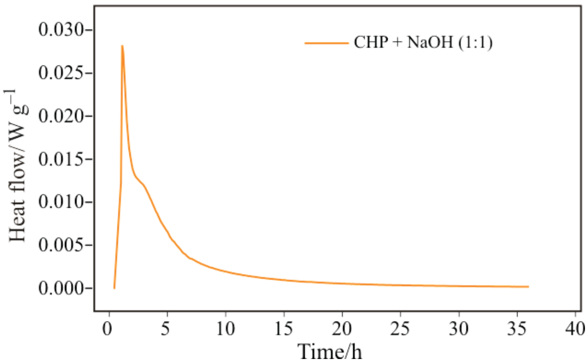

Fig. 6 Thermal curve for 80 mass% CHP+NaOH by TAM at 90°C

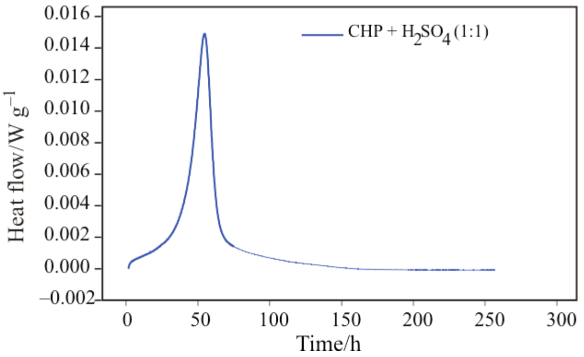

Fig. 7 Thermal curve for 80 mass% CHP and 3N H_2SO_4 by TAM at 90°C

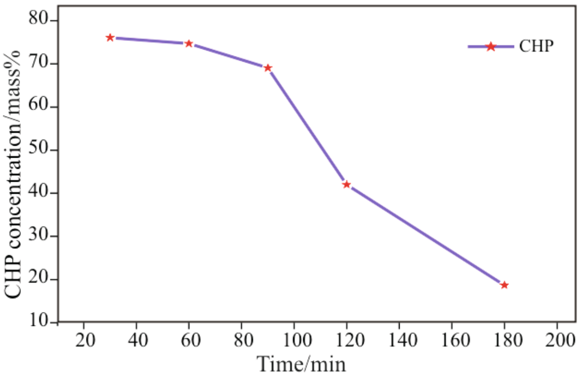

Fig. 8 Concentration profile of CHP by HPLC after setting at an oven temperature of 150°C

as incompatible for CHP. TAM was used to observe the exothermic situation at low temperature time. Figure 5 shows the exothermic time was extended and the peak was smooth to follow the temperature drop for 80 mass% CHP. Figure 6 shows the reaction was substantially exothermic and the second peak extended. Figure 7 demonstrates the maximum peak ascends from 0.0065 to 0.0149 W g^{-1} when 80 mass% CHP was added to 3 N H_2SO_4. This confirmed that CHP mixed with H_2SO_4 is even more dangerous than CHP alone.

High performance liquid chromatograph (HPLC)

As planned, experiment was set 30 s at oven temperature of 150°C by Barnstead. Subsequently, we can clearly see a mild reaction to take from 30 to 90 min, and acceleration to clearly occurs after 90 min, as can be seen in Fig. 8.

Conclusions

OPs are very susceptible to thermal sources, as caused by their active (–O–O–) bond [12–16]. Their acid group and OH$^-$ group will be delimited from Lewis acid or Lewis base. When CHP came in contact with NaOH, the T_0 of exothermic reaction was reduced from 80 to 40°C; and when CHP mixed with H_2SO_4, T_0 of exothermic reaction was lessened from 80 to 53°C. It demonstrated the application of the isothermal microcalorimetry for investigating the autocatalytic exothermic decomposition of CHP. And as CHP mixed with NaOH we observed a reaction was induced; after that the reaction was accelerated with the autocatalytic reaction (induction, acceleration, poise and blight). In consequence, the entire hazard was increased. When CHP was mixed with NaOH or H_2SO_4, the process became even more dangerous. Accordingly, the process must be controlled when CHP are catalysts or pH is used to adjust to avoid heat accumulation, fire or even thermal explosion.

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References

1 K. M. Luo, J. G. Chang, S. H. Lin, C. T. Chang, T. F. Yeh, K. H. Hu and C. S. Kao, J. Loss Prev. Process Ind., 14 (2001) 229.
2 United Nations, Committee of Experts on the Transport of Dangerous Goods, 14th Revised Ed., USA 2005, p. 205.
3 H. G. Fisher and D. D. Goetz, J. Loss Prev. Process Ind., 6 (1993) 183.
4 R. J. Schmidt, Appl. Catal., 89 (2005) 280.
5 NFPA 43B, National Fire Protection Association, 2007, Quincy, MA, USA.

6 Y. W. Wang, C. M. Shu, Y. S. Duh and C. S. Kao, Ind. Eng. Chem. Res., 40 (2001) 1125.
7 STAR^e Software with Solaris Operating System, Operating Instructions, Mettler Toledo, Switzerland 2004.
8 H. Y. Hou, T. S. Liao, Y. S. Duh and C. M. Shu, J. Therm. Anal. Cal., 83 (2006) 167.
9 H. Y. Hou, Y. S. Duh, W. H. Lin, K. H. Hu and C. M. Shu, J. Therm. Anal. Cal., 85 (2006) 145.
10 Y. W. Wang, Y. S. Duh and C. M. Shu, J. Therm. Anal. Cal., 85 (2006) 225.
11 H. Y. Hou, C. M. Shu and Y. S. Duh, AIChE J., 47 (2001) 1893.
12 J. R. Chen, S. H. Wu, S. Y. Lin, H. Y. Hou and C. M. Shu, J. Therm. Anal. Cal., 93 (2008) 127.
13 S. H. Wu, Y. W. Wang, T. C. Wu, W. N. Hu and C.M. Shu, J. Therm. Anal. Cal., 93 (2008) 189.
14 R. H. Chang, J. M. Tseng, J. M. Jehng, C. M. Shu and H. Y. Hou, J. Therm. Anal. Cal., 83 (2006) 57.
15 J. M. Tseng, R. H. Chang, J. J. Horng, M. K. Chang and C. M. Shu, J. Therm. Anal. Cal., 85 (2006) 189.
16 J. M. Tseng, Y. Y. Chang, T. S. Su and C. M. Shu, J. Hazard. Mater., 142 (2007) 765.

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