



## Kinetic and chemical characterization of thermal decomposition of dicumylperoxide in cumene

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### ABSTRACT

Dicumylperoxide (DCP) is one of the most used peroxides in the polymer industry. It has been reported that its thermal decomposition can result in runaway phenomena and thermal explosions with significant economic losses and injuries to people. In the present paper thermal behaviour of dicumylperoxide in cumene was investigated over the temperature range of 393–433 K under aerated and de-aerated conditions. The results indicated that when oxygen was present, the decomposition rate did not follow a simple pseudo-first order kinetic as previously reported in literature. A satisfactory fit of the experimental data was, in this case, achieved by means of kinetic expression derived under the assumption of an autocatalytic scheme of reaction. The reaction rate was, on the contrary, correctly described by a pseudo-first order kinetic in absence of oxygen. Under both aerated and de-aerated conditions, chemical analysis showed that the decomposition mainly resulted in the formation of acetophenone and dimethylphenylcarbinol with minor occurrence of 2,3-dimethyl-2,3-diphenylbutane. The formation of methane and ethane was also invariably observed while the appearance of cumylhydroperoxide as a reaction intermediate was detected under only aerated conditions. Therefore, two reaction schemes were proposed to explain system behaviour in the presence of oxygen and after its purging.

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### 1. Introduction

Dicumylperoxide (DCP) is one of the most used peroxides in the polymer industry [1]. It is extensively utilized as a cross-linking agent for polyethylene, ethylene vinyl acetate copolymers and as a curing agent for unsaturated polystyrene. Moreover, it can form as a reaction intermediate in chemical process of practical relevance. Particularly, the appearance of DCP as a reaction intermediate has been recently observed by our group during the analysis of the thermal decomposition of cumylhydroperoxide (CHP) in cumene (CUM) [2]. It is, in this context, of great concern to note that thermal decomposition of DCP can likely lead, as a consequence, to temperature control failure and/or process disturbances, to the occurrence of runaway phenomena [3,4]. These may give rise to reactor explosions with significant economic losses and injuries to people. A case of reactor explosion caused by the thermal decomposition of DCP occurred, for example, in 2003 in Taiwan and has been thoroughly described in [5]. Therefore, a detailed kinetic and chemical characterization of the thermal decomposition of DCP is essential to ensure safe operation of chemical processes of practical relevance.

Despite the extensive use of DCP in industrial applications and its intrinsic danger, few studies have been presented providing a detailed analysis of the thermal decomposition of such peroxide. The little data available refer to different processing conditions making it impossible to assess the reliability of the proposed kinetic expressions by comparison between different studies. Two studies have been presented, in particular, over the past decade. In the first one by Marco et al. [6] the decomposition of DCP was investigated in ethylbenzene while in a second study presented by Wu et al. [5] the behaviour of the peroxide in the presence of dimethylphenylcarbinol and cumylhydroperoxide was analyzed. Both studies proposed to describe the decomposition rate of DCP by means of an  $n$ th-order kinetic with Arrhenius dependence on the temperature. The same type of kinetic expression was proposed in an older paper by Bailey and Godin [7] for the thermal decomposition of DCP in de-aerated cumene. The kinetic parameters reported in these three papers [5–7] suggest a dependence of the thermal decomposition rate of DCP on the employed solvent and/or the presence of oxygen. However, it is important to stress that indications about the uncertainty of the estimated kinetic parameters are only provided in [6] for the DCP decomposition in aerated solutions of ethylbenzene. On the contrary, uncertainty measure is not presented for the DCP decomposition in dimethylphenylcarbinol [5] while confidence intervals are computed only for the activation energy when de-aerated cumene is employed as a solvent [7].

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### Nomenclature

$A_i$	Pre-exponential factor ( $\text{min}^{-1}$ ) or ( $\text{L mol}^{-1} \text{min}^{-1}$ )
$E_i$	Activation energy ( $\text{kJ mol}^{-1}$ )
$C_i^0$	Initial concentration of $i$ th species ( $\text{mol L}^{-1}$ )
$C_{Rj}$	Concentration of $i$ th radical species ( $\text{mol L}^{-1}$ )
$C_i$	Concentration of $i$ th species ( $\text{mol L}^{-1}$ )
$T$	Temperature (K)
$R$	Universal constant of gas ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$k_j$	Kinetic constant for $j$ th reaction ( $\text{min}^{-1}$ ) or ( $\text{L mol}^{-1} \text{min}^{-1}$ )
$t$	Time (min)
$u$	Conversion degree (dimensionless)
$r$	Number of groups of data collected in all the experiments (dimensionless)
$p$	Number of parameters to be estimated (dimensionless)
$m$	Total number of experimental data (dimensionless)
$q_i$	Sum of the squares (dimensionless)

### Greek symbol

$\sigma$	Percentage standard deviation (dimensionless)
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Therefore, the confidence intervals of the kinetic parameter values estimated with different solvents might actually overlap. In this case, no information about the dependence of the DCP decomposition rate on processing conditions might be inferred. Therefore, further analysis needs to be performed in order to clearly describe how the employed solvent and the presence of oxygen affect the thermal decomposition of DCP.

In this paper, the thermal decomposition of DCP in cumene is investigated. As previously mentioned, DCP can be formed as intermediate during CHP decomposition and it can decompose leading to the development of runaway phenomena. It is important to remark, in this context, that CHP production is typically carried out by a reaction between oxygen and cumene [8]. Therefore, it is of great importance to investigate the kinetic behaviour of DCP in the presence of oxygen. Moreover, the sole study of DCP thermal decomposition in cumene was presented in [7] and performed under de-aerated conditions. It is also important to note that a completely non-chain mechanism of the DCP decomposition process was proposed in [7] in contrast with what is found for numerous other peroxides exhibiting a partial radical-induced decomposition mechanism (see for example [9] for di-tert-butyl-peroxide). Therefore, the present work investigates the DCP thermal decomposition in cumene under aerated and de-aerated conditions. The objective is to provide reliable kinetic expressions for the DCP decomposition rate and elucidate, based on the identification of the main intermediates and products, the relevant reaction pathways. Particular attention is focused on the effect of oxygen.

## 2. Materials and methods

All the experimental runs were carried out using an oil bath whose temperature was controlled by an Heydolph EKT 3001 heating plate. For all experiments, a series of sealed glass tubes were filled with DCP solutions in cumene at a concentration of around  $0.6 \text{ mol L}^{-1}$ . For runs performed in absence of oxygen, the glass tubes were previously purged by means of an argon stream. In both cases (with and without oxygen) the tubes were placed into the oil bath, taken out of it after the desired reaction time and rapidly cooled. The samples were recovered with acetone, diluted with acetonitrile and submitted to HPLC analysis. These were performed by

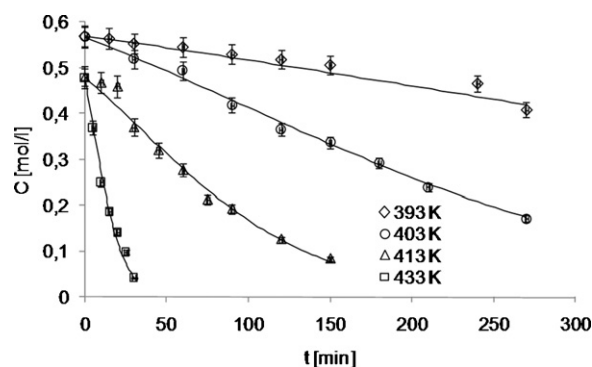


Fig. 1. DCP concentration decay during isothermal decomposition runs in the presence of oxygen. Symbols – experimental data; continuous lines – calculated concentrations.

means of a 1100 Hewlett Packard HPLC equipped with a Synergi 4  $\mu$  Fusion RP-80 column and a diode array detector. The mobile phase was (v/v%) 65% of acetonitrile and 35% of a buffer solution (5.0%  $\text{CH}_3\text{OH}$ , 0.4%  $\text{H}_3\text{PO}_4$  and 94.6%  $\text{H}_2\text{O}$ ), with a flow of  $10^{-3} \text{ L min}^{-1}$ . The signals at wavelengths of 210 and 240 nm were used for quantitative analysis. The oven temperature was set at 305 K. Gas analysis was performed on a Chromatograph HP 5890 equipped with a FID detector and a PPU column ( $30 \text{ m} \times 0.53 \text{ mm}$ ) with an oven set 313 K and a helium flow of  $7.0 \text{ mL min}^{-1}$ . All the reagents were purchased from Sigma–Aldrich and were used as received.

## 3. Results and discussion

### 3.1. Kinetic investigations

In Fig. 1 the concentration data against the reaction time for DCP thermal decomposition in cumene collected during four isothermal runs at 393, 403, 413 and 433 K in the presence of oxygen were shown.

For each investigated temperature, the runs were repeated three times and the average of the DCP concentration values collected at each instant were reported in the diagrams along with the error bars. A first attempt to identify the kinetic law governing the thermal decomposition of DCP was performed by means of a simple pseudo-first order kinetics as previously used by other authors [6,7]. A Fisher's test was performed [10] to assess the possibility to correctly describe the DCP decomposition rate by means of such model (null hypothesis). With this aim, the collected experimental data were partitioned into groups corresponding to the same reaction time and temperature and the following ratio was computed:

$$v_0 = \frac{q_1/(r-p)}{q_2/(m-p)} = 2.1 \quad (\text{a})$$

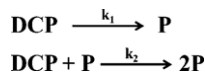
where  $r$  is the number of groups of data,  $p$  is the number of the parameters to be estimated,  $m$  is the total number of experimental data,  $q_1$  is the sum of the squared deviations of the average values of the groups from the values predicted with the utilized model,  $q_2$  is the sum of the squared deviations of each experimental data from the average value of the corresponding group. The computed  $v_0$  value is then compared with a critical value  $C = 1.605$ , derived from the table of the  $F$ -distribution for a significance level equal to 5% with  $((r-p), (m-r))$  degrees of freedom. The results of the test are reported in Table 1.

Since the computed  $v_0$  was found larger than  $C$ , the null hypothesis was rejected imposing to consider different kinetic models.

A careful analysis of the collected experimental data showed that the evolution of the DCP concentration approximately follows a s-shaped pattern. This suggested that an autocatalytic kinetic model could be more adequate than a simple pseudo-first order

**Table 1**  
Analysis of variance (first-order model).

Source of variation	Degrees of freedom	Sum of squares	Mean square
Deviation of means from regression	$r - p = 35 - 2 = 33$	$q_1 = 1.7 \times 10^{-2}$	$q_1 / (r - p) = 5.17 \times 10^{-4}$
Within groups (deviation from mean)	$m - r = 105 - 35 = 70$	$q_2 = 1.74 \times 10^{-2}$	$q_2 / (m - r) = 2.49 \times 10^{-4}$
Total	$m - p = 103$	$q = 3.45 \times 10^{-2}$	

**Scheme 1.** Simple reaction network for autocatalytic decomposition of DCP.

kinetic model to describe the DCP decomposition rate. To prove it, the simple autocatalytic reaction scheme described in **Scheme 1** is considered. Based on such scheme, the following kinetic equation was derived:

$$\frac{du}{dt} = A_2 \cdot \exp\left(\frac{-E_2}{RT}\right) \cdot C_{\text{DCP}}^0 \cdot (1 - u) \cdot \left(u + \frac{A_1 \cdot \exp(-E_1/RT)}{A_2 \cdot \exp(-E_2/RT) \cdot C_{\text{DCP}}^0}\right) \quad (\text{b})$$

The Fisher test was repeated to assess the reliability of such model (see **Table 2**).

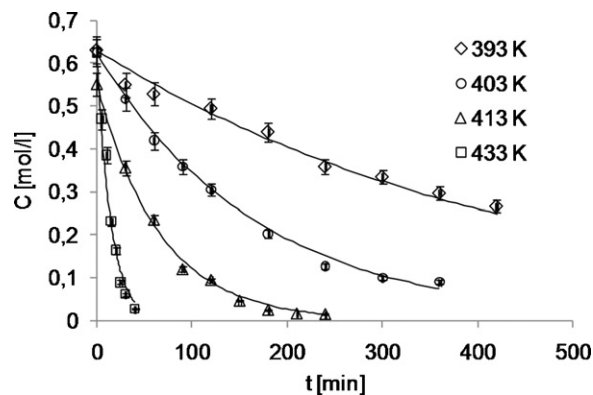
In this case, a critical value  $C = 1.615$  was derived from the table of the  $F$ -distribution for a significance level equal to 5% with  $((r - p), (m - r))$  degrees of freedom.

Hence, the value  $v_0 = 0.93 < C = 1.615$  was found clearly suggesting the possibility to effectively employ the proposed autocatalytic model. This is also apparent from **Fig. 1**, showing a comparison between the experimental data and those calculated by means of the autocatalytic model (continuous line). The computed optimal values of the kinetic parameters are given in **Table 3**.

Unfortunately, due to the complexity of the decomposition mechanism, the identification of an intermediate species which can behave as  $P$  in **Scheme 1** is not possible.

When the runs were repeated after purging the oxygen from the system, different results were found. For example, the data collected during isothermal runs carried out at 393, 403, 413 and 433 K, were satisfactorily fitted by means of a simple pseudo-first order kinetics (**Fig. 2**). In this case, a Fischer's test was again performed demonstrating that a pseudo-first order kinetic correctly describes the decomposition rate for a significance level equal to 1% (calculation not shown).

Based on the simultaneous modelling of the results of the four runs by means of a pseudo-first order kinetic equation, values of the pre-exponential factor and of the activation energy equal to  $(3.9 \pm 0.2) \times 10^{14} \text{ min}^{-1}$  and  $129.9 \pm 0.2 \text{ kJ/mol}$  were found respectively (with percentage standard deviations equal to 5.1%

**Fig. 2.** DCP concentration decay during isothermal decomposition runs in the absence of oxygen. Symbols – experimental data; continuous lines – calculated concentrations.

(393 K), 6.5% (403 K), 7.7% (413 K), 10.4% (433 K)). It is noteworthy to observe that the value found for the activation energy was significantly different from that reported by Bailey and Godin [7]. On the contrary, nothing could be said for the pre-exponential factor since no indication about the uncertainty of the value computed for such parameter was given in [7]. However, to prepare the basis for the development of a single model capable to simulate the system behaviour at varying the experimental conditions (including the presence of oxygen) a better understanding of the DCP thermal decomposition process in cumene was necessary. A detailed investigation on the main reaction pathways through which the process itself develops was thus undertaken.

### 3.2. Chemical investigations

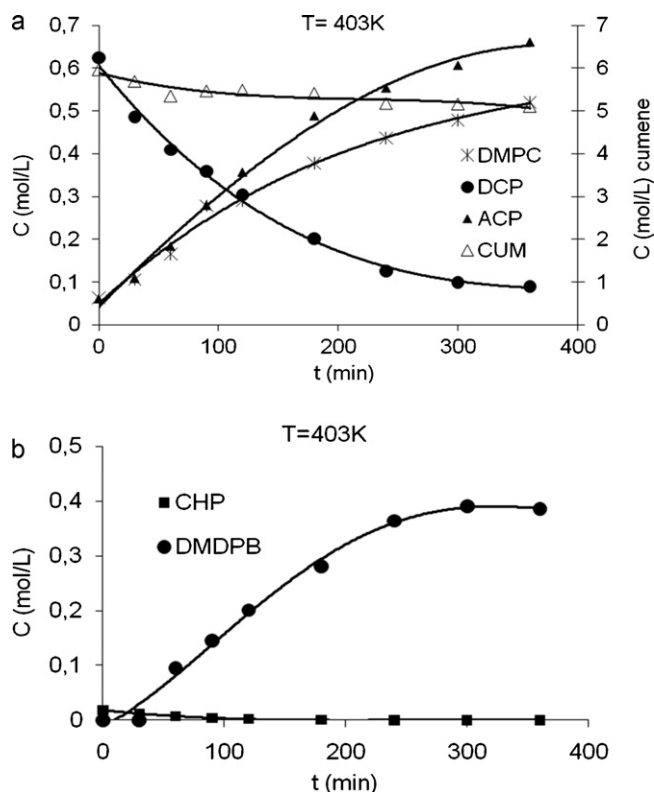
The distribution of the intermediates and products recorded during a decomposition run at 403 K in cumene, after removing oxygen from the reacting system, is shown in **Fig. 3a** and **b**. The results indicated that, at the beginning of the run, cumylhydroperoxide (CHP) was present in the reacting solution, being this species a common impurity of commercial cumene. Analytical data also indicated that during the decomposition of DCP different intermediates and products formed as mainly acetophenone (ACP) and dimethylphenylcarbinol (DMPC) and at lower concentra-

**Table 2**  
Analysis of variance (autocatalytic model).

Source of variation	Degrees of freedom	Sum of squares	Mean square
Deviation of means from regression	$r - p = 35 - 4 = 31$	$q_1 = 7.16 \times 10^{-3}$	$q_1 / (r - p) = 2.31 \times 10^{-4}$
Within groups (deviation from mean)	$m - r = 105 - 35 = 70$	$q_2 = 1.74 \times 10^{-2}$	$q_2 / (m - r) = 2.49 \times 10^{-4}$
Total	$m - p = 101$	$q = 2.46 \times 10^{-2}$	

**Table 3**  
Best estimated values of the kinetic parameters and percentage standard deviation for DCP thermal decomposition in the presence of oxygen (autocatalytic model).

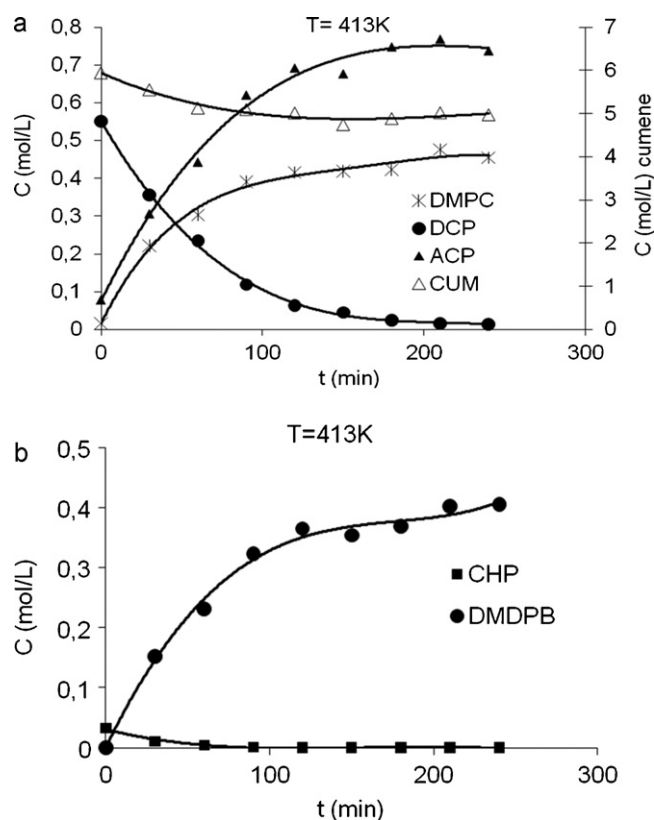
$A_1$ ( $\text{L min}^{-1}$ )	$E_1$ (kJ/mol)	$A_2$ ( $\text{L mol}^{-1} \text{ min}^{-1}$ )	$E_2$ (kJ/mol)	$\sigma$ (393 K) %	$\sigma$ (403 K) %	$\sigma$ (413 K) %	$\sigma$ (433 K) %
$1.9 \times 10^{15} \pm 0.2 \times 10^{15}$	$133.8 \pm 0.3$	$7.3 \times 10^{14} \pm 0.3 \times 10^{13}$	$134.9 \pm 0.2$	5.0	6.5	8.6	10.9



**Fig. 3.** (a) Distribution of intermediates and products during DCP thermal decomposition at  $T=403\text{ K}$  in the absence of oxygen  $[\text{DCP}]_0=0.62\text{ mol L}^{-1}$ . Dimethylphenylcarbinol (DMPC), dicumylperoxide (DCP), acetophenone (ACP), cumene (CUM). (b) Distribution of intermediates and products during DCP thermal decomposition at  $T=403\text{ K}$  in the absence of oxygen  $[\text{DCP}]_0=0.62\text{ mol L}^{-1}$ . Cumylhydroperoxide (CHP), 2,3-dimethyl-2,3-diphenylbutane (DMDPB). (In these figures, continuous lines do not represent calculated data.)

tions 2,3-dimethyl-2,3-diphenylbutane (DMDPB), CHP and traces of alpha-methylstyrene (AMS). In particular, it could be observed that after 360 min about 86% of the initial DCP disappeared leading mainly to the formation of ACP and DMPC. The formation of gaseous products such as methane and ethane was also detected during the experiments. It is noteworthy to observe that the identified products satisfactorily accounted for the disappearance of the substrate and for the partial consumption of cumene. In fact the total amount of aromatic rings present at the beginning of the run was the same as the one found in the analyzed products at the end of the experiments.

Similar results were observed at 413 K (Fig. 4a and b), the sole difference being represented by a shorter reaction time required for a complete disappearance of DCP.

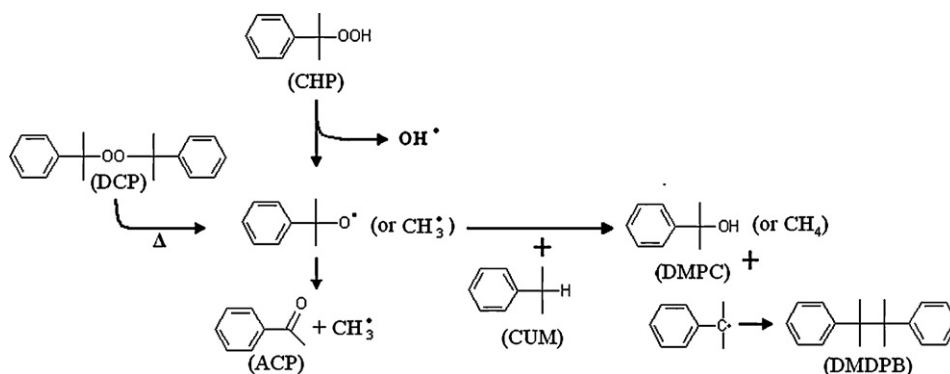


**Fig. 4.** (a) Distribution of intermediates and products during DCP thermal decomposition at  $T=413\text{ K}$  in the absence of oxygen  $[\text{DCP}]_0=0.55\text{ mol L}^{-1}$ . Dimethylphenylcarbinol (DMPC), dicumylperoxide (DCP), acetophenone (ACP), cumene (CUM). (b) Distribution of intermediates and products during DCP thermal decomposition at  $T=413\text{ K}$  in the absence of oxygen  $[\text{DCP}]_0=0.55\text{ mol L}^{-1}$ . Cumylhydroperoxide (CHP), 2,3-dimethyl-2,3-diphenylbutane (DMDPB). (In these figures, continuous lines do not represent calculated data.)

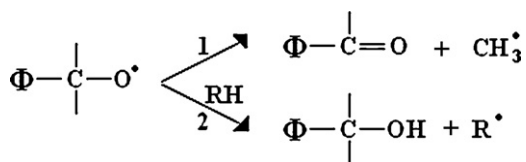
Based on these observations, Scheme 2 could be proposed to account for the system behaviour in absence of oxygen.

The homolysis of O–O bond of DCP gave rise to the formation of two cumyloxy radicals for each molecule of DCP. The formation of the two main decomposition products, ACP and DMPC, was strictly related to the behaviour of these radicals. This species could undergo a  $\beta$ -scission (path 1 in Scheme 3) leading to the formation of ketone and a methyl radical or react with an H-donor to form carbinol (path 2) [11].

The high concentration at which an H-donor as cumene was present made it possible for path 2 to significantly compete with

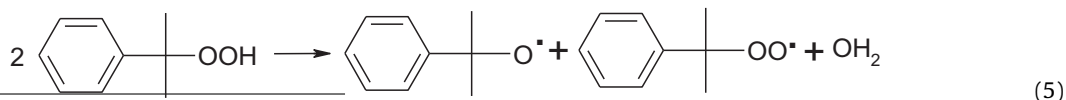


**Scheme 2.** Pathways proposed for the thermal decomposition of DCP in the absence of oxygen.

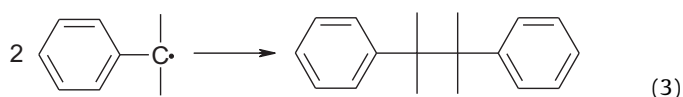
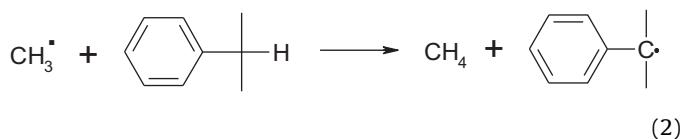
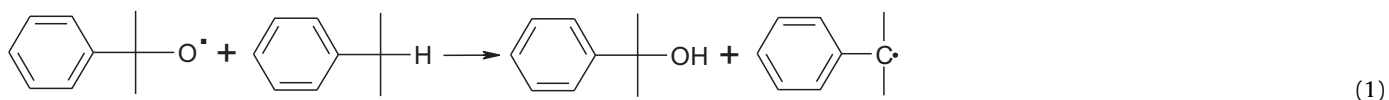


**Scheme 3.** Competitive reactions involving cumyloxy radicals.

path 1 (Scheme 3) thus allowing the appearance in the solution of both DMPC and ACP at comparable concentrations.



In the absence of O<sub>2</sub> cumyl radicals which easily formed as a result of an H-abstraction from cumene by cumyloxy and methyl radicals could just undergo some terminating reactions as, for example, that leading to the formation of DMDPB:



In the case of a non-chain mechanism, as proposed by Bailey and Godin [7] and according to the reactions reported above, DMDPB would form in a ratio of 1 mole per mole of DCP. A simple look to Figs. 3a and b (or 4a and b) indicated that the moles of DMDPB formed in the runs in the absence of oxygen carried out during the present investigation were a little higher than one half of those of the initial DCP. Therefore, it could be thus concluded that cumyloxy and methyl radicals underwent some other reactions in addition to (1) and (2) which did not generate cumyl radicals. For example, the formation of ethane as a result of a cross termination of methyl radicals supported this view.

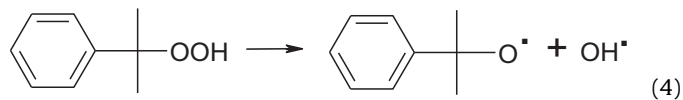
The results recorded at 403 K when the runs are repeated in the presence of oxygen are shown in Fig. 5a and b.

ACP, DMDPB and DMPC were again found to form as reaction products. However, unlike the case of de-aerated solutions, CHP was formed in this case as a reaction intermediate. In particular, the CHP concentration rapidly increased and then gradually decreased after reaching a maximum concentration value of ~0.23 mol L<sup>-1</sup>. It had to be stressed that also in the presence of oxygen the identified and analyzed products satisfactorily accounted (in terms of aromatic rings) for the disappearance of DCP and CHP and for the partial conversion of cumene. Similar results were obtained at 393 and 413 K (data not shown).

To explain this result, the reaction pathways made possible by the presence of oxygen had to be identified. For example, it could be proposed that in the presence of oxygen cumyl radicals, which form according to the reactions (1) and (2), were readily converted to cumylperoxy radicals. These peroxidic species could in principle abstract a hydrogen atom both from cumene and also from DCP

molecules. Last attack, which results into the formation of CHP and the radical species (I) (Scheme 4) and represented a pathway of disappearance of DCP (in addition to the homolysis of the –O–O–bond), was only possible in an aerated system provided that, for the adopted DCP concentrations, it could kinetically compete with hydrogen abstraction from cumene.

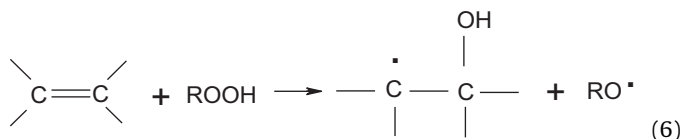
CHP could decompose to generate some radicals according to the following reactions:



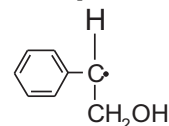
In Scheme 4 it was proposed that the radical (I) decomposed to form cumylperoxy radical and a molecule of alpha-methylstyrene. However, due to the low concentration at which alpha-

methylstyrene was found in the solution the occurrence of some other reactions in which this species was involved leading to the formation of chemical species among those analyzed in the present investigation-had to be put forward. It has been reported that hydroperoxides are capable of reacting with olefins to generate radical species [12].

Emanuel et al. [12] proposed that the reaction between a hydroperoxide and an olefin resulted in the formation of an alkoxy radical and a radical containing an alcoholic function in the alpha position:

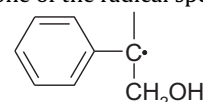


The same authors calculated that in the case of tert-butylhydroperoxide and styrene the path leading to butoxy radical and



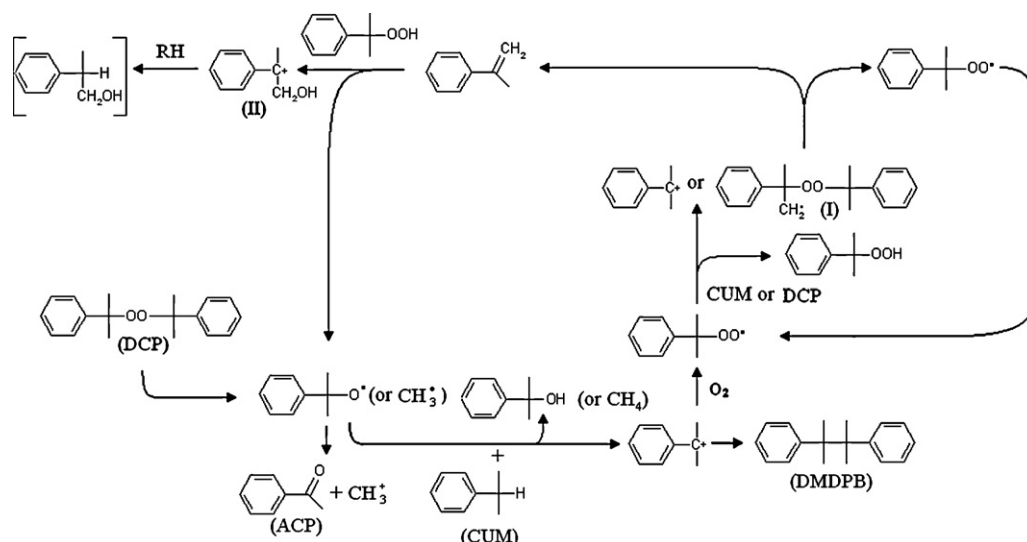
was energetically the most favourable.

According to these observations it could be proposed that a direct reaction between cumylhydroperoxide and alpha-methylstyrene occurred leading to the formation of a molecule of cumyloxyradical and one of the radical species (II):



A simple calculation by a group contributing method for gas phase for the reaction between alpha-methylstyrene and cumenehydroperoxide gave a heat of reaction of –6.6 kcal/mole (the heats of formation used for this calculation were, at atmospheric pressure and T=298 K: –19.4 kcal/mole (cumenehydroperoxide), 28.6 kcal/mole (alpha-methylstyrene), 9.7 kcal/mole (cumyloxyradical) and –7.1 kcal/mole (alphahydroxycumylradical) [13]), thus indicating that it was energetically favoured. The





**Scheme 4.** Pathways proposed for the thermal decomposition of DCP in the presence of oxygen.

species II could abstract a hydrogen atom from the solvent leading to the formation of 2-phenyl-1-propanol. However, its presence in the reacting mixtures could just be inferred since any attempt to demonstrate it failed due to the very similar (chromatographic and UV absorption) properties of this species and carbinol. This fact prevented any possibility to measure separately the concentration of the two species in the reacting mixture in which all the data

reported in figures as carbinol had to be considered as the sum of their concentrations.

The presence at trace levels of 2-phenylpropanal – which could arise from alpha-methylstyrene oxide – indicated that the formation of the latter from radical (I), as could be proposed based on literature suggestions [14], could be neglected.

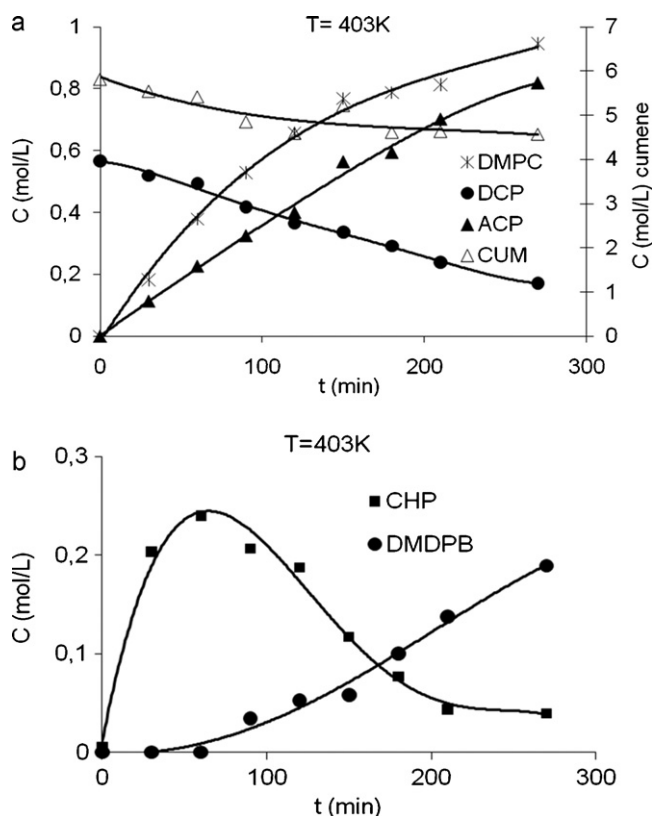
Following the results reported above, it was clear that generally speaking DCP consumption during its thermal decomposition could be ascribed both to the O–O homolysis and to the attack of different reactive radicals on its molecules. The nature and the stationary concentrations in the solution of these radicals depended on the operating conditions (solvent, presence of oxygen, initial substrate concentrations and temperature). In particular, when oxygen was purged from the system the dominating radical species, cumyl radical, was not capable of abstracting a hydrogen atom from DCP and the decomposition of the latter proceeds all through the simple O–O homolysis. In the presence of oxygen, cumyl radicals were converted into cumylperoxy ones which attack DCP and sustain its radical-induced decomposition. Therefore, it was clear that any model aiming to simulate the system behaviour by varying the experimental conditions had to be based on a detailed reaction network to allow the calculation of the concentrations of the relevant radical species present in the reacting medium.

#### 4. Conclusions

The decomposition of dicumylperoxide in cumene was studied in the temperature range of 393–433 K with and without the presence of oxygen.

A preliminary kinetic analysis indicated that different reaction kinetics are required to describe the substrate decay: when oxygen was present autocatalytic reaction kinetics could be successfully used whereas in the absence of oxygen a simple pseudo-first order could be adopted.

Chemical investigations indicated that the decomposition of dicumylperoxide in cumene mainly resulted in the formation of ACP and DMPC with minor occurrence of DMDPB and the presence of cumylhydroperoxide in the system as a reaction intermediate, the formation of AMS being observed at trace levels. The formation of methane and ethane was also observed. A reaction scheme was proposed to explain the results observed in the experiments in the presence of oxygen. A second scheme could be derived from the previous one to account for the results collected when oxygen was



**Fig. 5.** (a) Distribution of intermediates and products during DCP thermal decomposition at  $T=403\text{K}$  in the presence of oxygen  $[\text{DCP}]_0=0.57\text{ mol L}^{-1}$ . Dimethylphenylcarbinol (DMPC), dicumylperoxide (DCP), acetophenone (ACP), cumene (CUM). (b) Distribution of intermediates and products during DCP thermal decomposition at  $T=403\text{K}$  in the presence of oxygen  $[\text{DCP}]_0=0.57\text{ mol L}^{-1}$ . Cumylhydroperoxide (CHP), 2,3-dimethyl-2,3-diphenylbutane (DMDPB). (In these figures, continuous lines do not represent calculated data.)

purged from the system just providing that the pathway leading to cumylperoxy radicals through the addition of oxygen to cumyl radicals was ruled out.

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