

Kinetic Modeling of Dicumyl Peroxide Thermal Decomposition in Cumene

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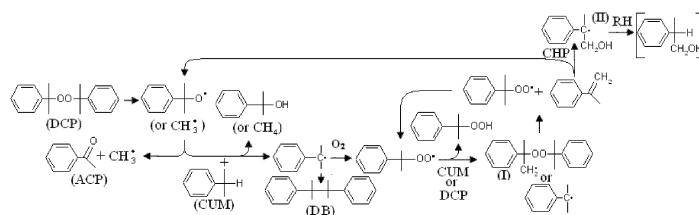
The present study aims to propose a detailed network of reactions through which the Dicumylperoxide (DCP) decomposition in cumene is supposed to occur. On the basis of this network a kinetic model is developed and successfully used to estimate the unknown kinetic parameters.

1. Introduction

Organic peroxides are dangerous materials widely used in chemical and process industry. Many incidents have been reported in the industrial sites in which they are used often due to runaway phenomena (Whu et al, 2008). A kinetic characterization of their thermal decompositions is thus useful both for the industrial applications and safety considerations. DCP is one of the most used peroxide in the polymer industry as cross-linking agent for polyethylene and ethylene vinyl acetate copolymers. In previous investigations the thermal decomposition of this species was studied by the Authors. The decomposition of DCP in cumene was studied in the temperature range 393-433 K from kinetic and chemical point of view, with and without the presence of oxygen. The results indicate that when oxygen is present the decomposition process is regulated by simple autocatalytic kinetics whereas after oxygen purging good results are obtained by modelling the substrate decay using a pseudo-first order kinetic equation. Chemical investigations indicate that the decomposition of DCP results mainly in the formation of acetophenone and dimethylphenylcarbinol with minor occurrence of 2,3-dimethyl-2,3-diphenylbutane and the presence of cumene hydroperoxide (CHP) as a reaction intermediate. On the basis of these results the present work is devoted to the development and validation of a single detailed kinetic model capable of predicting the concentration profiles of the involved species when a solution of DCP in cumene undergoes thermal decomposition at varying the starting conditions (temperature, substrate concentration, presence of oxygen etc.). An attempt to extend the modelling to the thermal decomposition of CHP in cumene is also done.

2. Model development

Scheme 1 depicts the reaction network through which the thermal decomposition of DCP in cumene develops according to the information collected during a previous investigation. However, other reactions are necessary to complete the reaction network. In tab. 1 all the reactions considered in the model are listed (see Table 2 for the acronyms of the species). On the basis of this list, the material balance for all the species participating to the process is written as an ordinary differential partial equations.



Scheme 1

For each species the balance equation is written as the sum of the rates of the reactions of consumption and generation to which the species participates:

$$\frac{dC_i}{dt} = \sum_n \pm k_n \cdot \prod_j C_j = \sum_n \pm A_n \cdot e^{-\frac{E_n}{RT}} \cdot \prod_j C_j \quad (1)$$

The oxygen transfer from the gas phase to the liquid solution is accounted for under the hypothesis of a “fast kinetic regime of absorption with reaction”:

$$\frac{dn_{O_2}}{dt} = V_{liq} \cdot K_{La} \cdot (C^* - C_{O_2}) \quad (2)$$

$$\frac{dC_{O_2}}{dt} = K_L a \cdot (C^* - C_{O_2}) - \sum_{i=1}^n K_i \cdot C_i \cdot C_{O_2} \quad (3)$$

$$C^* = \frac{1}{H} \cdot P_{O_2} = \gamma \cdot P_{O_2} = \gamma \cdot (n_{O_2}^0 - n_{O_2}) \cdot R \cdot T \cdot V_{gas}^{-1} \quad (4)$$

V_{liq} was equal to $0,15 \cdot 10^{-3}$ L and was kept constant during each run. The reciprocal of Henry constant for oxygen, γ , was fixed to $2.5 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$ and considered independent upon the temperature in the investigated range (Denisov et al, 1977).

Therefore the model consists of a system of 41 ordinary differential equations which needs to be solved according to proper initial conditions (for $t=0$: $C_{O_2} = C^{*0}$, $C_i = C_i^0$ where i is one of the n species taking part to the process) in order to test the developed kinetic model by comparing the concentration profiles calculated at varying the reaction time with those recorded during the runs. It is clear that the key to a successful kinetic model for the process is represented by the correct assignment of the values to the large number of kinetic parameters. From this point of view, all the reactions reported in tab. 1 can be divided into three groups. A first one including few of them for which reliable values of kinetic parameters were found in the literature and consequently adopted in the model. It is noteworthy to observe that for some specific reactions being more than one single value reported for its parameters (see reaction 1) the determination of reliable values was achieved as a result of an optimization procedure. A second group of reactions is represented by those for which no specific data for the parameters were found, although approximate values could be derived by analogy based on molecular similarities (see, for example, t-BuO and cumyloxy radicals). In this case the values taken from the literature were used as initial data for the optimization procedure. In the third group all the reactions are considered for which no data at all were available (n.a. in the table) from the literature. For the overall mass-transfer coefficient K_{La} a value equal to 1 min^{-1} was adopted.

Table 1: Reaction included in the model

n	REACTION	Real/ Analog	optimized	References	k (l/mol) ^g ·s ⁻¹	Ea Kcal/mol
1	CHP→R1+R5	R R	yes	Emmanuel, 1976 Bhattacharya, 2008	10 ^(12,3±0,1)	33,3±0,8
2	2CHP→R1+R4+W	R	no	Swern, 1970	10 ^{7,7}	26,0
3	DCP→2R1	R	no	Beiley, 1956	10 ^{14,7}	34,5±0,5
4	R1→ACP+R3	R R	yes	Baignèe, 1983 Bhattacharya, 2008	10 ^(9,8±0,1)	4,9±0,2
5	R3+CUM→MET+R2	R	no	Hendry, 1974	10 ^(8,4±0,5)	8,5±1,0
6	R1+CUM→DC+R2	A	yes	Hendry, 1974	10 ^(8,4±0,4)	3,8±0,2
7	R2+OX→R4	A	yes	Emmanuel, 1976	10 ^(7,2±0,3)	0
8	2R2→DB	A	yes	Denisov, 1977	10 ^(7,0±0,3)	3,0±0,3
9	R4+CUM→CHP+R2	A	yes	Hendry, 1974	10 ^(7,2±0,2)	12,1±0,5
10	R4+R2→DCP	A	yes	Denisov, 1977	10 ^(8,2±0,3)	3,6±0,3
11	2R3→ET	A	yes	Denisov, 1977	10 ^(9,4±0,1)	1,1±0,2
12	R5+CUM→W+R2	A	yes	Hendry, 1974	10 ^(8,5±0,1)	14,5±0,5
13	2R5→WX	A	yes	Denisov, 1977	10 ^(8,4±0,5)	0,5±0,1
14	R5+R2→DC	A	yes	Denisov, 1977	10 ^(8,7±0,1)	0,9±0,2
15	R2+R3→M	A	yes	Denisov, 1977	10 ^(9,1±0,2)	0,5±0,3
16	R4+DCP→CHP+R6	A	yes	Hendry, 1974	10 ^(9,2±0,3)	17,7±0,7
17	R6→AMS+R4	n.a.	yes		10 ^(8,2±0,4)	15,2±1,0
18	AMS+CHP→R7+R1	n.a.	yes		10 ^(8,2±0,3)	21,5±1,0
19	R7+CUM→AL+R2	n.a.	yes		10 ^(8,4±0,1)	23,0±1,1
20	R1+DCP→DC+R6	A	yes	Hendry, 1974	10 ^(9,0±0,6)	8,6±0,9
21	R1+CHP→DC+R8	A	yes	Hendry, 1974	10 ^(9,3±0,2)	11,4±4,0
22	R8→AMS+R11	A	yes		10 ^(6,6±0,1)	18,2±2,0
23	R4+DC→CHP+R9	A	yes	Hendry, 1974	10 ^(9,3±0,1)	17,3±1,5
24	R9→AMS+R5	n.a.	yes		10 ^(8,2±0,3)	22,5±0,5
25	R3+DCP→MET+R6	R	no	Hendry, 1974	10 ^(9,0±0,5)	13,2±1,0
26	AMS+CHP→DCP	n.a.	yes		10 ^(5,1±0,1)	22,0±0,4
27	R4+CHP→CHP+R8	A	yes	Hendry, 1974	10 ^(7,2±0,2)	15,6±1,2
28	R3+OX→R10	A	yes	Emmanuel, 1976	10 ^(4,2±0,3)	0
29	R10+DCP→B+R6	A	yes	Hendry, 1974	10 ^(8,2±0,3)	12,3±0,9
30	R10+CHP→B+R8	A	yes	Hendry, 1974	10 ^(8,4±0,7)	8,9±1,9
31	R3+DC→MET+R9	R	no	Hendry, 1974	10 ^(9,0±0,5)	13,2±1,0
32	R1+DC→DC+R9	A	yes	Hendry, 1974	10 ^(9,3±0,2)	4,8±1,0
33	R3+CHP→MET+R8	R	no	Hendry, 1974	10 ^(9,0±0,5)	13,2±1,0
34	WX→2R5	A	yes	Beiley, 1956	10 ^(13,4±0,2)	24,0±1,5
35	R4+R3→F	A	yes	Denisov, 1977	10 ^(9,2±0,2)	6,6±1,6
36	2R4→DCP+OX	A	yes	Denisov, 1977	10 ^(8,4±0,1)	4,9±0,6
37	2R10→G+OX	A	yes	Denisov, 1977	10 ^(9,2±0,3)	1,0±0,3
38	R5+CHP→W+R8	n.a.	yes		10 ^(9,1±0,2)	14,2±0,2
39	R11+CHP→WX+R8	n.a.	yes		10 ^(7,3±0,2)	16,4±1,0
40	R1+CHP→DC+R4	n.a.	yes		10 ^(8,4±0,2)	3,7±0,3
41	R3+CHP→MET+R4	n.a.	yes		10 ^(8,5±0,3)	6,9±0,5
42	R5+CHP→W+R4	n.a.	yes		10 ^(8,6±0,5)	14,4±1,2

43	R10+CHP→B+R4	n.a.	yes	$10^{(8,1±0,5)}$	$3,6±0,8$
44	R7→R12	n.a.	yes	$10^{(8,2±0,3)}$	$23,0±2,0$
45	R12+CUM→AL+R2	n.a.	yes	$10^{(8,2±0,5)}$	$16,2±0,7$
46	R12+DCP→AL+R6	n.a.	yes	$10^{(7,2±0,3)}$	$21,4±0,6$
47	R12+CHP→AL+R8	n.a.	yes	$10^{(8,2±0,3)}$	$17,0±0,4$
48	R5+AMS→R7	n.a.	yes	$10^{(8,2±0,4)}$	$11,1±0,5$
49	R4→AMS+R11	n.a.	yes	$10^{(3,2±0,1)}$	$4,7±0,3$
50	2R11→WX+OX	n.a.	yes	$10^{(8,3±0,6)}$	$2,0±0,4$

Table 2: Acronyms of the species included in the model

species	Abb	species	Abb	species	Abb
$[C_6H_5C(CH_3)_2]_2$	DB	$C_6H_5C(CH_3)_2OH$	DC	$C_6H_5COO\cdot(CH_3)_2$	R4
$C_6H_5C(O)CH_3$	ACP	$C_6H_5C(CH_3)_2OOH$	CHP	$HO\cdot$	R5
CH_3OOH	B	$[C_6H_5C(CH_3)_2O]_2$	DCP	$C_6H_5(CH_3)_2(CO)_2(CH_3)(CH_2\cdot)$	R6
CH_3CH_3	ET	$C_6H_5C(CH_3)_2H$	CUM	$C_6H_5\cdot$	
H_2O	W	$C_6H_5C(CH_3)=CH_2$	AMS	$C_6H_5C\cdot(CH_3)(CH_2OH)$	R7
CH_3OOCH_3	G	$C_6H_5C(CH_3)_2OOCH_3$	F	$C_6H_5(CH_3)(CH_2\cdot)COOH$	R8
O_2	OX	$C_6H_5CH(CH_3)CH_2OH$	AL	$C_6H_5(CH_3)(CH_2\cdot)COH$	R9
H_2O_2	WX	$C_6H_5CO\cdot(CH_3)_2$	R1	$CH_3OO\cdot$	R10
$C_6H_5C(CH_3)_3$	M	$C_6H_5C\cdot(CH_3)_2$	R2	$HO_2\cdot$	R11
CH_4	MET	$CH_3\cdot$	R3	$C_6H_5(CH_3)(CH_2O\cdot)CH$	R12

3. Experimental

For all the experiments a series of sealed, magnetically stirred, glass tubes were filled with DCP solutions in cumene with a concentration equal to 0.6 mol/L. For runs performed in absence of oxygen, the glass tubes were previously purged with a nitrogen stream. In both the cases (with and without oxygen) the tubes were placed into the oil bath withdrawn from it after the desired reaction time and rapidly cooled. The samples were recovered with acetone, diluted with acetonitrile and submitted to HPLC analyses. These were performed by means of a 1100 Hewlett Packard HPLC equipped with a Synergi 4 μ Fusion RP-80 column and a diode array detector. Gas analysis was performed on a Chromatograph HP 5890 equipped with a FID detector and a PPU column (30m x 053 mm) with an oven set 313 K and an helium flow of 7.0 ml/min.

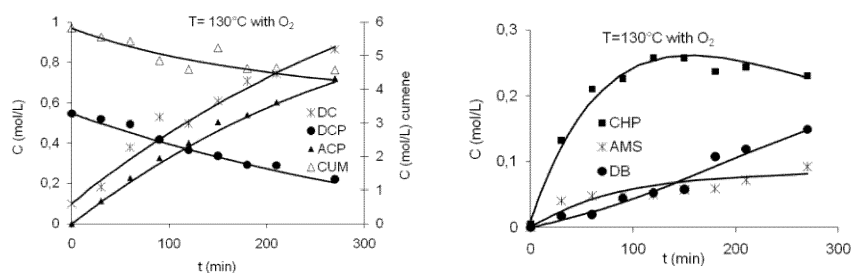
4. Results and discussion

During the present investigation 11 runs on DCP thermal decomposition were carried out starting from different initial conditions. For each run about 10 concentration data of 8 species were recorded. The results of 9 of the runs performed during the present work were simultaneously used in a single optimization procedure to estimate the unknown kinetic parameters, based on the minimization of an objective function defined as :

$$\varphi = \sum_{i=1}^f \sum_{j=1}^k \sum_{l=1}^n (y_{i,j,l} - c_{i,j,l})^2 \quad (5)$$

In which y and c are the calculated and experimental concentration and n , k , f are, respectively, the number of experimental data recorded in each experiment, of the substances and the of the experiments used in the optimization procedure.

In figs. 1 and 2 some examples of comparison of calculated (continuous lines) and experimental data (symbols) are shown. At a first sight, the proposed model seems to be capable to well simulate the system behavior. However, for a more quantitative analysis of the results of the optimization procedure an examination of the data and statistical indices reported in table 1 is necessary. A careful analysis of them indicates that for each of the estimated kinetic parameters very low uncertainties are calculated and that the mean overall percentage standard deviation (5,47%) in the runs is comparable with those associated with the analytical determinations of each species, thus supporting a good reliability of the model. To confirm this, the model was successfully validated by using the results of the runs not included in the optimization procedure. In this case, the model was used just to simulate the concentration profiles of the species of interest *without any further adjustment* of previously estimated kinetic parameters (Figs. 3).



Figures 1a/1b: DCP decomposition with O_2 , $T=130^\circ C$

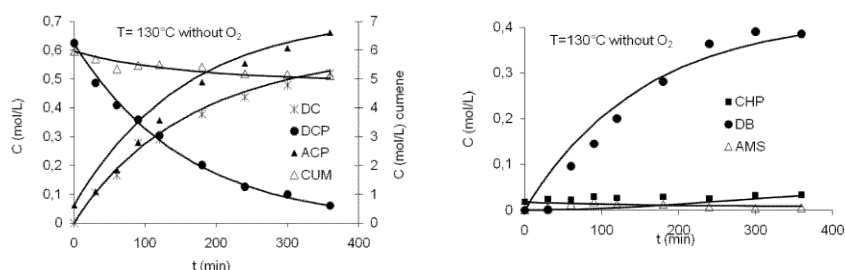


Figure 2a/2b: DCP decomposition without O_2 , $T=130^\circ C$

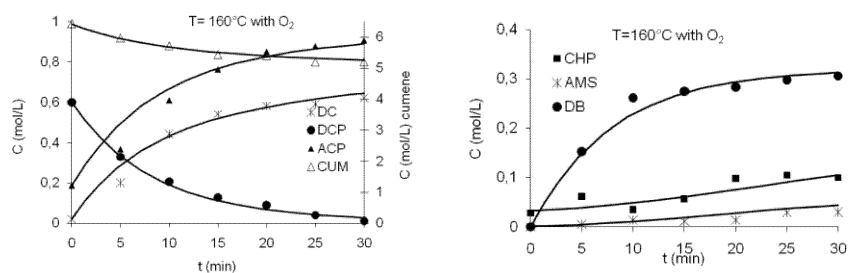


Figure 3a/3b: DCP decomposition with O_2 , $T=160^\circ C$

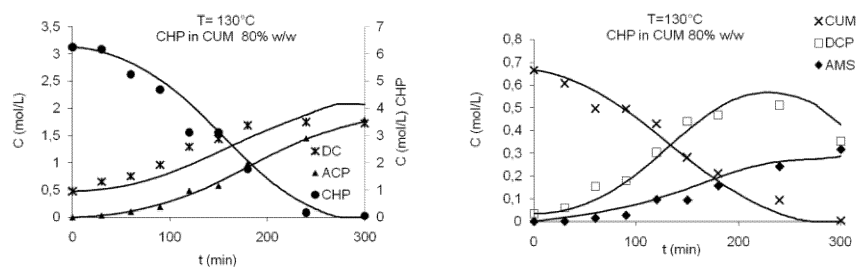


Figure 4a/4b: CHP decomposition, $T=130^{\circ}\text{C}$

Figs. 3 shows the good agreement between the calculated and experimental results thus confirming the reliability of the proposed model. An attempt was also done to apply the developed and validated model to simulate the results collected during the thermal decomposition of cumene hydroperoxide in cumene (Figs 4). Good results are obtained also in this case.

5. Conclusions

In the present work a model was proposed to simulate the thermal decomposition of DCP in cumene. This model was validated by means of the data collected during the experimental runs and unknown kinetic parameters were estimated. An attempt to extend its use to the thermal decomposition of cumene hydroperoxide in cumene was also successfully done.

References

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