Thermal Decomposition of Cumene Hydroperoxide: Chemical and Kinetic Characterization

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Thermal decomposition process of cumene hydroperoxide (CHP) in cumene has been investigated by different researchers from chemical and kinetic point of view although its reactive characteristics have not yet been fully identified. The major discrepancy in the literature data is represented by different reaction n*th-order and autocatalytic kinetics suggested. In the present work CHP thermal decomposition is studied by means of isothermal experiments, adiabatic and scanning calorimetry on commercial hydroperoxide samples. The most simple autocatalytic scheme is adopted for the analysis of the data collected on CHP solutions in cumene at different initial concentrations (80%–30% w/w) allowing to estimate the kinetic parameters regulating the process. A characterization of the intermediate and product distribution at varying reaction time is attempted. The effect on the system reactivity of the addition of small quantities of carbinol or acetophenone or α-methylstyrene to the CHP solution in cumene is also studied.* © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 1579–1584, 2008
Keywords: cumene hydroperoxide, thermal decomposition, autocatalytic kinetics, decomposition products, calorimetry

Introduction

Cumene hydroperoxide (CHP) is an important intermediate for the production of phenol (along with acetone)[1] and dicumylperoxide. It is also used as an initiator in polymerization processes.[2] It is currently produced through the oxidation with air of cumene. Incidents have been documented in the past in the oxidation reactors,[3] vacuum evaporator[4] and storage tanks.[5] For example, Kletz reported that an explosion occurred in an oxidation column when—as a result of a problem to the feed—the liquid inside was left at 382 K without cooling and exploded after 5 h from the beginning of the process deviation.[6] Due to its tendency to undergo violent thermal decomposition, its behavior has been investigated by different researchers[3,7] from chemical and kinetic points of view, although its reactive characteristics have not yet been fully identified. In particular the major discrepancy among the literature data is represented by the order of reaction for the decomposition of CHP in cumene. Different *n*th order ($n = 1/2$ for Duh et al., $n = 1$ for K. Hattori et al.), and autocatalytic kinetics[8] have been proposed, from which no clear indications may be derived when a prediction of the system behavior is required. It is noteworthy to observe that very different data may be obtained for example in the calculation of adiabatic time-to-maximum rate (TMR) of a CHP

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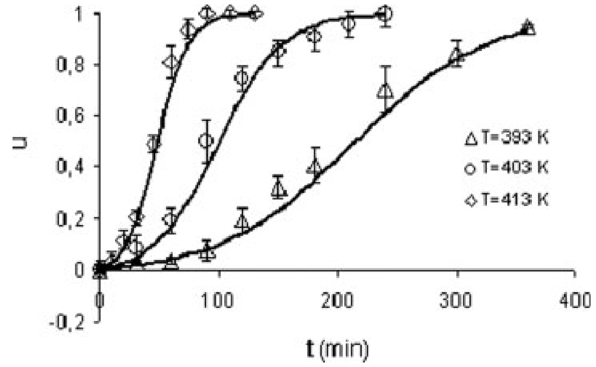


Figure 1. Conversion of CHP against the time during isothermal runs on solutions in cumene (80% w/w).

solution when the kinetic parameters given in the literature are used. TMRs at a temperature of 364 K of 12.7 min and 1,478 min are obtained for 80% CHP solution in cumene by using Hattori's and Duh et al.'s kinetics, respectively. Obviously these data are of poor applicability when the knowledge of the time for an emergency intervention is required in a site in which CHP is produced or used. Dimethylphenylcarbinol (carbinol), cumylperoxide, phenol and methane have been reported as the main CHP thermal decomposition products in some old papers, along with the effect of the solvent used in the experiments.[9] However, a literature survey did not provide any data on the distribution against time of the intermediates and products recorded during the decomposition process mainly starting from CHP solution at concentration of interest for practical applications. This work aims at clarifying these topics through a new investigation of the reaction kinetics of CHP thermal decomposition by using different experimental approaches and intermediates, and products identification and quantification. Kinetic runs are, thus, carried out under isothermal conditions and by means of scanning (DSC) and adiabatic calorimetry. Solutions at different initial CHP concentrations are submitted to the investigation to evaluate if the discrepancies observed among the data reported in the literature may be ascribed to this variable.

Table 1. Temperatures at the Maximum and Heats of Reaction Recorded During DSC Runs Performed on 80% CHP Solutions in Cumene at Varying the Heating Rate

v (K/min)	Maximum (K)	q (J/g)
5	457,6	1189
7,5	465,3	1231
10	468,7	1200
12,5	473,5	1256

The thermal decomposition process is also followed from a chemical point of view by the analysis of intermediates and products distribution at varying reaction time. The catalytic role of identified species is also evaluated.

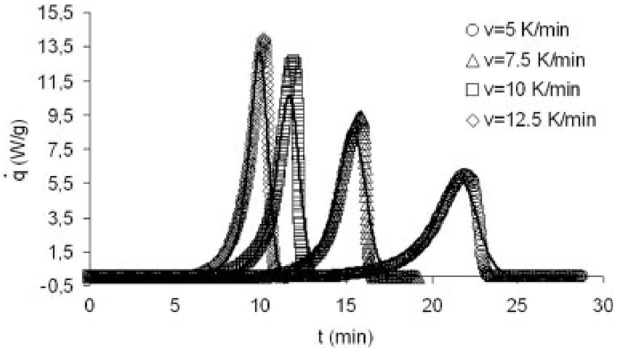


Figure 2. Power generated per unit of mass during DSC experiments on 80% CHP solution in cumene at varying the heating rate.

Experimental

The experimental runs were carried out by means of different calorimetric devices. For the adiabatic experiments was used an A.R.C. calorimeter (by Columbia Scientific Industries), while for the DSC experiment a Q10 thermal analysis was used. All the isothermal runs were carried out using an oil bath, where the temperature was controlled by a Heidolf EKT 3001 heating plate. In this case a series of sealed glass tubes previously filled with CHP solutions of different concentrations ranging from $1.8 \div 5.4$ mol/L were placed into the oil bath, the tubes were then extracted and rapidly cooled after the desired reaction time. These samples were recovered with acetone, diluted with acetonitrile and submitted to HPLC analysis. This was performed by means of a 1090 Hewlett Packard HPLC equipped with a Synergi 4μ Fusion RP-80 column and a diode array detector. The mobile phase was (V/V-%) 65% of Acetonitrile and 35% of a solution formed by 5% methanol, 0.4% H_3PO4 and 94.6% H_2O, with a flow of 10^{-3} l min^{-1}. The oven temperature was set at 305 K.

The gases recovered during the isothermal runs were analyzed by using a gas chromatograph (HP 6890 Series) equipped with a TCD and FID detector.

The A.R.C. runs were performed in Hastelloy C bombs with the following set parameters: waiting time 10 min, heat step temperature 10 K, heat rate threshold value 0.02 K min^{-1}.

Moreover, preliminary runs have been carried out by reacting the same solution both in glass vials and metal reactors (hastelloy C) in order to check the existence of any surface effect. The results of these runs indicated that metal surfaces adopted in the present investigation do not affect the system reactivity.

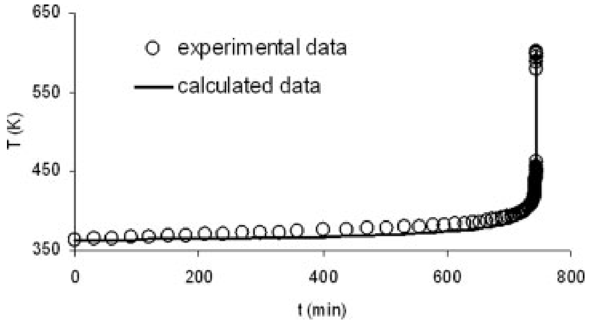


Figure 3. Thermal behavior of 80% solution of CHP in cumene under adiabatic conditions.

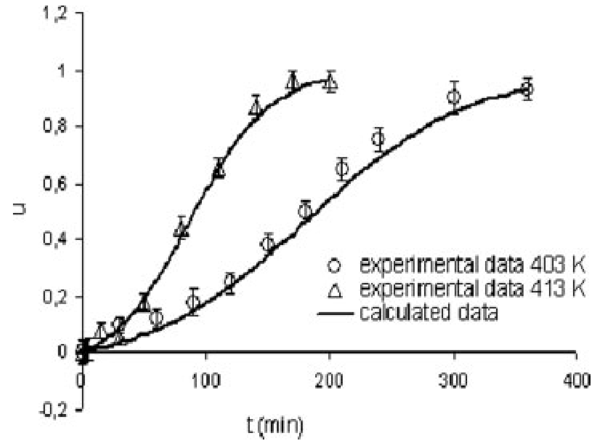


Figure 4. Conversion of CHP against the time during isothermal runs on solutions in cumene (30% w/w).

Results and Discussion

Figure 1 illustrates the decomposition of CHP (80% w/w in cumene) as a function of time under isothermal conditions, at 393, 403 and 413 K (symbols). In all cases the diagram of the conversion of CHP against the time follows a s-shaped curve, which undoubtedly suggests that the decomposition process is regulated by autocatalytic kinetics.

The results of DSC experiments on 80% CHP solution in cumene at different heating rate are shown in Figure 2 (symbols). The effect of heating rate on the temperature maximum (T_{max}), and on the heats of reaction is reported in Table 1.

From Table 1 it is evident that the measured heats of reaction in the runs performed on the same solution are very close.

The thermogram recorded under adiabatic conditions on 80% CHP solution in cumene is shown in Figure 3 (symbols).

From the recorded adiabatic temperature rise and the weight of the sample used for the run a heat of reaction of 1073 J/g is calculated, which well agrees with the mean value of 1219 J/g obtained from DSC experiments. The investigation has been successively extended to study the decomposition of more diluted CHP solutions in cumene to assess the effect of this variable. Figures 4, 5 and 6 illustrate the results obtained for CHP decomposition under isothermal (403 K, 413 K), dynamic (scanning) and adiabatic conditions, respectively, (symbols) starting from a 30% CHP solution in cumene. The shape of the diagrams recorded under isothermal conditions on a 30% CHP solutions in cumene also suggests in this case an autocatalytic behavior.

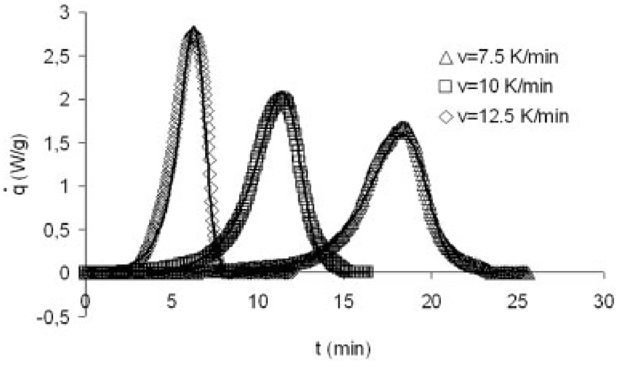


Figure 5. Power generated per unit of mass during DSC experiments on 30% CHP solution in cumene at varying the heating rate.

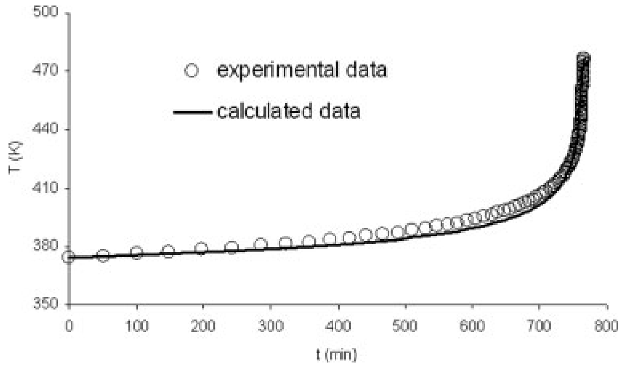


Figure 6. Thermal behavior of 30% solution of CHP in cumene under adiabatic conditions.

According to previous observations an overall simple autocatalytic Scheme 1 is proposed to develop kinetic models capable of describing the system behavior.

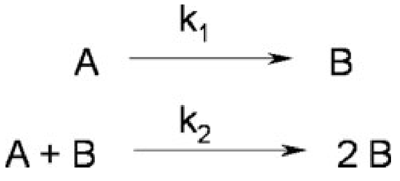
On the basis of this scheme, three mathematical models can be written for isothermal, scanning and adiabatic runs (Table 2) which can then be used to simulate the system behavior under different reacting conditions.

In particular the three models have been used along with an optimization procedure which allowed the best estimation of kinetic parameters k_{10}, Ea_1, k_{20}, Ea_2. This procedure relies on the minimization of an objective function F defined as following

$$F = \sum_{j=1}^{m} \sum_{i=1}^{n} (C_{i,j} - Y_{i,j})^2$$

where $C_{i,j}$ and $Y_{i,j}$ are the measured (experimental) concentration of the substrate, and that calculated by the model at each reaction times, respectively, n being the number of sampling times in a single run, and m is that of the runs whose data have been used for the optimization. All the experimental results collected during this investigation have been simultaneously used for the estimation of the parameters. The best estimated values obtained with this procedure are reported in Table 3.

Determination coefficients (r^2) between 0.93 and 0.99 have been obtained by analyzing the experimental data with the



Scheme 1. Proposed autocatalytic kinetic scheme.

Table 2. Mathematical Models Used to Simulate the System Behavior During Isothermal, Scanning and Adiabatic Runs, Where $k_i = k_{i0} \exp(-Ea_i/(R \cdot T))$

Conditions	Material Balance	Thermal Balance
Isothermal	$\frac{du}{dt} = k_2 \cdot C_A^0 \cdot (1-u) \cdot \left(u + \frac{k_1}{k_2 \cdot C_A^0}\right)$	$\frac{dT}{dt} = 0$
Scanning	$\frac{du}{dt} = k_2 \cdot C_A^0 \cdot (1-u) \cdot \left(u + \frac{k_1}{k_2 \cdot C_A^0}\right)$	$\dot{q} = cp \cdot \varphi \cdot \frac{dT}{dt} = \frac{du}{dt} \cdot (-\Delta H)$
Adiabatic	$\frac{du}{dt} = k_2 \cdot C_A^0 \cdot (1-u) \cdot \left(u + \frac{k_1}{k_2 \cdot C_A^0}\right)$	$\frac{dT}{dt} = \frac{du}{dt} \cdot (+\Delta T_{ad})$

Table 3. Best Estimated Values of Kinetic Parameters, k_{10}, Ea_1, k_{20}, Ea_2, . $k_i = k_{i0} \exp(-Ea_i/(R \cdot T))$

i	Ea_i	k_{i0}
1	108520.1 ± 5.2 J/mol	$(1.06 \pm 0.05) \cdot 10^{11}$ 1/min
2	97193.7 ± 8 J/mol	$(2.83 \pm 0.07) \cdot 10^{10}$ 1/(mol · min)

proposed models. In Figures 1–6 the results calculated by the models using the best estimated values for the parameters are shown by continous lines. A careful examination of these figures indicates that the quality of the fitting between calculated and experimental results is in some cases partially satisfactory (see for example the Figures 3 and 6) although low-values of the uncertainties on the best estimates and high-determination coefficients were obtained during the analysis of the data. As a first attempt this behavior may be ascribed to a limited capability of the proposed overall reaction scheme to describe the studied decomposition process probably due to the great complexity of the latter.

In order to shed some light on the mechanism of the thermal decomposition process of CHP in cumene an attempt to identify the intermediates and products at varying reaction time was performed. In Figures 7 and 8 the concentrations of all identified species are reported against time during a run at 393 K starting from 80% CHP solution in cumene.

Acetophenone and carbinol are the main products identified in the reacting solution during the CHP decomposition process with a minor occurrence of α-metylstyrene, dicumylperoxide and phenol. Gaschromatographic analyses of the gases evolved and collected during the experimental runs indicated the presence of methane and oxygen as the main gaseous products. The formation of acetophenone and carbinol can be easily explained through the steps reported in Scheme 2.

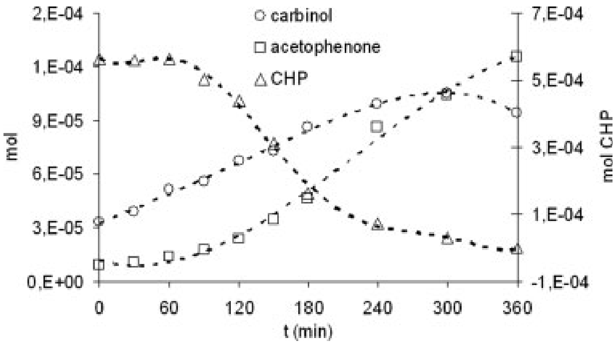


Figure 7. Concentrations of the intermediates and products against the time identified during an isothermal run (T = 393 K) on a 80% CHP solution in cumene.

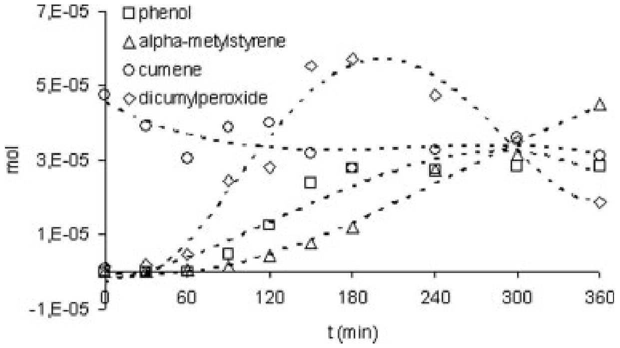
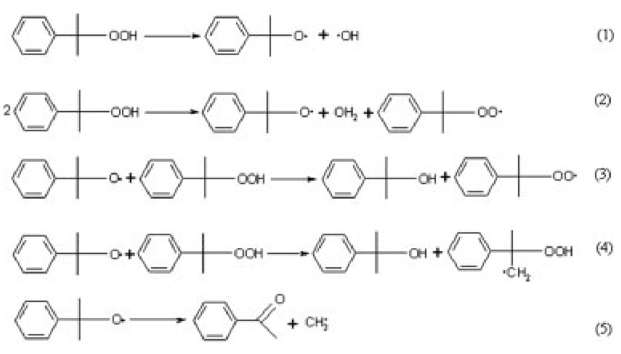


Figure 8. Concentrations of the intermediates and products against the time identified during an isothermal run (T = 393 K) on a 80% CHP solution in cumene.

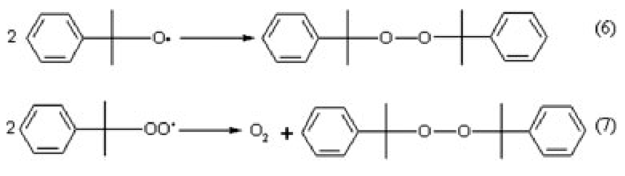
That is, the homolysis (unimolecular or bimolecular) of —O—O— CHP bond initiates the decomposition process which is sustained by the propagation reactions (3) and (4), and the cleavage (5). The formation of acetophenone through the reaction (5), is accompanied by that of methyl radicals, which may extract a hydrogen atom from the other species in the reacting solution, thus, resulting in generation of methane found during this investigation.

To account for the formation of dicumylperoxide, both the terminating reactions (6) and (7) can be considered (Scheme 3).

The occurrence of the last reaction (7) is consistent with the appearance of the evolved oxygen gas. As it is evident



Scheme 2. Possible steps for the formation of acetophenone and carbinol.



Scheme 3. Formation of dicumylperoxide.

from the profiles in Figure 8, cumene peroxide is also significantly consumed during the process, probably due to its known tendency to undergo thermal decomposition.[8]

α-metylstyrene may form from the attack of cumyloxy radicals to a CHP molecule (reaction 8), followed by the expulsion of HO_2 species (reaction 9), as well as through a terminating reaction (reaction 10), cumyl radical being formed through a H-abstraction from cumene (Scheme 4).

Further experiments under isothermal conditions have been carried out to assess if some of the identified species may exert a catalytic effect on CHP decomposition. The data reported in Figure 9 indicate that the addition of small quantities (comparable with those reported for the single species in Figures 7 and 8) of α-methylstyrene or acetophenone or carbinol to 80% CHP solution in cumene causes a remarkable increase in the reactivity of the system.

A possible justification for this behavior may be found for each of the three species. α-methylstyrene can be supposed to be capable of reacting with CHP to produce reactive radical species. Literature indications support this hypothesis: Dikii et Yurzhenko reported that hydroperoxides react with α-methylstyrene to produce free radicals which initiate the polymerization of the latter.[10] The low-concentrations at which this species are found in the reacting solutions in this investigation are probably due to the relevance of this reaction within the CHP decomposition process.

The capability of ketones to accelerate the decomposition of hydroperoxides has been demonstrated in the past by Russian researchers,[11] who found that this was due to an interaction of the latter with the carbonyl group, the resulting species decomposing into free radicals at a higher velocity than hydroperoxide itself.

A direct interaction between added carbinol and hydroperoxide, (Scheme 5) with the formation of cumyloxy radicals[12] may be responsible for the enhanced system reactivity observed during the experimental runs.

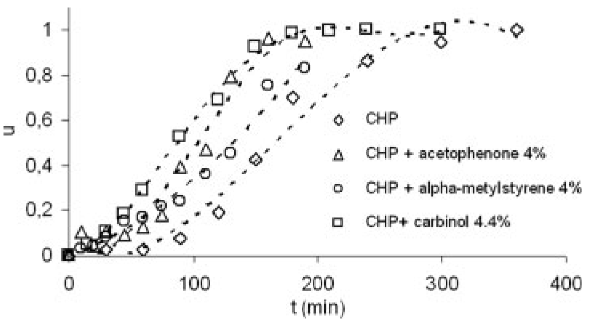


Figure 9. Effect of the addition of α-methylstyrene or acetophenone or carbinol to 80% CHP solution in cumene on the system reactivity at 393 K.

It may be stated that this reaction, and that between hydroperoxide and acetophenone give a significant contribution to the initiation of the decomposition process, even in a case where there was no addition of carbinol and/or acetophenone into the system, since these species can be formed during cumene oxidation stage, and are normally present in commercial cumene hydroperoxide solutions in cumene (see in the Figure 7 the solution composition at the time zero).

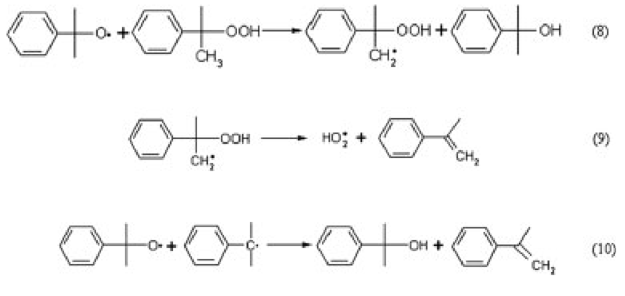
Minor occurrence of phenol, in agreement with what reported by Kharasch et al.[9] may be considered as the results of a rearrangement typically observed in acid medium,[13] which occurs at a limited extent even in the absence of acids. From the diagrams in the Figure 8 it can be easily observed that the concentration of cumene reduces during the decomposition process as a result of the hydrogen abstraction by the radicals present in the solution.

Comparison of some literature data with those predicted by the proposed model

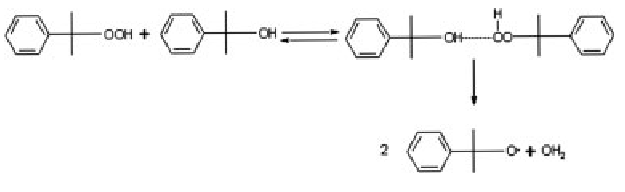
Since the concentrations of carbinol and acetophenone in CHP commercial samples do not vary significantly, the capability of the model developed in this work to predict the results collected by others has been evaluated. To this purpose, the data related to the temperature increase under adiabatic conditions during the thermal decomposition of 30 and 35% CHP solutions in cumene, starting, respectively, from 379.2 and 374.4 K, and reported by Duh et al.[14] have been analysed by means of the proposed model by trying to estimate the best kinetic parameters. As a result of this attempt a satisfactory capability of the model to simulate the temperature increase under adiabatic conditions was observed.

The new values of kinetic parameters obtained in this way are reported for comparison in the Table 4 along with those found on the data collected in this investigation.

It is evident that the values of the three sets are very close, although the differences among them are slightly higher than the experimental errors. This moderate discrepancy can be tentatively ascribed to a (small) difference in the concentra-



Scheme 4. Formation of α-methylstyrene.



Scheme 5. Interaction between carbinol and cumene.

Table 4. Comparison of Best Estimated Values of Kinetic Parameters

	Ea_1 [J/mol]	k_{10} [1/min]	Ea_2 [J/mol]	k_{20} [l/(mol·min)]
Present work	108520.1 ± 5.2	$(1.06 \pm 0.05) \cdot 10^{11}$	97193.7 ± 8	$(2.83 \pm 0.07) \cdot 10^{10}$
From Duh et al.'s data 35% wt CHP	107478.5 ± 5.1	$(1.53 \pm 0.01) \cdot 10^{11}$	101822.2 ± 10	$(1.94 \pm 0.01) \cdot 10^{10}$
From Duh et al.'s data 30% wt CHP	108256.3 ± 5.0	$(1.39 \pm 0.03) \cdot 10^{11}$	99487.7 ± 6	$(1.16 \pm 0.05) \cdot 10^{10}$

tions of the secondary products (carbinol and acetophenone) in the hydroperoxides samples used in the two investigations (no indications about this point have been found in the quoted paper), whose influence on the reactivity of the system has been discussed above. Moreover, it is important to stress that the results of this modeling attempt indicate that also the data taken from the literature may be analyzed by using an autocatalytic model in agreement with what has been observed in this investigation.

Due to these considerations, it can be concluded that the autocatalytic character of CHP thermal decomposition—which was put forward in the past only by some researchers – is supported by the data collected during the present investigation, and also by those taken from the literature and considered in this article for comparison.

Conclusions

Thermal decomposition process of CHP in cumene has been studied by means of isothermal experiments, adiabatic and scanning calometry on commercial hydroperoxide samples. Data collected on CHP solutions in cumene at initial concentrations ranging from 80 to 30% have confirmed as suggested by some researchers in the past that the decomposition process is regulated by autocatalytic kinetics. The adoption of the simplest autocatalytic scheme to describe the system behavior enabled the estimation of the kinetic parameters regulating the decomposition process, although in some cases the comparison between experimental and calculated data resulted partially satisfactory. This behavior may be tentatively ascribed to a limited capability of the proposed overall reaction scheme to describe the studied decomposition process probably due to the great complexity of the latter.

Successive investigations allowed to characterize the intermediate and product distribution at varying reaction time. Moreover, it has been demonstrated that the addition of small quantities of carbinol or acetophenone or α-methylstyrene to the CHP solution in cumene enhances the reactivity of the system. Therefore, this could explain the discrepancies in the results obtained by different research groups when CHP samples containing carbinol and acetophenone at concentrations significantly different from those normally found in commercial samples are used to assess its decomposition kinetics.

Further works are, thus, required to develop new models based on detailed reaction schemes in which the initial concentration of carbinol and acetophenone is considered.

Notation

C_j^0 = initial concentration of j-th species, mol l^{-1}
cp = mean specific heat of reacting mixture, J K^{-1} g^{-1}
Ea_i = activation energy of reaction, for i-th reaction, kJ mol^{-1}
k_i = kinetic constant of reaction for i-th reaction, l mol^{-1} min^{-1}
k_{i0} = pre-exponential factor of reaction for i-th reaction, l mol^{-1} min^{-1}
R = universal costant of gas, J mol^{-1} K^{-1}
t = time, min
T = temperature, K
$\dot{q}$ = power per unit of mass, W g^{-1}
u = conversion, dimensionless
v = heating rate, K min^{-1}

Greek letters

ΔH = heat of overall reaction, kJ mol^{-1}
ΔT_{ad} = adiabatic temperature rise, K
φ = thermal inertia, dimensionless

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