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Hierarchical kinetic simulation for autocatalytic decomposition of cumene hydroperoxide at low temperatures

**Jiann-Rong Chen · Shyh-Yuch Cheng ·
Min-Hao Yuan · Arcady A. Kossoy ·
Chi-Min Shu**

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Abstract A hierarchical set of kinetic models were proposed and discussed for simulation of autocatalytic decomposition of cumene hydroperoxide (CHP) in cumene at low temperatures. The hierarchy leads from a formal model of full autocatalysis, which is based on conversion degree as a state variable, through a two-stage autocatalytic concentration-based model to a meticulous multi-stage model of the reaction. By the ForK (Formal Kinetics) and DesK (Descriptive Kinetics) software, developed by ChemInform Saint Petersburg (CISP) Ltd., the related kinetic parameters and their significance have also been estimated and elucidated. Through this best-fit approach, it is possible to formulate a systematic methodology on the kinetic studies for thermal decomposition of typical organic peroxides with autocatalytic nature, specifically at low temperature ranges.

Keywords Autocatalytic decomposition · Best-fit approach · Cumene hydroperoxide (CHP) · Kinetic parameters · Meticulous multi-stage model

Nomenclature

E_i	Activation energy of the i stage, J mol^{-1}
E_{ki}	Activation energy of the i stage for model k, J mol^{-1}
k_{0i}	Frequency factor of the i stage, mol^{1-n}/(L^{n-1} s) = M^{1-n} s^{-1}
k_{k0i}	Frequency factor of the i stage for model k, mol^{1-n}/(L^{n-1} s) = M^{1-n} s^{-1}
n_i	Reaction order of i stage, dimensionless
n_{ij}	Reaction order of i stage for the species j, dimensionless
n_{ki}	Reaction order of i stage for model k, dimensionless
n_{kij}	Reaction order of i stage for model k for the species j, dimensionless
Q	Heat production, kJ/kg, kJ mol^{-1}
dQ/dt	Heat production rate, kJ min^{-1} kg $^{-1}$
Q_i^{∞}	Heat effect of i stage, kJ mol^{-1}
Q_{ki}^{∞}	Heat effect of i stage for model k, kJ mol^{-1}
R	Gas constant (8.314), J mol^{-1} K^{-1}
r_i	Reaction rate of i stage, mol (L s)$^{-1}$ = M s^{-1}
r_{ki}	Reaction rate of i stage for model k, mol (L s)$^{-1}$ = M s^{-1}
TMR_{iso}	Time to maximum rate under isothermal conditions, h
T	Temperature, °C, K
t	Time, min, h
$[X]$	Concentration of a species X, k mol m^{-3}

J.-R. Chen
General Education, Hsiuping Institute of Technology, 11,
Gong-Ye Road, Dali, Taichung County 41280, Taiwan, ROC

J.-R. Chen · C.-M. Shu (✉)
Doctoral Program, Graduate School of Engineering Science
and Technology, National Yunlin University of Science and
Technology, 123, University Road, Sec. 3, Douliou,
Yunlin 64002, Taiwan, ROC
e-mail: shucm@yuntech.edu.tw

S.-Y. Cheng
Department of Occupational Safety and Hygiene, Chia-Nan
University of Pharmacy and Science, 60, Erh-Jen Road, Sec.1,
Jente, Tainan 71710, Taiwan, ROC

M.-H. Yuan
Graduate Institute of Environmental Engineering, National
Taiwan University, 1, Sec. 4, Roosevelt Road, Taipei 10617,
Taiwan, ROC

A. A. Kossoy
ChemInform Saint Petersburg (CISP) Ltd, 14 Dobrolubov Ave,
197198 St. Petersburg, Russia

Greek letters

α	Degree of conversion (range 0–1)
$d\alpha/dt$	Rate of degree of conversion, 1 s^{-1}

Introduction

Cumene hydroperoxide (CHP) is widely used as an initiator in polymerization, especially for the acrylonitrile-butadiene-styrene (ABS) copolymer in Taiwan, and has been used in producing phenol and acetone by catalytic cleavage [1–5]. Many incidents have been caused by its thermal instability or reactive incompatibility. Runaway incidents can occur in oxidation reactors, vacuum condensation reactors, or storage tanks.

Autocatalytic reactions are considered to be hazardous because of unexpected initiation and sudden heat evolution even in an isothermal environment. The way to illustrate the autocatalytic behavior would be the use of a more complex model of full autocatalysis. This model includes two parallel stages that can be schematically represented as:

$A \rightarrow B + \text{products}$ – initiation stage;

$A + B \rightarrow 2B + \text{products}$ – self-accelerating stage;

where A and B stand for CHP and product-catalyst. This scheme results in the following mathematical model:

$$\frac{d\alpha}{dt} = r_1 + r_2 \tag{1}$$

$$r_1 = k_{01} e^{-E_1/RT} (1-\alpha)^{n_1} \tag{2}$$

$$r_2 = k_{02} e^{-E_2/RT} \alpha^{n_{21}} (1-\alpha)^{n_{22}} \tag{3}$$

$$\frac{dQ}{dt} = Q_1^{\infty} r_1 + Q_2^{\infty} r_2 \tag{4}$$

The model is capable of reproducing the main features of pronounced self-acceleration, i.e., induction, acceleration and decay periods, and hence can be successfully used for fitting autocatalytic data (for instance, a similar model had been applied by Beckmann and co-workers [6]). Figure 1a and b display that this model can be used to achieve a reasonable quality of data fits for the CHP decomposition. The estimates of kinetic parameters are presented in Table 1.

To a greater or lesser extent this model is capable of reflecting some specific features of the reaction. Nevertheless, it is a formal model that uses the degree of conversion (α) as state variables and hence does not allow in-depth study. Therefore, a more adequate and conventional way is highly desired for the investigation of the CHP decomposition as a system.

This can be done by means of current methodology using a numerical approach [7, 8]. In the present study this approach and the state-of-the-art flexible and efficient DesK (Descriptive Kinetics) software were used. Ultimately, the best way to depict this autocatalytic phenomenon would be to rely upon detailed simulation using a meticulous model. Nonetheless, the simple two-stage concentration-based model was created first to demonstrate the evolution of the models.

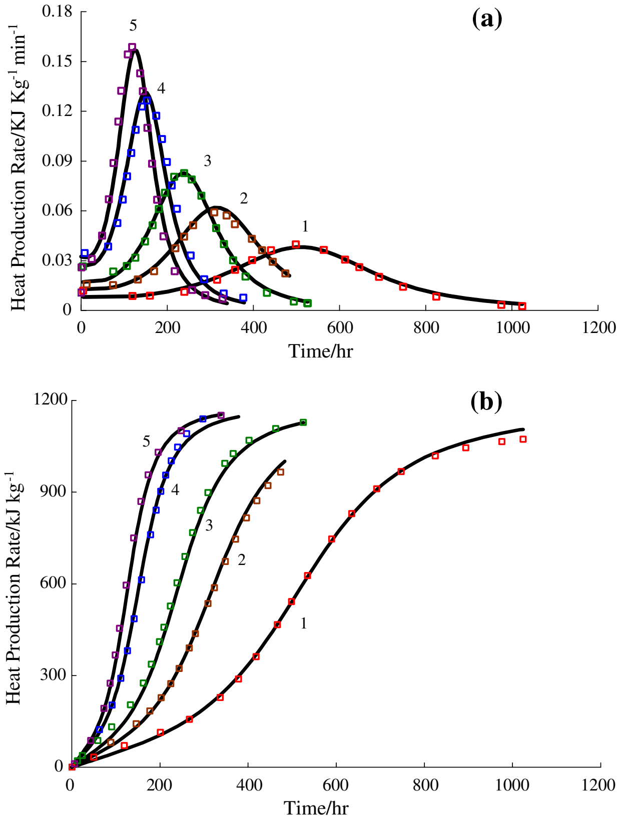

Fig. 1 Comparison of numerical simulations (——) and experimental data (□□□□) at 1—75 °C, 2—80 °C, 3—83 °C, 4—88 °C and 5—90 °C for **a** heat production rate and **b** heat production by the formal model of full autocatalysis

Mode of decomposition

Scheme A—the two-stage autocatalytic model

Since the formal two-stage model of full autocatalysis provides a reasonable fitting of the whole set of experimental data, it was of particular interest whether the concentration-based model of similar complexity could be used for fitting data. The hypothetical reaction scheme which is reduced from Sykes [9] as denoted in Scheme 1, results in the following two-stage autocatalytic model:

$$r_{a1} = k_{a01} e^{-E_{a1}/RT} [C_6H_5C(CH_3)_2OOH]^{n_{a1}} \tag{5}$$

Table 1 Kinetic parameters for the formal model for full autocatalysis of CHP decomposition in cumene

Kinetic parameters
$r_1 = 7.42 \times 10^8 \cdot \exp(-102,470/RT) \cdot (1-\alpha)^{1.80}$;
$Q_1^\infty = 567.5\,\mathrm{kJ\,kg^{-1}}$
$r_2 = 9.60 \times 10^9 \cdot \exp(-95,810/RT) \cdot \alpha^{4.02}(1-\alpha)^{3.00}$;
$Q_2^\infty = 1,831.2\,\mathrm{kJ\,kg^{-1}}$

$$r_{a2} = k_{a02}e^{-E_{a2}/RT}[C_6H_5C(CH_3)_2OOH]^{n_{a21}}[C_6H_5OH]^{n_{a22}} \tag{6}$$

Concentration rate changes are represented by the linear combinations of the rates of the two reactions with the corresponding stoichiometric coefficients:

$$d[C_6H_5C(CH_3)_2OOH]/dt = -r_{a1} - r_{a2} \tag{7}$$

$$d[CH_3COCH_3]/dt = r_{a1} + r_{a2} \tag{8}$$

$$d[C_6H_5C(CH_3)_2OOH]/dt = r_{a1} - r_{a2} + 2r_{a2} \tag{9}$$

To fit the calorimetric data from the heat flux microcalorimeter, TAM (Thermal Activity Monitor), the model should be supplemented with the equation for rate of heat generation:

$$\frac{dQ}{dt} = Q_{a1}^\infty r_{a1} + Q_{a2}^\infty r_{a2} \tag{10}$$

In Table 2, the kinetic parameters estimated by using DesK on the basis of the four isothermal curves (temperature range 75–88 °C) provided good data fits, as can be seen in Fig. 2a and b. Although the two-stage concentration-based model is more conventional for chemists and chemical engineers, it is merely a rough descriptive model that might not be useful for a detailed analysis of the decomposition process.

Scheme B—the meticulous model

The thermal decomposition of CHP in different organic solvents has been studied thoroughly [2, 10–14]. Solvent involvement in the process of thermal decomposition has been confirmed [1, 2, 15]. Most of the CHP actually decomposes via radical induced decomposition pathways [10, 16]. Certain significant phenomena incorporating the attraction of the active hydrogen atom at the α-position or ·OH induced hydrogen bonding were proposed in the elucidation of the typical decomposition kinetics [14, 17–19]. That the hydroperoxide might form dimers in some solvents at lower temperatures, even at 70 °C, was verified by IR spectrometry. Based on this information, a thermal decomposition of CHP was proposed that follows scheme B, as defined in Scheme 2, and as suggested by Hiatt et al. and Duh et al. [10, 16, 17]. This scheme results in the following mathematical model:

$$C_6H_5C(CH_3)_2OOH \xrightarrow{r_{a1}} CH_3COCH_3 + C_6H_5OH$$

$$C_6H_5C(CH_3)_2OOH + C_6H_5OH \xrightarrow{r_{a2}} CH_3COCH_3 + 2C_6H_5OH$$

* Phenol is supposed to be the product-catalyst and the acetone is the product.

Scheme 1 The two-stage autocatalysis model (scheme A) for the decomposition of CHP

Table 2 Kinetic parameters for the model for scheme A of CHP decomposition in cumene

Kinetic parameters
$r_{a1} = 2.64 \times 10^5 \cdot \exp(-95,210/RT) \cdot [C_6H_5C(CH_3)_2OOH]^{4.00}$;
$Q_{a1}^\infty = 208.3\,\mathrm{kJ\,mol^{-1}}$
$r_{a2} = 9.42 \times 10^6 \cdot \exp(-97,230/RT)\cdot$
$[C_6H_5C(CH_3)_2OOH]^{2.48}[C_6H_5OH]^{2.34}$;
$Q_{a2}^\infty = 252.7\,\mathrm{kJ\,mol^{-1}}$

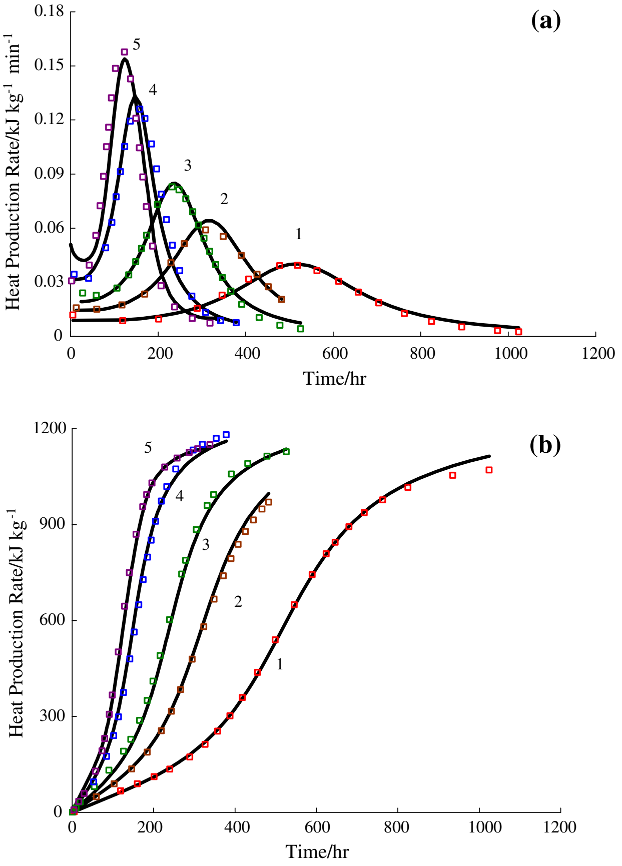

Fig. 2 Comparison of numerical simulations (——) and experimental data (□□□) at 1—75 °C, 2—80 °C, 3—83 °C, 4—88 °C and 5—90 °C for **a** heat production rate and **b** heat production by the simplified concentration-based model (scheme A)

$$2C_6H_5C(CH_3)_2OOH \xleftrightarrow{r_{b1f},\ r_{b1b}} (C_6H_5C(CH_3)_2OOH)_2$$

$$C_6H_5C(CH_3)_2OOH \xrightarrow{r_{b2}} C_6H_5C(CH_3)_2O\cdot + \cdot OH$$

$$C_6H_5C(CH_3)_2O\cdot \xrightarrow{r_{b3}} C_6H_5COCH_3 + \cdot CH_3$$

$$C_6H_5C(CH_3)_2H + \cdot CH_3 \xrightarrow{r_{b4}} CH_4 + C_6H_5C(CH_3)_2\cdot$$

$$C_6H_5C(CH_3)_2H + \cdot OH \xrightarrow{r_{b5}} H_2O + C_6H_5C(CH_3)_2\cdot$$

$$C_6H_5C(CH_3)_2O\cdot + C_6H_5C(CH_3)_2H \xrightarrow{r_{b6}} C_6H_5C(CH_3)_2OH + C_6H_5C(CH_3)_2\cdot$$

$$C_6H_5C(CH_3)_2O\cdot + \cdot OH \xrightarrow{r_{b7}} C_6H_5OH + CH_3COCH_3$$

$$C_6H_5C(CH_3)_2\cdot + \cdot OH \xrightarrow{r_{b8}} C_6H_5CH_3C = CH_2 + H_2O$$

$$2C_6H_5C(CH_3)_2\cdot \xrightarrow{r_{b9}} (C_6H_5C(CH_3)_2)_2$$

Scheme 2 The homolytic decomposition scheme (scheme B) of CHP

$$r_{b1f} = k_{b01f}e^{-E_{b1f}/RT}[C_6H_5C(CH_3)_2OOH]^{n_{b1f}} \tag{11}$$

$$r_{b1b} = k_{b01b}e^{-E_{b1b}/RT}[(C_6H_5C(CH_3)_2OOH)_2]^{n_{b1b}} \tag{12}$$

$$r_{b2} = k_{b02}e^{-E_{b2}/RT}[C_6H_5C(CH_3)_2OOH]^{n_{b21}} \tag{13}$$

$$r_{b3} = k_{b03}e^{-E_{b3}/RT}[C_6H_5C(CH_3)_2O\cdot]^{n_{b31}} \tag{14}$$

$$r_{b4} = k_{b04}e^{-E_{b4}/RT}[C_6H_5C(CH_3)_2H]^{n_{b41}}[\cdot CH_3]^{n_{b42}} \tag{15}$$

$$r_{b5} = k_{b05}e^{-E_{b5}/RT}[C_6H_5C(CH_3)_2H]^{n_{b51}}[\cdot OH]^{n_{b52}} \tag{16}$$

$$r_{b6} = k_{b06}e^{-E_{b6}/RT}[C_6H_5C(CH_3)_2O\cdot]^{n_{b61}}[C_6H_5C(CH_3)_2H]^{n_{b62}} \tag{17}$$

$$r_{b7} = k_{b07}e^{-E_{b7}/RT}[C_6H_5C(CH_3)_2O\cdot]^{n_{b71}}[\cdot OH]^{n_{b72}} \tag{18}$$

$$r_{b8} = k_{b08}e^{-E_{b8}/RT}[C_6H_5C(CH_3)_2\cdot]^{n_{b81}}[\cdot OH]^{n_{b82}} \tag{19}$$

$$r_{b9} = k_{b09}e^{-E_{b9}/RT}[C_6H_5C(CH_3)_2\cdot]^{n_{b91}} \tag{20}$$

Based upon Eqs. 11–20, the concentration models could be readily expressed as follows:

$$d[C_6H_5C(CH_3)_2OOH]/dt = -r_{b2} - 2r_{b1f} + r_{b1b} \tag{21}$$

$$d[(C_6H_5C(CH_3)_2OOH)_2]/dt = r_{b1f} - r_{b1b} \tag{22}$$

$$d[C_6H_5C(CH_3)_2O\cdot]/dt = r_{b2} - r_{b3} - r_{b6} - r_{b7} \tag{23}$$

$$d[\cdot OH]/dt = r_{b2} - r_{b5} - r_{b7} - r_{b8} \tag{24}$$

$$d[C_6H_5COCH_3]/dt = r_{b3} \tag{25}$$

$$d[\cdot CH_3]/dt = r_{b3} - r_{b4} \tag{26}$$

$$d[C_6H_5C(CH_3)_2H]/dt = -r_{b4} - r_{b5} - r_{b6} \tag{27}$$

$$d[CH_4]/dt = r_{b4} \tag{28}$$

$$d[C_6H_5C(CH_3)_2\cdot]/dt = r_{b4} + r_{b5} + r_{b6} - r_{b8} - 2r_{b9} \tag{29}$$

$$d[H_2O]/dt = r_{b5} + r_{b8} \tag{30}$$

$$d[C_6H_5C(CH_3)_2OH]/dt = r_{b6} \tag{31}$$

$$d[C_6H_5OH]/dt = r_{b7} \tag{32}$$

$$d[C_6H_5COCH_3]/dt = r_{b3} \tag{33}$$

$$d[C_6H_5CH_3C = CH_2]/dt = r_{b8} \tag{34}$$

$$d[(C_6H_5C(CH_3)_2)_2]/dt = r_{b9} \tag{35}$$

$$\frac{dQ}{dt} = \sum_{i=1}^{9} Q_{bi}^{\infty} r_{bi} \tag{36}$$

The meticulous decomposition scheme proposed in our previous work [2], along with others, is believed to be superior to the simplified concentration-based and formal full autocatalytic models in terms of degree of accuracy. However, the lack of concentration profiles during decomposition tests by the adiabatic calorimeter, such as VSP2 (Vent Sizing Package 2), and some other peculiarities of the adiabatic mode impeded the kinetics evaluation proposed in Eqs. 21–36. In this study this model was used for evaluating kinetics on the basis of a more exhaustive set of experimental data regarding the decomposition of 80 mass% solution CHP in cumene, which was investigated using the TAM, under isothermal conditions, starting from 75 to 90 °C. All the kinetic parameters of the model were estimated by simultaneous processing of four data sets that correspond to 75, 80, 83, 88 and 90 °C by using the DesK software, which resulted in satisfactory data fits shown in Fig. 3a and b. The values of kinetic parameters are listed in Table 3. The following important observations have been made in the course of parameter estimation.

- The reversible dimerization stage, reactions (b1f) and (b1b), can have a considerable impact upon the reaction course through the reversible consumption of CHP. Therefore, reliable estimates of kinetic parameters for these stages are particularly required. Nevertheless, in this study only their coarse estimates have been obtained. Additional concentrational data from some independent measurements are necessary for getting more precise estimates of equilibrium constant with the following specification of reaction enthalpy.
- The reaction (b6) was found to be extremely slow; therefore, it was removed from further consideration.
- The set of kinetic parameters found does not represent the unique solution of the estimation problem. Additional experimental data are required for obtaining more accurate estimates of the parameters. First, concentration data for the various species must be acquired over the course of the reaction to complement the overall calorimetric responses. Even knowing only the final composition of the reacting mixture might be very helpful for this purpose. Furthermore, conducting calorimetric experiments with the mixtures of different

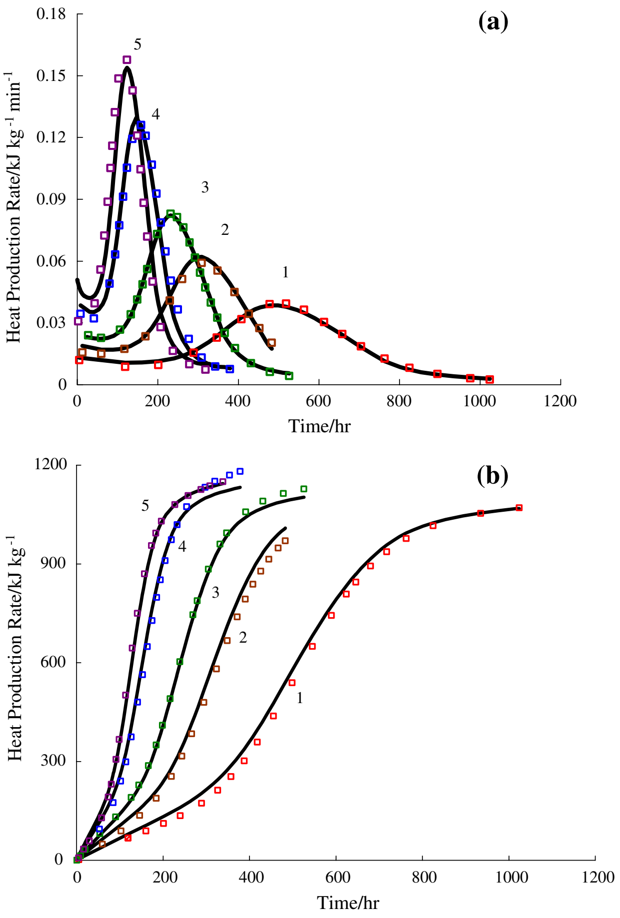

Fig. 3 Comparison of numerical simulations (——) and experimental data (□□□) at 1—75 °C, 2—80 °C, 3—83 °C, 4—88 °C and 5—90 °C for **a** heat production rate and **b** heat production by the meticulous concentration-based model (scheme B)

initial compositions would be very useful for obtaining more accurate estimates of model parameters for the proposed Scheme 2 in particular and for the creation of a more accurate model in general.

Only four out of the five data sets were used for estimating parameters for each of the three models. The fifth data set, for the 90 °C experiment, was not used in the model development, but was used to test the ability to extrapolate the models, based on the other four experiments. The correspondence between simulated and experimental 90 °C data, which is displayed in Figs. 1–3, somewhat demonstrates the ability of the models to predict the thermal behavior of the reaction.

Discussion

In spite of the previously mentioned observations concerning the parameter estimation for the meticulous model, it is much more detailed than the other ones considered. Therefore, comparing its predicting abilities with those of the formal autocatalysis scheme and the simple concentration-based model (scheme A) was of considerable interest.

All these models allow reaction simulation under certain conditions, provided that the initial composition of a mixture is the same as was investigated (i.e., 80 mass% solution of CHP in cumene). For further comparison of the ability to extrapolate the models, the heat production rate at 70 °C was simulated. In Fig. 4, the results of the simulation demonstrate that all the models provide almost identical prediction of heat production rate. This confirms that, in general, the predictions of all the models are in reasonable agreement.

Both the concentrational models A and B can predict the influence of the initial concentrations in the solution for the decomposition. To determine this, the reaction, when controlled isothermally at 83 °C, has been simulated based on models A (Fig. 5a and b) and B (Fig. 6a and b). Both models predict a decrease of maximal heat production rate with the reduction of the initial concentration of CHP, but the predicted values of maximal rates and especially TMR_{iso} differ significantly. In addition, scheme B predicts the complex character of heat production rate for 90 mass% solution (Fig. 6a). The models also predict quite

Table 3 Kinetic parameters for the model for scheme B of CHP decomposition in cumene

Kinetic parameters
$r_{\mathrm{b1f}} = 1.07 \cdot \exp(-45{,}000/RT) \cdot [\mathrm{C_6H_5C(CH_3)_2OOH}]^{2.00};\quad Q^{\infty}_{\mathrm{b1f}} = 7.00\,\mathrm{kJ\,mol^{-1}}$
$r_{\mathrm{b1b}} = 15.32 \cdot \exp(-40{,}000/RT) \cdot [(\mathrm{C_6H_5C(CH_3)_2OOH})_2]^{1.00};\quad Q^{\infty}_{\mathrm{b1b}} = -7.00\,\mathrm{kJ\,mol^{-1}}$
$r_{\mathrm{b2}} = 7.09 \times 10^{8} \cdot \exp(-97{,}420/RT) \cdot [\mathrm{C_6H_5C(CH_3)_2OOH}]^{0.41};\quad Q^{\infty}_{\mathrm{b2}} = 57.30\,\mathrm{kJ\,mol^{-1}}$
$r_{\mathrm{b3}} = 2.29 \times 10^{7} \cdot \exp(-92{,}300/RT) \cdot [\mathrm{C_6H_5C(CH_3)_2O}\cdot]^{0.58};\quad Q^{\infty}_{\mathrm{b3}} = 1.32\,\mathrm{kJ\,mol^{-1}}$
$r_{\mathrm{b4}} = 1.08 \times 10^{10} \cdot \exp(-103{,}740/RT) \cdot [\mathrm{C_6H_5C(CH_3)_2H}]^{0.43}[\cdot\mathrm{CH_3}]^{1.23};\quad Q^{\infty}_{\mathrm{b4}} = 61.80\,\mathrm{kJ\,mol^{-1}}$
$r_{\mathrm{b5}} = 1.32 \times 10^{7} \cdot \exp(-86{,}780/RT) \cdot [\mathrm{C_6H_5C(CH_3)_2H}]^{1.12}[\cdot\mathrm{OH}]^{0.96};\quad Q^{\infty}_{\mathrm{b5}} = 1.96\,\mathrm{kJ\,mol^{-1}}$
$r_{\mathrm{b7}} = 9.58 \times 10^{7} \cdot \exp(-111{,}420/RT) \cdot [\mathrm{C_6H_5C(CH_3)_2O}\cdot]^{0.45}[\cdot\mathrm{OH}]^{4.33};\quad Q^{\infty}_{\mathrm{b7}} = 266.71\,\mathrm{kJ\,mol^{-1}}$
$r_{\mathrm{b8}} = 1.05 \times 10^{6} \cdot \exp(-93{,}320/RT) \cdot [\mathrm{C_6H_5C(CH_3)_2}\cdot]^{0.68}[\cdot\mathrm{OH}]^{4.94};\quad Q^{\infty}_{\mathrm{b8}} = 576.22\,\mathrm{kJ\,mol^{-1}}$
$r_{\mathrm{b9}} = 1.17 \times 10^{7} \cdot \exp(-91{,}450/RT) \cdot [\mathrm{C_6H_5C(CH_3)_2}\cdot]^{1.69};\quad Q^{\infty}_{\mathrm{b9}} = 3.63\,\mathrm{kJ\,mol^{-1}}$

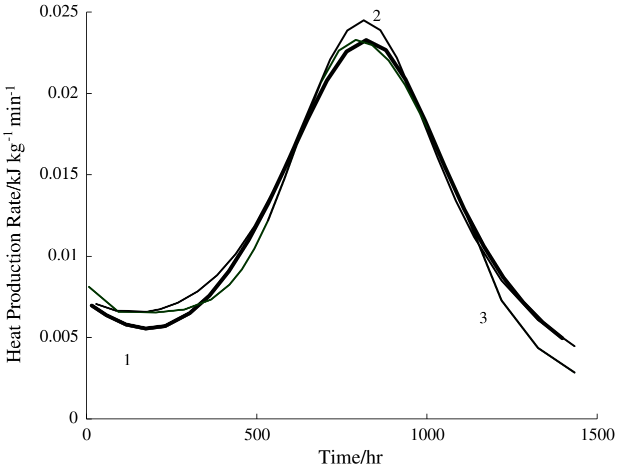

Fig. 4 Prediction of the decomposition of 80 mass% CHP solution at 70 °C by different models: 1—formal autocatalysis; 2—two-stage scheme A; 3—meticulous scheme B

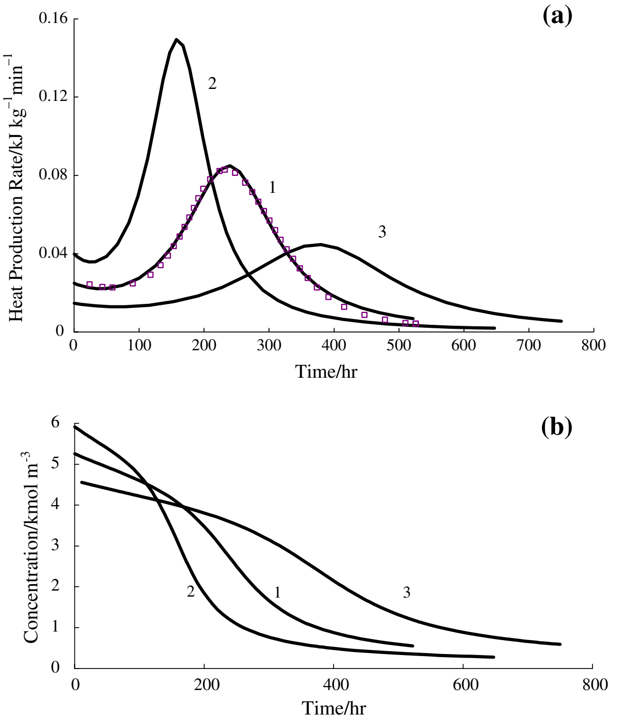

Fig. 5 Decomposition predictions with various CHP concentrations at 83 °C by scheme A for **a** heat production rate and **b** CHP concentration. CHP/cumene ratio (weight fractions): 1—0.8/0.2; 2—0.9/0.1; 3—0.7/0.3; 4—experimental data (□□□) for 80 mass% CHP solution

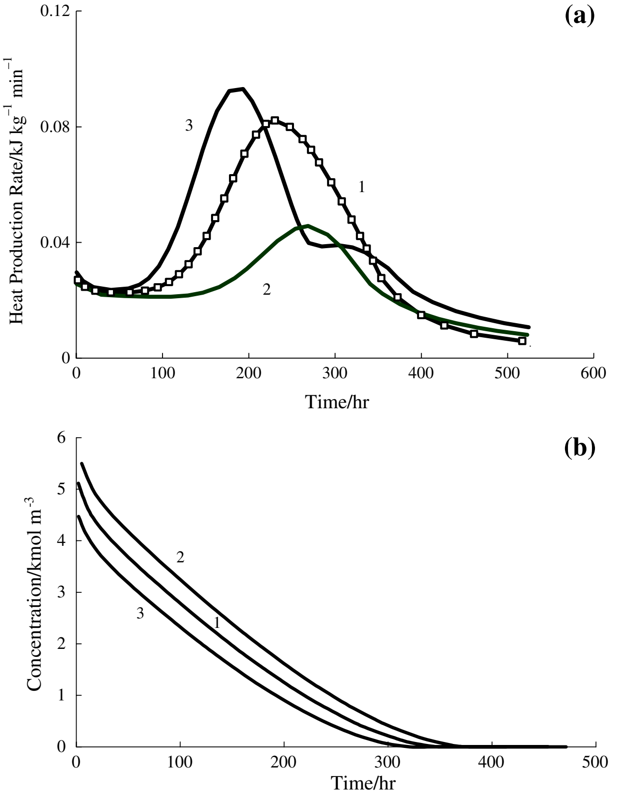

Fig. 6 Decomposition predictions with various CHP concentrations at 83 °C by scheme B for **a** heat production rate and **b** CHP concentration. CHP/cumene ratio (weight fractions): 1—0.8/0.2; 2—0.9/0.1; 3—0.7/0.3; 4—experimental data (□□□) for 80 mass% solution

different CHP profiles, as illustrated in Figs. 5b and 6b. The meticulous model is expected to give more realistic predictions. Nevertheless, the results clearly illustrate that running experiments with samples of different initial concentrations are highly desirable because they would give valuable information for model validation and for acquiring more accurate estimates of kinetic parameters.

Only the meticulous scheme B, in principle, can predict the influence of such factors as the presence of some radicals in the initial composition. To demonstrate this potential we simulated the decomposition of the 80 mass% CHP solution in cumene at 83 °C assuming that the initial mixture contains some small amount of radicals. We analyzed the effect of different radicals on the heat release. In all the cases the initial mixture was assumed to contain 4 mass% of a radical. The results of this sensitivity analysis can be seen in Fig. 7. The ·OH radical has a strong impact on the reaction, whereas the influences of $C_6H_5C(CH_3)_2O\cdot$ and $C_6H_5C(CH_3)_2\cdot$ were very weak. Then we investigated the effect of varying the ·OH concentration in the initial mixture (within the range 0–4 mass%). As expected, an increase of this contaminant concentration results both in a noticeable rise of maximal heat production rate and in a significant shortening of the TMR_{iso}, as diagramed in Fig. 8. Specifically, this means that the ·OH radical is the most dangerous contaminant from the thermal safety viewpoint.

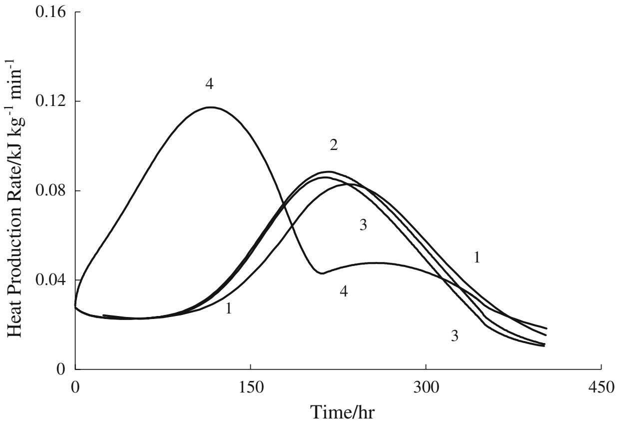

Fig. 7 Heat production rate v.s. time predictions, assuming elevated concentrations of different radical in the initial mixture at 83 CHP/cumene/radical ratio (weight fractions)—0.8/0.16/0.04: 1—no radicals (CHP/cumene—0.8/0.2); 2—$C_6H_5C(CH_3)_2O$; 3—$C_6H_5C(CH_3)_2$; 4—·OH

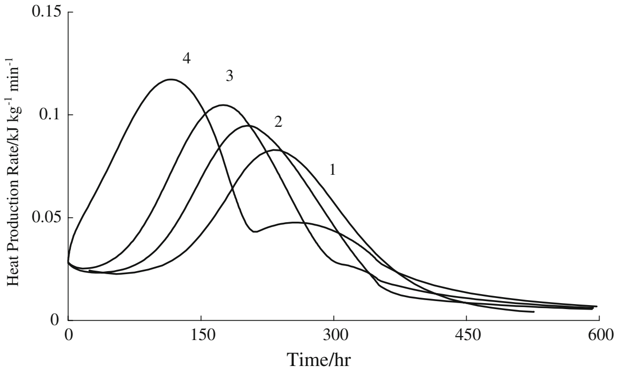

Fig. 8 Heat production rate v.s. time predictions, assuming various ·OH concentrations in t the initial mixture at 83 °C. CHP/cumene/·OH ratio (weight fractions): 1—0.8/0.2/0.0; 2—0.8/0.19/0.01; 3—0.8/0.18/0.02; 4—0.8/0.16/0.04

Conclusions

Mathematical simulation was systematically applied for the creation of a hierarchical set of kinetic models for the decomposition reaction of CHP. Simple two-stage autocatalytic models (both formal and concentrational) and the meticulous multi-stage model were shown to fit the available set of calorimetric data with almost the same quality. Of course, the prognostic abilities of the models differ significantly. Therefore, the choice of the model to use depends on the purpose of the investigation. The formal and simple concentrational models can be successfully applied for predicting the heat release of the mixture, provided that its composition is the same as was investigated. However, analyses with different mixture compositions or the presence of contaminants can be implemented only by using a detailed concentration-based model. The examples presented vividly illustrate the potential of kinetics-based simulation for the reactivity analysis of complex reactions.

Calorimetric data give valuable information for evaluating a reaction model. Nevertheless some additional data on the composition of reacting mixture are required to create an accurate complex multi-stage kinetic model.

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References

1. Hou HY, Shu CM, Duh YS. Exothermic decomposition of cumene hydroperoxide at low temperature conditions. AIChE J. 2001;47:1893–6.
2. Wang YW, Shu CM, Duh YS, Kao CS. Thermal runaway hazards of cumene hydroperoxide with contaminants. Ing Eng Chem Res. 2001;40:1125–32.
3. Chou YP, Huang JY, Tseng JM, Cheng SY, Shu CM. Reaction hazard analysis for the thermal decomposition of cumene hydroperoxide in the presence of sodium hydroxide. J Therm Anal Calorim. 2008;93:275–80.
4. Chen YL, Chou YP, Hou HY, I YP, Shu CM. Reaction hazard analysis for cumene hydroperoxide with sodium hydroxide or sulfuric acid. J Therm Anal Calorim. 2009;95:535–9.
5. Chen JR, Wu SH, Lin SY, Hou HY, Shu CM. Utilization of microcalorimetry for an assessment of the potential for a runaway decomposition of cumene hydroperoxide at low temperatures. J Therm Anal Calorim. 2008;93:127–33.
6. Beckmann JW, Wilkes JS, McGuire RR. 2,4,6-trinitrotoluene thermal decomposition: kinetic parameters determined by the isothermal differential scanning calorimetry technique. Thermochim Acta. 1977;19:111.
7. Kossoy AA, Benin AI, Smikalov PYu, Kasakov AN. A computerized system for research into the thermal safety of chemical processes. Thermochim Acta. 1992;203:77–92.
8. Kossoy AA, Podlevskikh N, Sheinman I. From calorimetric data via kinetic modeling to runaway simulation and reactor optimization (methodology and software). Proceedings of International Conference Assessment and Control of Chemical Processing Hazards, London, England 2000;24–5.
9. Sykes P. The guidebook to scheme in organic chemistry. 6th ed. Harlow: Longman; 1986. p. 128.
10. Hiatt R, Mill T, Irwin C, Castelman JK. Homolytic decompositions of hydroperoxides. II. Radical-induced decompositions of *t*-butyl hydroperoxide. J Org Chem. 1968;33:1421–8.
11. Howard JA, Chenier JHB, Yamada T. Absolute rate constant for hydrocarbon autoxidation. 32. On the self-reaction of 1,1-diphenylethylperoxyl in solution. Can J Chem. 1982;60:2566–72.
12. Furimsky E, Howard JA, Sewyn J. Absolute rate constant for hydrocarbon autoxidation. 28. A low temperature kinetic electron spin resonance study of the self-reactions of isopropylperoxy and related secondary alkylperoxy radicals in solution. Can J Chem. 1980;58:677–80.
13. Cowley LT, Waddington DJ, Wooley A. Reaction of oxygenated radicals in the gas phase, part 9 – self- reactions of isopropylperoxy radicals. J Chem Soc Faraday Trans. 1982;78:2535–46.

14. Shopova N, Ivanov S. Thermal decomposition of α-tetralyl hydroperoxide under non-isothermal conditions, without solvents. Thermochim Acta. 1944;231:193.
15. Chen CC, Shu CM, Yeh CA, Chen SC, Shyu ML. Autocatalytic decomposition of cumene hydroperoxide at low temperature conditions. The 17th Annual Conference of Asia Pacific Occupational Safety & Health Organization, Taipei, Taiwan, ROC 2001; p. 24–9.
16. Hiatt R, Chipcham J, Visser T. The induced decomposition of *tert*-butyl hydroperoxide. Can J Chem. 1964;42:2754–7.
17. Duh YS, Kao CS, Hwang HH, Lee WL. Thermal decomposition kinetics of cumene hydroperoxide. Trans IChemE. 1998;76:271.
18. Rotaru A, Kropidłowska A, Moanţă A, Rotaru P, Segal E. Thermal decomoposition kinetics of some aromatic azomonoehters. J Therm Anal Calorim. 2008;92:233.
19. Vlase T, Doca N, Vlase G, Bolcu C, Borcan F. Kinetics of non-isothermal decomposition of three irganox-type antioxidants. J Therm Anal Calorim. 2008;92:15–8.