Reactions of cumene hydroperoxide mixed with sodium hydroxide

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Abstract

Decomposition of cumene hydroperoxide (CHP) was undertaken in a free radical chain reaction. The peroxyl group is very active and unstable, while the remainder of the molecule is inert. CHP reacted with various concentrations of dilute sodium hydroxide as a catalyst to cleave at ambient and decomposition temperature. The products were verified by GC/MS, and were quantitatively analyzed by chromatography. CHP cleaved heterolytic with NaOH at 250 °C, whose major product was dimethylphenyl carbinol (DMPC); however, the main products become acetophenone and α-methylstyrene by cleaved homolytic pathway. The catalytic concentrations of NaOH significantly affected the branch ratios of DMPC under decomposition. Based on the experimental results, a radical cleavage mechanism was proposed. To sum up, the reaction parameters, such as temperature, Lewis base, etc., could affect the incompatibilities and decomposition pathways for proper CHP cleavage process. In addition, exothermic onset temperatures (T_0) and heat of decomposition (ΔH_d) of incompatible mixtures and CHP itself were studied by differential scanning calorimetry (DSC). Comparisons of T_0, ΔH_d and peak power were assessed to corroborate the severity of thermal hazards. From the decay rate of CHP concentration, the reaction order was determined to be 0.5, and the Arrhenius parameters were measured as $E_a = 92.1$ kJ/mol and frequency factor $A = 2.42 \times 10^{10}$ min^{-1}.
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1. Introduction

Organic peroxides are widely used as a source of free radicals to initiate a number of polymerization reactions, owing to the relatively weak oxygen–oxygen linkage (bond dissociation energy of 20–50 kcal/mol). However, organic peroxides also possess a potential hazard for which the peroxy radical is a pivotal factor. It may result in fire or explosion from contact with thermal sources, acid-catalyzed, base-catalyzed, metallic compounds, pollutants, and mechanical impact, etc. [1–3]. Based on the above-mentioned, organic peroxides are very unstable and active materials.

Cumene hydroperoxide (CHP) is produced via the oxidation of cumene with air in the presence of aqueous sodium carbonate as a catalyst. Even with various kinds of applications in the petrochemical industry, over 94.5% of the CHP

has been used in producing phenol and acetone through catalytic reaction [4]. Additional applicable purposes include use as a catalyst, a curing agent, and as an initiator for polymerization. CHP is an initiator for polymerization to produce the acrylonitrile–butadiene–styrene (ABS) resin [3], and is also a source material for producing dicumyl hydroperoxide (DCPO) by dehydration process in Taiwan and around the world. In the manufacturing process of DCPO, CHP is catalyzed by dilute about 45 mass% NaOH to yield α-cumyl alcohol (also called dimethylphenyl carbinol, DMPC) [5]. On 26 September 2003, inadequate control of a reaction led to the explosion of a DCPO production plant in Taiwan. The heat-releasing rate was much greater than the heat-removing rate in the batch reactor, and enormous pressure built up in the reactive system, exacerbated by improper venting and followed by an immediate explosion. Fires or explosions caused by the thermal runaway of organic peroxides have been important issues in the past three decades in Taiwan [6]. Incidents have been caused by thermal decomposition, external fire, and incompatibilities, because of thermal instability or reactive incompatibility of CHP. Calorimeters and

related methodologies for preventing reactive hazards of organic peroxides have been widely developed. DIERS (Design Institute for Emergency Relief Systems) technology of AIChE has also been useful for safe venting of runaway reactions incurred by organic peroxide in the early stages [7]. Runaway hazards and decomposition kinetics in various process conditions have been studied with various calorimeters, such as differential scanning calorimetry (DSC), thermal activity monitor (TAM), accelerating rate calorimeter (ARC), vent sizing package 2 (VSP2), and C80 [5–14]. However, the characteristics of decomposition and reaction mechanism reduced by base-catalyzed were not clearly identified for a long time.

The mechanism of free radical production from CHP involves the homolytic and heterolytic cleavage of the peroxide bond (–O–O–) to produce the cumoxyl radical. In this study, chromatographic instruments, GC/MS, GC and HPLC, were adopted to quantify the various concentrations of CHP and its related products. This study addressed the following objectives: (1) comparing and analyzing the various compositions of self-reactive or incompatible decompositions by chromatography, (2) acquiring the thermokinetics or hazards of CHP in cumene, and (3) proposing the possible decomposition mechanisms and major intermediate of CHP under base-catalyzed situations.

2. Experimental

CHP (Aldrich, 88 mass%) was prepared for thermal decomposition which was catalyzed by sodium hydroxide (NaOH) (Riede-de Haën, 99 mass%). As planned, NaOH was to be diluted for 1, 3, 6, and 9N with de-ionized water. Later, we used methanol (Mallinckrodt, 99.9 mass%) as the solvent to dilute the aromatic compounds. Because the boiling point and molecular weight of methanol were lower and less than aromatic compounds, it could be readily separated from solvent and aromatic compounds by GC/MS.

2.1. Reactants and catalyst

Samples of CHP (0.5 mL) were mixed with NaOH solutions (1, 3, 6, and 9N; 0.5 mL) in a glass vessel. This vessel was put inside a stainless steel one which was then placed in a high temperature furnace to create an isothermal condition. The conversion, selectivity, rate of CHP decomposition and the compositions of product were analyzed by GC/MS, GC, and HPLC.

2.2. Instruments and methods

2.2.1. Thermal decomposition analysis by DSC
Calorimetric measurements were conducted by using a Mettler TA8000 DSC 821^e system which can acquire the heat flow for CHP under thermal decomposition. The heating rate was set at 4 °C/min in the range of 30–300 °C. For an isothermal decomposition reaction, CHP was heated to 120, 130, 140, 150, and 160 °C, and held for enough time to assure CHP decomposed completely.

2.2.2. Analyses by various chromatography
Thermal decomposition of CHP and its decomposition products was determined by GC/MS Agilent 5973 Network. The conversion and selectivity rate were analyzed by an Agilent 6890 gas chromatograph (GC) equipped with a capillary column HP-1 (30 m × 250 μm × 0.25 μm); the decomposition products were quantified by both FID detector and HPLC equipped with a column Zorbax Eclipse XDB-C18 [4.6 mm × 250 mm (5 μm)] and an Agilent diode-array detector.

3. Results and discussion

3.1. Thermal hazard analysis

The heat of decomposition (ΔH_d) and exothermic onset temperature (T_0) of CHP can be obtained by DSC dynamic scanning tests. The heat flow curves versus temperature for the thermal decomposition of 88 mass% CHP and CHP mixed with 1N NaOH were recorded and depicted in Fig. 1. Thermal curves indicate conspicuous reactivity for CHP with NaOH solution; the exothermic peak was clearly altered from single to twin peaks and the T_0 of the first peak decreased from 109 to 60 °C. In the initial interaction of NaOH with CHP reaction, salts were generated and existed in the form of peroxy anions, ROO$^-$, and alkoxy anions, RO$^-$. Since the free radicals were presumably formed in the thermal decomposition of CHP under the influence of base or the hydroxy ion, the first peak of the related reaction obviously induced the second (main) exothermic peak. The experiments show the decomposition of CHP with NaOH solution may undergo a different mechanism in comparison to CHP itself. The DSC data are summarized in Table 1.

According to a previous study by Schmidt [15], CHP has to be operated at a mild temperature for safety reasons. Typically, the operating temperature of cumene oxidation for producing CHP is 82–90 °C, and the CHP accelerated thermal decomposition temperature is around 95–100 °C or more [15]. If sufficient heat of reaction is provided, CHP cleaved and catalyzed by
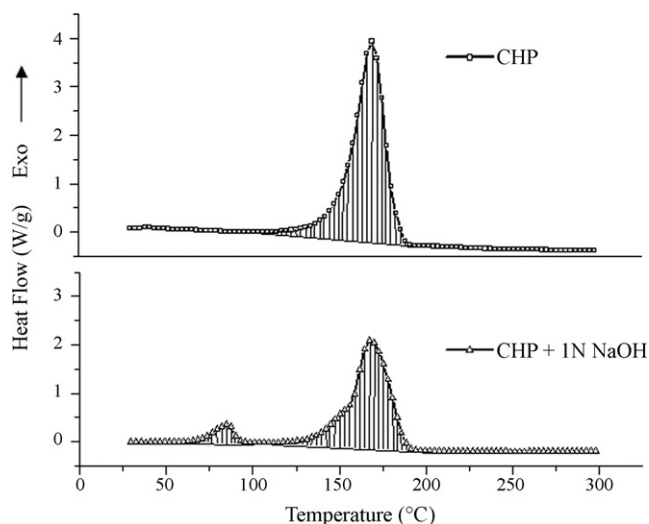

Fig. 1. Heat production vs. temperature for thermal decomposition of CHP and catalyzed by NaOH from DSC.

Table 1

Heat of decomposition and initial exothermic temperature of CHP with NaOH solution

Sample	T_0 (°C)	1st peak		2nd peak	
		T_p (°C)	ΔH (J/g)	T_p (°C)	ΔH (J/g)
CHP 88 mass%	109	–	–	170	1382
CHP 88 mass% + 1N NaOH	60	86	76	168	852

NaOH might reach the accelerated decomposition temperature. An overall investigation could establish the reason why the aforementioned batch reactor tanks exploded.

3.2. Thermal decomposition mechanisms for CHP and CHP/NaOH solution

3.2.1. Chromatographic data of the CHP decomposition

The composition of CHP was mainly CHP, cumene, 2-phenyl-2-propanol (DMPC), and acetophenone (AP). The components after CHP decomposition were determined by using HPLC at ambient temperature (Table 2). The conversion process can be inferred from the composition of the products. The decomposed products of CHP in liquid phase at various isothermal temperatures (120, 130, 140, 150, and 160 °C) proved the presence of acetone, α-methylstyrene (AMS), AP, DMPC, and phenol, which were clearly identified by use of a normal phase separation column associated within HPLC. Moreover, combining the heat flow curves with the ratios of CHP decomposition products, the variation of concentration could be regarded as direct evidence for proposing ΔH_d with respect to CHP concentration at isothermal tests. The ratios of decomposition at various isothermal temperatures are shown in Figs. 2–6.

Cleavage of the O–O bond of CHP molecule can be either heterolytic or homolytic. The number of electrons on a cleaved oxygen atom is the difference between heterolytic and homolytic cleavage. DMPC was produced through the heterolytic O–O scission of CHP; on the other hand, AP was yielded through the homolytic scission of the hydroperoxide [16].

Decomposition of CHP with catalyst, NaOH solution, yielded organic products, which were DMPC, AMS, AP, and copolymer. The GC/MS chromatographs for decomposition products of CHP mixed with NaOH solution are in Figs. 7 and 8.

3.2.2. Homolytic decomposition

Bryant et al. [17], Suppes and McHugh [18] and Lyavinets [19] proposed that the cleavage of CHP was through a free radi-

Table 2

Average composition products of CHP 88 mass% in 95% confidence limits

Compound	Standard deviation (S.D.)	Average (mass%)	95% confidence limit[a] (%)
CHP	2.27	88.0	88.0 ± 2
Cumene	0.02	4.6	4.6 ± 0.2
AP	0.15	3.3	3.3 ± 0.2
DMPC	0.19	2.5	2.5 ± 0.2

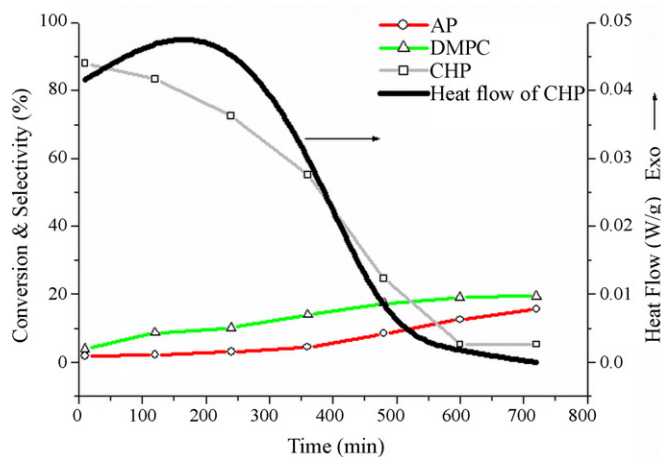[a] Data performed as mean ± S.D. of five experiments.

Fig. 2. Comparison of CHP at 120 °C on conversion, selectivity, and heat flow.
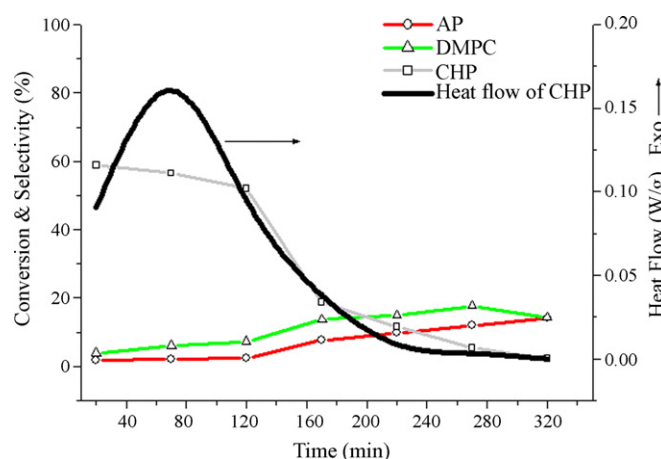

Fig. 3. Comparison of CHP at 130 °C on conversion, selectivity, and heat flow.

cal reaction and passed through β-scission to generate AP. This study investigated CHP mixed with NaOH solution in a high temperature furnace for 3 h under 200 °C isothermal condition. In the isothermal condition, a series of CHP homolytic scissions were carried out, and the reaction and thermal decomposition of CHP/NaOH solution was confirmed completely. Fig. 9
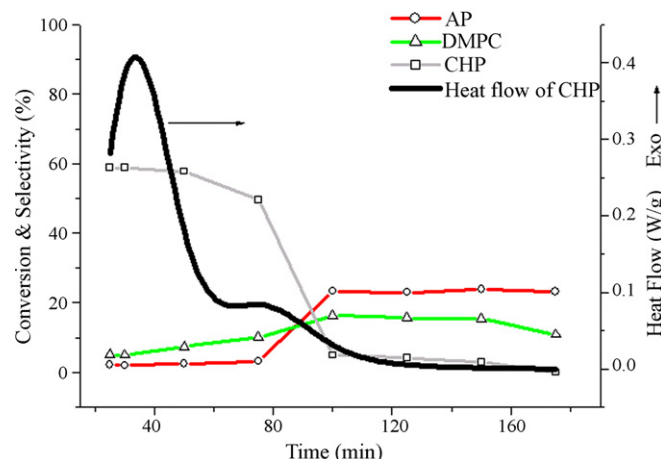

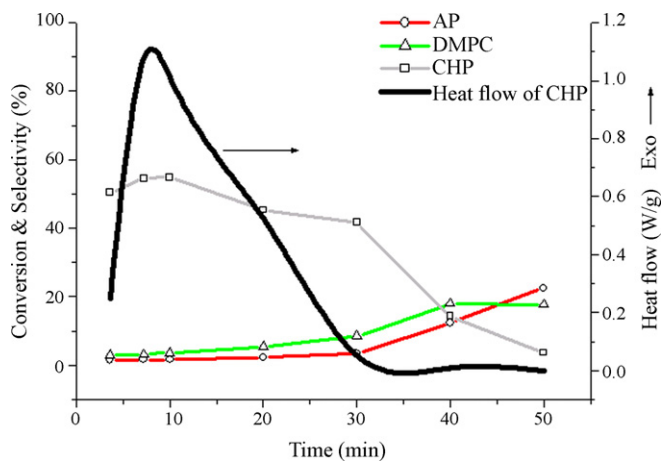Fig. 4. Comparison of CHP at 140 °C on conversion, selectivity, and heat flow.

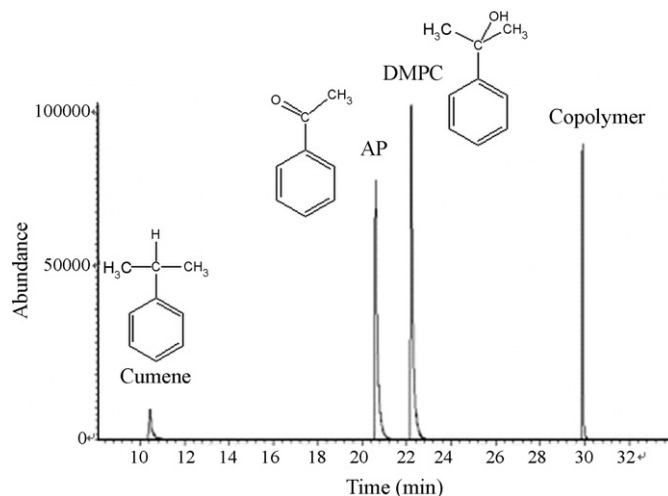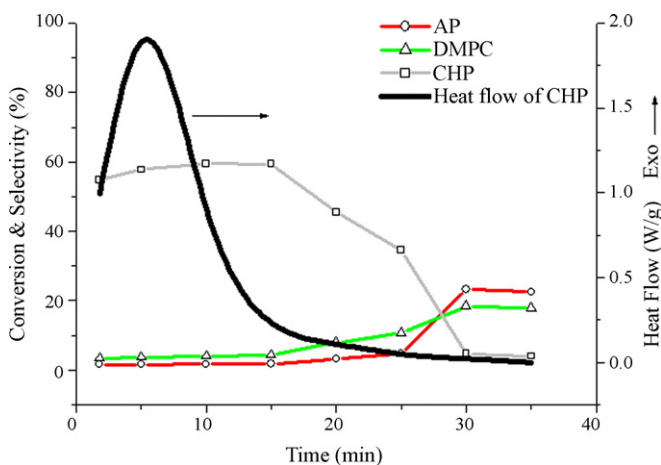Fig. 5. Comparison of CHP at 150 °C on conversion, selectivity, and heat flow.

Fig. 6. Comparison of CHP at 160 °C on conversion, selectivity, and heat flow.

clearly demonstrates the relative concentrations of cumene, AP, DMPC, and AMS. Based on CHP radical mechanism by Sato and Shimizu [16] and He et al. [20], NaOH has a significant influence on the conversion of CHP, and with increasing the concentration of NaOH, the ratio of DMPC increased rapidly.
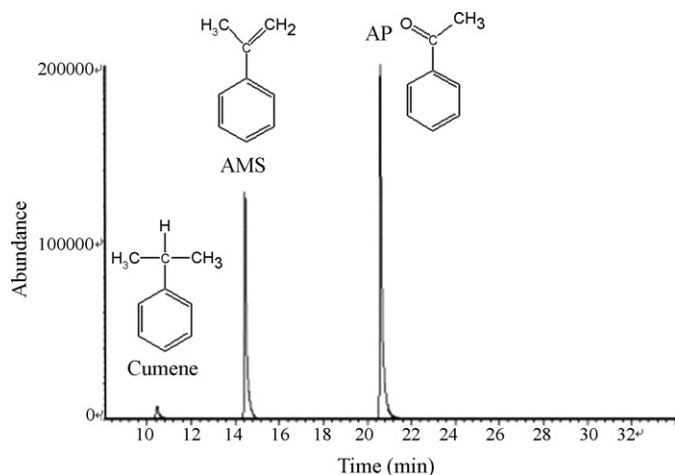

Fig. 7. Product analysis of the homolytic decomposition of CHP mixed with NaOH by GC/MS.

Fig. 8. Product analysis of the heterolytic decomposition of CHP mixed with NaOH by GC/MS.

Moreover, for the other decomposition products, AP, the selectivity decreased while the concentration of hydroxides increased. In the homolytic decomposition of CHP induced by NaOH solution, high concentration of NaOH (9N) could lead to a DMPC ratio of 90%. Table 3 lists the major decomposition products and selectivity through the homolytic and heterolytic cleavage. At elevated concentration of NaOH solution (1, 3, 6, and 9N), most of the products were the same but occurred in different ratios.

3.2.3. Heterolytic decomposition

The concentration of CHP–NaOH mixture decomposition products was analyzed by GC equipped with FID at 250 °C, high inject temperature, which made the sample vaporize and cleave rapidly; the cleavage group of the peroxyl group was present through heterolytic scission. Here, the base-catalyzed route to AP, DMPC, and AMS was also depicted. For the effect of various concentrations of NaOH on the CHP decomposition reaction, the selectivity is illustrated in Fig. 10. CHP catalyzed with 1N NaOH could yield the most amount of DMPC, and the interaction of NaOH with CHP revealed that salts were formed. These salts
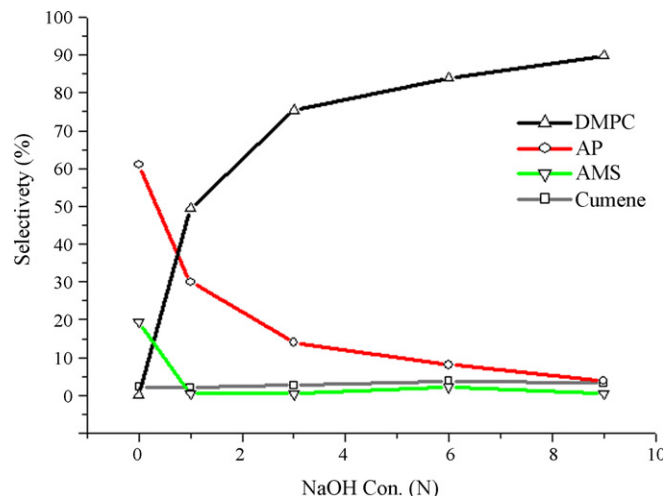

Fig. 9. Variation of CHP for selectivity by NaOH in homolytic scission.

Table 3
Principal decomposition products and selectivity through the homolytic and heterolytic cleavages

Sample	Homolytic decomposition products (mass%)				Heterolytic decomposition products (mass%)			
	Cumene	AP	DMPC	AMS	Cumene	AP	DMPC	AMS
88 mass% CHP	2.23	61.02	0	19.49	6.35	13.93	49.99	–
88 mass% CHP + 1N NaOH	2.20	29.91	49.41	0.54	6.31	11.40	71.75	–
88 mass% CHP + 3N NaOH	2.68	14.00	75.46	0.48	2.99	4.30	28.63	–
88 mass% CHP + 6N NaOH	3.86	8.15	83.86	2.24	2.18	5.00	23.67	–
88 mass% CHP + 9N NaOH	3.33	3.81	89.81	0.56	3.76	5.19	23.09	–

exist in the form of peroxy anions with a relatively little-solvated anion, ROO⁻ [9]. The results showed that by enhancing the concentration of hydroxides (exceed 1N NaOH), the crystallization increased, but the selectivity of DMPC decreased instead.

GC/MS spectrometry verified that CHP reacted with NaOH to form AP and DMPC by homolytic and heterolytic pathways; the proposed decomposition mechanisms of CHP cleaved with NaOH were proposed in Scheme 1.

3.3. Decomposition kinetics

The kinetic analysis results for 80 mass% CHP at various isothermal conditions were conducted by HPLC (UV–vis). Isothermal analysis provided more reliable kinetic data without thermal lag effect and maintained great thermal equilibrium using an nth order model [21].

The decomposition rate law for CHP decay concentration can be written as the following equation:

$$r = -\frac{dC}{dt} = kC_{CHP}^m \tag{1}$$

where r, k, C_{CHP}, and m denote the rate of reaction, the rate constant, the concentration of CHP, and the reaction of order, respectively. Eq. (1) could be integrated and turned into the following equation:

$$-\int dC_{CHP} \frac{1}{C_{CHP}^m} = \int k\, dt \tag{2}$$

Homolytic scission
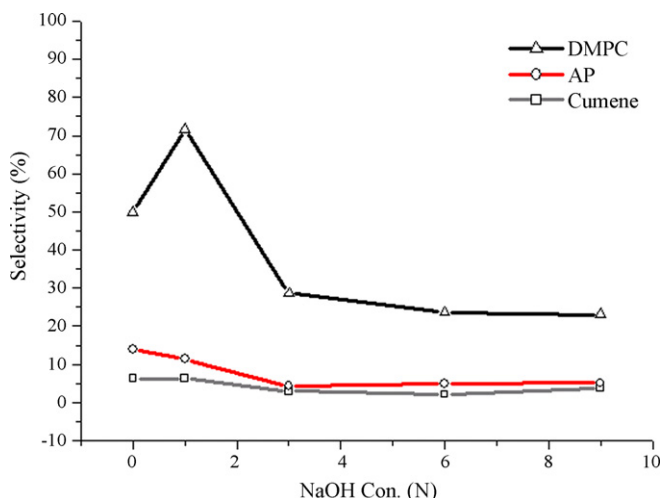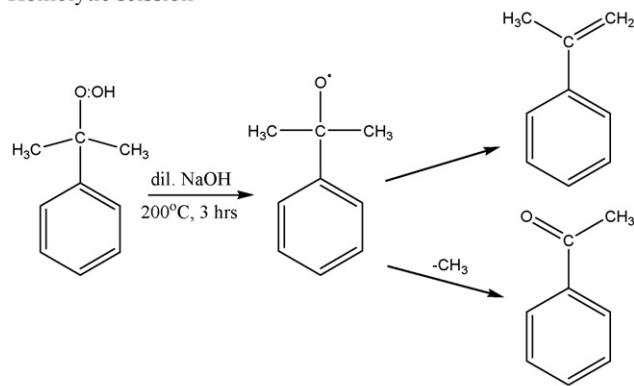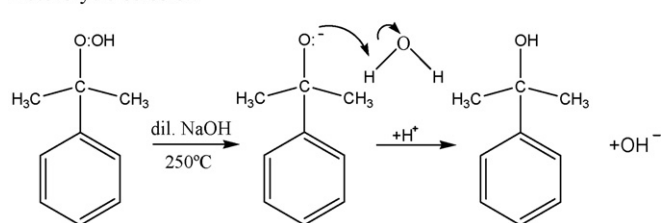
Heterolytic scission

Scheme 1. Proposed decomposition mechanisms of CHP cleaved with NaOH.

The previous studies of Duh and co-workers [9,12] have revealed that the reaction order of 80 mass% CHP decomposition was 0.5. Based on the results, the rate constants are displayed in Table 4 where it is apparent that the associated standard deviations are high.

$$k = A \exp\left(\frac{-E_a}{RT}\right) \tag{3}$$

where A, E_a, R, and T represent frequency factor, activation energy, gas constant and absolute temperature. Furthermore, Eq.

Table 4
Kinetic parameters for the degradation of CHP

Temperature (°C)	k (min⁻¹)
120	0.014
130	0.024
140	0.057
150	0.071
160	0.179

Fig. 10. Variation of CHP for selectivity by NaOH in heterolytic scission.

(3) could be expressed in logarithmic form:

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \tag{4}$$

By plotting $\ln k$ versus $1/T$, a straight line could be obtained and the kinetic parameters of activation energy could be achieved from the slope. The Arrhenius plot constructed from the isothermal decomposition results in calculation of E_a and A as: $E_a = 92.1$ kJ/mol and $A = 2.42 \times 10^{10}$ min^{-1}.

4. Conclusions

Thermal hazards and reaction products of the CHP in the presence of NaOH solution were studied by DSC and chromatography. In this work, incompatible reaction led to complicated phenomena, lower exothermic onset temperature and adiabatic temperature rise from the first peak can trigger a thermal runaway or explosion. Furthermore, the base-catalyzed route to AMS, AP, and DMPC were clearly identified. This comparative study was focused on the incompatible characteristics of CHP mixed with alkaline solution undergoing homolytic and heterolytic scission. At elevated concentration of NaOH, the decomposition products were the same but occurred in different ratios.

Additionally, thermal kinetics of CHP was calculated and performed by chromatographic and calorimetric instruments under various isothermal tests and confirmed by systematic methodologies. The reaction order of CHP in cumene was determined to be 0.5. The results can be used to assess the thermal runaway or reactive hazard potential of organic peroxide and applied for emergency relief system design.

Acknowledgements

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