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REACTIVE INCOMPATIBILITY OF CUMENE HYDROPEROXIDE MIXED WITH ALKALINE SOLUTIONS

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Cumene hydroperoxide (CHP) is classified as a flammable hazard in NFPA 43B. Fires or explosions induced by thermal hazards ascribed to the unstable hydroperoxyl or peroxyl groups are often reported. This sequence studies is aimed at the decomposition phenomena associated with the reactive and incompatible characteristics of CHP mixed with alkaline solutions. Various alkalines were used for comparing the relative impact of bases and effects on concentrations. Exothermic onset temperatures and heats of decomposition of these incompatible mixtures were performed by differential scanning calorimetry (DSC). Comparisons of exothermic onset temperature, peak power, heat of decomposition, etc., were assessed to verify the severity of incompatible hazards in these systems. When mixed with a small amount of the hydroxides (in the production or storage of CHP), CHP will be more labile or unstable because of lower exothermic temperature. In addition, to elucidate the final products and propose mechanisms of the reaction of CHP mixed with alkaline solution, the analytical results were carried out by GC/MS and IR. The exhibited reactivity was complicated and significantly affected by the alkaline solutions. The reaction schemes have been proposed in this study. These results are especially important in process safety design for producing CHP and its related compounds, such as phenol, α-cumyl alcohol (CA), acetophenone (AP), and dicumyl peroxide (DCPO).

Keywords: *alkaline solutions, cumene hydroperoxide, DSC, incompatible characteristics, thermal hazards*

Introduction

A wide variety of organic peroxides are available for the commercial needs of polymer manufacturers. They can be used as curing agents, initiators, hardeners, cross-linking agents, or drying accelerators. However, organic peroxides may cause severe fire and explosion incidents because of their thermal instability and reactive incompatibilities during transport, storage, or processing [1]. Decomposition of organic peroxides is accompanied by a substantial amount of heat and gas release, and in the case of thermal explosion or thermal runaway, will result in disaster. CHP is a typical organic hydroperoxide. It is produced via the oxidation of cumene with air in the presence of aqueous sodium carbonate as a catalyst, and has been used primarily in the production of acetone and phenol. CHP is also used as a catalyst for rapid polymerization, especially in redox systems, as a curing agent for unsaturated polyester resins, an initiator for polymerization of styrene and acrylic monomer, and a chemical intermediate for the cross-linking agent, DCPO, in Taiwan and around the world. Because its exceptional reactivity and oxidative capacity are widely used in research laboratories and industries, information on the hazards of CHP and its forming chemicals is published in the literature. A series of tests have been carried out to examine and evaluate the basic thermal hazards and kinetics of CHP decomposition properties [2–4]. Besides, chemical contaminations can accelerate decomposition of CHP. Accordingly, care should be taken to avoid mixing with contaminants, strong mineral acids, bases, and metals. These will initiate a rapid decomposition even at ambient temperature [5–7]. The results of the tests have proven helpful in establishing safe handling, storage, transportation, and disposal guidelines.

Basically, CHP is intrinsically unstable and reactive due to its relatively weak –O–O– linkage (bond-dissociation energy of 20 to 50 kcal mol^{-1}) [8] and hydroperoxy radical which is sensitive to heat and incompatible with many materials, such as acids, bases, metals, ions, etc. [5, 7]. Runaway incidents can occur in oxidation reactors, vacuum condensation reactors, or storage tanks [2, 9]. CHP is widely used now, yet its properties, reaction mechanisms and the procedures for safe handling remain a mystery to be explored. After many continuing researches and discussions, in 1986, the National Fire Protection Associations (NFPA),

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43B Code ‘Storage and Handling of Organic Peroxide Formulations’ classified CHP as a flammable type or class III [10]. In addition, the United Nations has even suggested that the transportable temperature must be lower than the SADT (self-accelerating decomposition temperature) in any specific commercial package [11], and the U.S. Department of Transportation (DOT) classified it as a hazardous material subject to packaging, storage and transportation.

The studies of runaway hazards and decomposition kinetics in various process conditions, as supported from open literature, have made certain progress. However, the reactive characteristics or thermal hazards of CHP with alkaline solution have not been clearly identified yet. In summary, this study addressed the following objectives: comparison of the thermokinetics or hazards among various alkalines with CHP in cumene itself; and characterization of the effects of various concentrations of hydroxides and strengths of base by calorimetry.

Experimental

Materials and methods

Samples

An 80 mass% solution of CHP in cumene purchased directly from the supplier was measured to determine both density and concentration, and then stored at 4°C. Standard alkaline solutions of KOH, NaOH, LiOH and $NH_{3(aq)}$ were delicately prepared. As planned, the concentration of contaminants was 1, 3 and 9 N, the dosage of CHP to hydroxides was chosen at a ratio of about 3:1. The typical phenomenon of CHP reacting with various ratios of NaOH was selected for comparative study. In addition, to simulate the effect of chloride ion, a screening thermal curve of CHP mixed with NaCl was also corroborated.

Differential scanning calorimetry (DSC)

Dynamic screening experiments were performed on a Mettler TA8000 system coupled with a DSC 821 measuring cell that can withstand pressures as high as 100 bar. STAR^e software system was used for acquiring thermal curves and data analysis [12]. The scanning rate for the temperature-programmed ramp was chosen to be 4 K min^{-1} for sustaining thermal equilibrium within the reaction system.

Gas chromatography/mass spectroscopy (GC/MS)

The reaction products were determined and analyzed by using an Agilent 5973 GC/MS system, Agilent 19091S-433 gas chromatograph with a 30.0 m×250 μm×0.25 μm column, 80–180°C (10°C min^{-1}), injection temperature, 280°C; detect temperature, 280°C. The products were determined by comparing with the standard mass spectrometry of organic compounds, and fragmentation pattern.

Infrared spectrometry (IR)

The decomposition experiments of CHP/NaOH mixtures were carried out in the ampoules under an isothermal oven temperature of 180°C after complete decomposition. The decomposition products were identified by IR spectrometer, Shimadzu 8400S, of which the resolution of detection was set as 0.85 cm^{-1}.

Results and discussion

Thermal runaway decomposition scanning on DSC measurements

The onset temperature (T_0) and heat of decomposition (ΔH) of CHP with various hydroxides, NaOH, KOH, LiOH, and $NH_{3(aq)}$ can be acquired by using a DSC dynamic scanning test. From DSC thermal curves, Fig. 1 shows the typical heat flow curves *vs*. temperature for the thermal decomposition of 80 mass% CHP in cumene solution with various hydroxides. Thermal curves indicate the reactivity for CHP with impurities of aqueous hydroperoxides; the T_0 conspicuously decreased and impelled the reaction process to be complicated. The exothermic peak apparently changed from a single to twin peaks, which reveals that the reaction between CHP and hydroxides will be totally different from CHP itself, indicating that the hydroxide ion played the main role in the incompatible hazards. The exothermic onset of the first peak was close to 53°C. Moreover, adiabatic temperature rise from the first peak can cause the thermal decomposition of the second (main) exothermic peak to happen before CHP alone, and will lead to the worst exothermic hazard in the case of inadvertent mixing.

Data on CHP with impurities are listed in Table 1. The pH values of different hydroxides were between 11.5 and 13.9; however, no matter what kind of alkaline impurities, when mixed with hydroxide ions, CHP will be more hazardous and unstable because of lower exothermic onset temperatures. This will exacerbate the thermal hazard of the CHP or enhance the risk of handling CHP. The hydroxide ion dramatically reduced the onset temperature from 110°C to 53±5°C, indicating clearly that the hydroxide ions will increase the thermal hazard of CHP and raise the chance of triggering a runaway reaction. These experiments reveal that the thermal decomposition of CHP with various hydroxide ions could undergo a different decomposition pathway or mechanism in comparison to the CHP in cumene. CHP in cumene solution with small amount of water was conducted to determine the effect of water and used as a blank test compared to the incompatible systems. Apparently, the pure water blank test did not decrease the exothermic onset temperature in the thermal decomposition of CHP. Data on reaction of CHP with NaCl demonstrate that sodium ion (Na^+) or chloride ion ($Cl^–$) had not accelerated the thermal decomposition of CHP in cumene.

Furthermore, the characteristic curves of heat flow and reciprocal temperature recorded with DSC calorimeter at different dosing ratios of CHP/NaOH. In Figs 2 and 3, it appears that the mixture reactivity strongly depends on the ratio. In fact, as the dosing ratio increases from 20:1 to 1:1 and the concentration of NaOH from 1 to 9 N, the heat of decomposition decreases from nearly 1200 to 330 J g^{-1}. Small amounts of NaOH induce the initial decomposition behaviors and moderate the main thermal behavior of CHP in cumene. Hence, we can consider that in the first stage of the interaction of NaOH with CHP reaction, salts are formed. These salts exist in the form of peroxy anions with a relatively little-solvated anion, $ROO^–$ [13, 14]. As CHP decomposes, the composition of peroxy anions changes in favor of alkoxy anions, $RO^–$ [14]. The major route to products and thermal hazards should be relying on the interaction of CHP with alkoxy anions.

Physical data on thermal analyses are listed in Table 2. With the dose of hydroxide ion being raised, the total heat of decomposition was curtailed from 1214 to 336 J g^{-1} instead. This indicates that the injected reactant, NaOH, will react with CHP to produce another product via the other mechanisms; besides, the exothermic temperature and the heat of decomposition were strongly changed.

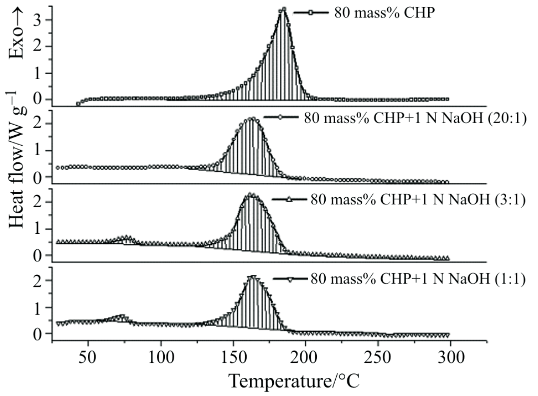

Fig. 2 Thermal decomposition comparison of CHP with various dosing ratios of NaOH by DSC tests

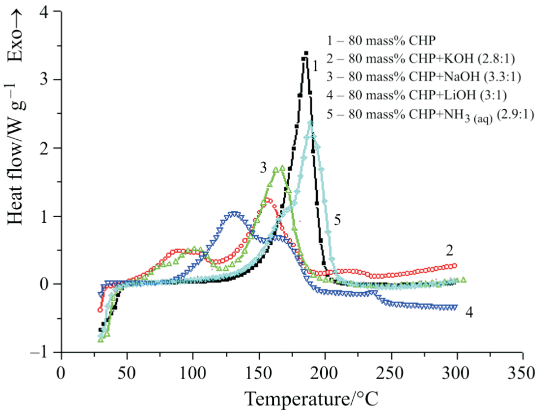

Fig. 1 Thermal decomposition of CHP with various alkalines compared to CHP itself in cumene by DSC tests

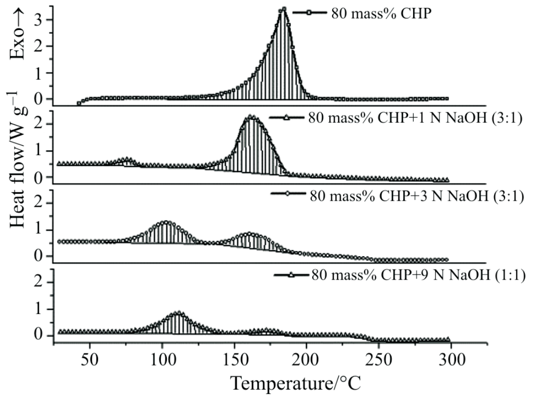

Fig. 3 Thermal decomposition comparison of CHP with various concentrations of NaOH by DSC tests

Table 1 Heat of decomposition and initial exothermic temperature of CHP with various alkalines

Experiment	80 mass% CHP/ mg	Incompatiblity			CHP/contaminant ratio	T_0/°C	T_{peak2}/°C	ΔH/J g^{-1}
		material	mass/mg	pH value				
1	5.6	–	–	–	–	110	188	1.214
2	6.4	1 N KOH	3	13.9	2.8:1	55	157	1.077
3	5.0	1 N NaOH	1.5	13.4	3.3:1	58	164	1.126
4	5.9	1 N LiOH	1.8	12.1	3:1	48	164	1.010
5	5.8	1 N $NH_{3\,(aq)}$	2.0	11.5	2.9:1	54	187	1.099
6	3.2	H_2O	1.3	7.9	2.5:1	100	165	1.107
7	6.5	NaCl	2.4	7.6	2.7:1	105	155	1.135

T_{peak2} – 2nd peak temperature

Table 2 Heat of decomposition and initial exothermic temperature of CHP with various dosing ratios and concentrations

Experiment	80 mass% CHP/ mg	NaOH concentration/N	CHP/NaOH ratio	T_0/°C	1st peak		2nd peak		Total ΔH/J g^{-1}
					T/°C	ΔH/J g^{-1}	T/°C	ΔH/J g^{-1}	
1	5.6	–	–	110	–	–	188	1214	1214
2	5.7	1	20:1	55	72	5	164	952	957
3	4.8	1	3:1	52	77	43	163	849	892
4	4.5	1	1:1	49	73	50	163	792	842
5	4.8	3	3:1	58	112	232	164	216	448
6	5.8	9	1:1	59	115	313	173	23	336

Spectroscopic analyses of the products after decomposition

To identify the main reactions occurring in CHP/NaOH mixtures, the temperature and the composition pattern of the reaction system had to be measured by GC/MS and IR runs. At temperatures exceeding 130°C, the principal potential decomposition products of CHP mixed with NaOH are α-methylstyrene (AMS), acetophenone (AP), 2-phenyl-2-propanol (which is also called CA), and phenol [5]. The chromatography of the three main products after incompatible reaction from GC/MS is shown in Fig. 4. The mass spectra of products were accorded with the standard mass spectrometry and fragmentation pattern.

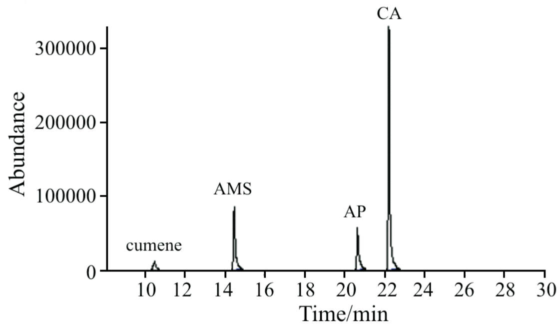

Fig. 4 Product analysis of the incompatible decomposition of CHP mixed with NaOH by GC/MS

The application of IR spectroscopy to the analysis of the final products can be regarded as direct evidence for proposing the decomposition mechanism of CHP with NaOH. Figure 4 illustrates infrared absorption spectra for various products in an incompatible process after decomposition. From the variations on functional groups, the varied products were assessed and identified as AMS, AP, and CA, while the vapor mixtures were not definitely probed. CHP in the presence of strong bases in nonaqueous media may decompose at 40–90°C to ketone without forming free radicals [13]. The analyzed IR spectra were focused on the 4000–400 cm^{-1} spectral region. The reaction was performed in aqueous solution of CHP/NaOH mixtures. The 1800–500 cm^{-1} spectral region was expected to go through important change during the reaction. A detailed investigation by means of IR analysis on both products and by-product was therefore carried out. In the fingerprint region, peaks at 1683, 1175 and 1160 cm^{-1} seem to be characteristic for the main products, AP and CA, and 556 and 591 cm^{-1} for the by-product, AMS. The higher intensity bands in the IR, at 1683 cm^{-1}, were assigned to the carbonyl stretching, and the presence of a band at 1160 and 1175 cm^{-1} seems to establish the existence of the tertiary alcohol stretching and the carbon–oxygen single bond. We chose to compare the reaction mixture with final product to show the main functional groups' evolution during the experiment. As illustrated in Fig. 5, rapid distinction of the three species was allowed.

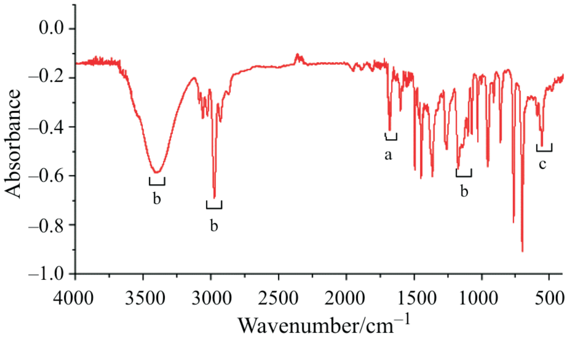

Fig. 5 Infrared spectra of CHP with NaOH catalyzed after complete decomposition; characteristic functional groups of a – AP, b – CA and c – AMS

Based on the analysis of products, a radical reaction mechanism was presumed, which is disclosed in Fig. 6. These reveal the decomposition pathways initiated by these additives are significantly different or there were nonequal branching ratios in the decomposition mechanism. CHP decomposed via complicated pathways in various solvents that are called free radical 'induced' decomposition [15, 16]. CHP had two primary reactions from elevated temperature to form (1) CA through reaction exposure of cumene solvent and (2) AP plus methanol by thermal decomposition without solvent [5, 7]. Furthermore, under the influence of strong acids, the reaction mainly results in the formation of phenol and acetone [17, 18]. The base-catalyzed route to AP, CA, AMS and methanol was also depicted. Following the mentioned mechanisms, a semi-empirical method with bond strengths in diatomic molecules was derived from molecule structure for the type of heat of reaction under investigation [19]. The reaction coordinate *vs*. potential energy of CHP via different pathways is recorded in Fig. 7. The reactant at various energies was controlled to exceed the activation barrier (E_a), deriving four reaction pathways with corresponding heats of reaction. The shortage of elementary data of E_a is seen to be uncertain, which needs further study on reaction dynamics. According to thermodynamics, the reaction might incline to generate relatively steady products, which are AP and methanol.

IR spectrometry verified that the CHP in cumene might react with each other to form CA and AP; the evident decomposition mechanism of CHP was proposed. Scheme 1 shows the homolytic decomposition of CHP is influenced by the reaction solvent present in the reactor [5, 13, 17, 20].

1. $C_6H_5(CH_3)_2COOH + C_6H_5(CH_3)_2CH \xrightarrow[KT]{} 2C_6H_5(CH_3)_2COH$

or

2. $C_6H_5(CH_3)_2COOH \rightarrow C_6H_5(CH_3)_2CO\bullet + HO\bullet$

3a. $C_6H_5(CH_3)_2CO\bullet \rightarrow CH_3COC_6H_5 + CH_3\bullet$

3b. $CH_3\bullet + C_6H_5(CH_3)_2CH \rightarrow CH_4 + C_6H_5(CH_3)_2C\bullet$

4. $HO\bullet + C_6H_5(CH_3)_2CH \rightarrow H_2O + C_6H_5(CH_3)_2C\bullet$

5. $C_6H_5(CH_3)_2CO\bullet + C_6H_5(CH_3)_2CH \rightarrow C_6H_5(CH_3)_2COH + C_6H_5(CH_3)_2C\bullet$

6. $2C_6H_5(CH_3)_2C\bullet \rightarrow [C_6H_5(CH_3)_2C-]_2$

Scheme 1 Mechanistic pathway for homolytic decomposition of CHP

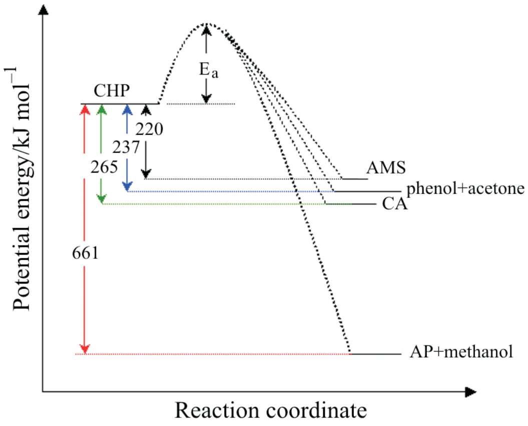

Fig. 7 Analysis of the decomposition of CHP path on the potential energy

Decomposition of CHP mixed with alkaline solutions

From thermal analysis under the influence of NaOH, the CHP, like most hydroperoxides, is a weak acid [17]. Hence, we can consider that in the first step of the decomposition mechanism of CHP with NaOH, salts are formed which exist in the form of ion pairs with relatively little solvated anion in the system [13]. From the data on thermal analysis of CHP in cumene with additional influences of NaOH, the characteristics and mechanisms were remarkably different from CHP itself. The sodium cation (Na^+) had no effects in the solution, namely, the various products formed in the decomposition of intermediate hydroperoxide under the influence of the base or the hydroxy ion. The decomposition mechanism of CHP was proposed under alkaline in the following Scheme 2.

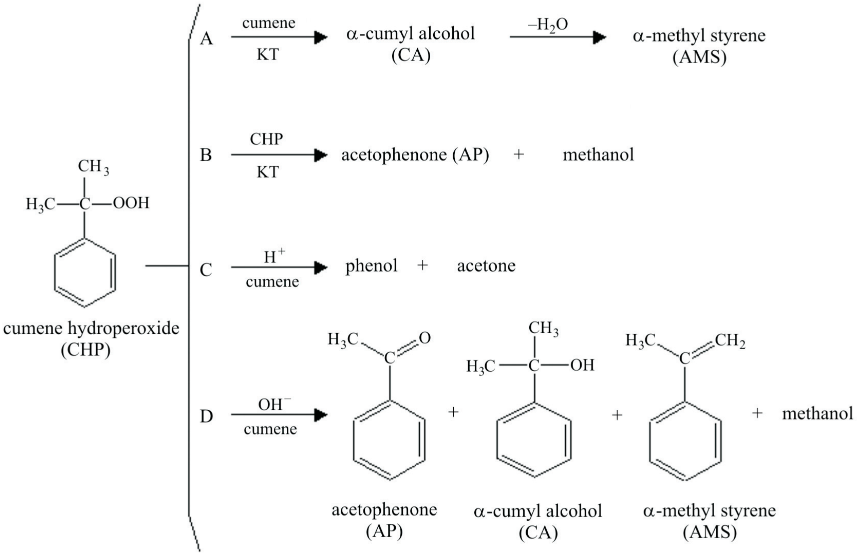

Fig. 6 Selected reaction pathways of CHP

7. $C_6H_5C(CH_3)_2OOH+NaOH\rightarrow$
$C_6H_5C(CH_3)_2OO^-Na^++H_2O$

8. $C_6H_5C(CH_3)_2OO^-+C_6H_5C(CH_3)_2OOH\rightarrow$
$C_6H_5(CH_3)_2CO^-+C_6H_5(CH_3)_2COH+O_2$

9a. $C_6H_5(CH_3)_2CO^-+C_6H_5(CH_3)_2COOH\rightarrow$
$CH_3COC_6H_5+CH_3OH+C_6H_5(CH_3)_2CO\bullet$

9b. $C_6H_5(CH_3)_2CO^-+CH_3(C_6H_5)CHOH\rightarrow$
$C_6H_5(CH_3)_2COH+HO(CH_3)(C_6H_5)C\bullet$

10. $HO(CH_3)(C_6H_5)C\bullet+C_6H_5C(CH_3)_2OOH\rightarrow$
$CH_3COC_6H_5+H_2O+C_6H_5(CH_3)_2CO\bullet$

11. $2HO(CH_3)(C_6H_5)C\bullet\rightarrow$
$CH_3COC_6H_5+CH_3(C_6H_5)CHOH$

Scheme 2 Mechanistic pathway for alkaline decomposition of CHP

Conclusions

Identification of the incompatible reaction of organic peroxides is crucial since these materials can generate catalysts that could lead to a lower exothermic onset temperature and trigger a thermal runaway or explosion. The alkaline decomposition of CHP leads to the formation of economic products, CA, AP and AMS, but the thermal curves induced by sodium hydroxide on CHP decompositions will result in the most hazardous situations, two exothermic peaks and lower onset temperatures. Obviously, CHP reacts violently by thermal activation, or acids, bases and other impurities. In this study, the reactive incompatibility of CHP mixed with alkaline solution was confirmed by systematic methodologies. The reactive hazards of CHP were also proposed.

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