A CONTRIBUTION TO THE STUDY OF THERMAL DECOMPOSITION OF CUMENE HYDROPEROXIDE

R. Rado and I. Chodák

Institute of Polymers,
Slovak Academy of Sciences, 809 34 Bratislava

Received February 28th, 1972

An analysis of the kinetics and mechanism of thermal decomposition of cumene hydroperoxide in n-heptane within 120–170°C is presented. It follows from the results that besides the homolytic dissociation of peroxidic bond also a chain process is involved in the decomposition of this peroxide. The kinetic analysis suggests a considerable participation of methyl radicals in this process. These radicals are formed through the fragmentation of primary cumyloxy radicals. The rate constants of both processes that are kinetically monomolecular have been expressed by corresponding Arrhenius equations.

Thermal decomposition of cumene hydroperoxide has been a subject of interest of several authors[1–5]. From the published data it follows that even a pure radical decomposition of this peroxide is not a simple reaction. The thermal dissociation is accompanied by several consecutive or parallel elementary processes.

Using kinetic analysis of the mechanism of decomposition reaction we attempted to describe the overall decomposition of cumene hydroperoxide more quantitatively *i.e.* including the loss of this compound caused by a chain process. For this reason the overall rate of peroxide decomposition was determined. The kinetics of primary monomolecular process were established by the inhibition of the chain reaction. Finally, when eliminating the original initiation step, the rate and order of the induced decomposition could be determined. The experiments were carried out in n-heptane within temperature region 120–170°C.

EXPERIMENTAL

Cumene hydroperoxide was purified by isolating its sodium salt from a commercial product. The salt was then decomposed by acetic acid and the peroxide formed was separated by distillation at 65°C/0·2 Torr. The peroxide obtained was 99·1% pure (iodometrical assay). n-*Heptane* employed as a reaction medium for peroxide decomposition was of analytical grade and it was used without further purification. The purification of N-phenyl-β-naphthylamine, used as a radical scavenger, was effected by four times repeated recrystallization from ethanol; M.p. 108°C was identical with tabelled data for a pure compound[6].

To be able to determine the amount of peroxide decomposition due to chain reaction and that caused by other processes the experiments were performed also at temperature conditions at which the decomposition of cumene hydroperoxide was negligible; however, the chain reaction could be initiated by some other more thermoreactive peroxide. Cumyl peroxide was selected for this purpose. Its decomposition gives cumyloxyradicals similarly as cumene hydroperoxide, the exception being that cumyl peroxide decomposes exclusively via a monomolecular reaction[7]. The quantitative determination of cumene hydroperoxide using iodometric method is not impaired by the presence of cumyl peroxide. *Cumyl peroxide* (Perkadox SB) was three times recrystallized from cool ethanol. M.p. of that product was 39°C (corresponding literature value[8] is 39·2°C).

Samples of n-heptane containing cumene hydroperoxide of a given concentration, N-phenyl-β-naphthylamine and cumyl peroxide, respectively, were, after purging with purified nitrogen and freezing down, sealed into glass tubes. The sample tubes were immersed into a thermostated oil bath. The initial concentration of cumene hydroperoxide in samples as well as the concentration after the decomposition was determined by the volumetric determination of iodine, evolved from potassium iodide in glacial acetic acid, by titration with 0·01M solution of sodium thiosulphate. The results represent a mean value of two parallel measurements.

RESULTS AND DISCUSSION

It follows from the results obtained by the above described manner that both the inhibited decomposition of cumene hydroperoxide and the overall thermal decomposition appear as monomolecular reactions no matter whether the corresponding kinetic expression is plotted against time (Fig. 1) or whether the initial concentration of peroxide was used (Fig. 2). In spite of the fact that the non-inhibited decomposition appears as a first order reaction, its rate exceeds that of the inhibited process performed at otherwise identical conditions (Fig. 2). Judging from this observation the peroxide loss should then be accounted for by two kinetically monomolecular re-

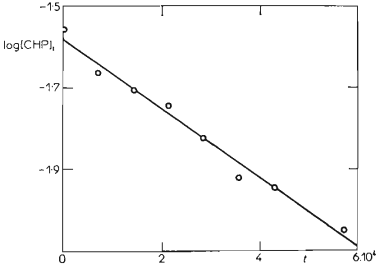

FIG. 1

Logarithm of Cumene Hydroperoxide Concentration ($[CHP]_t$ in mol/l) *vs* Time (in s)
Reaction carried out in n-heptane at 140·0°C.

actions: homolytic dissociation process and consecutive chain decomposition induced by free radicals formed in the primary initiation act.

The numerical value for the rate constant of a spontaneous decomposition of peroxide (k_1) can then be obtained from the slope [exp $k_1 t$] of the dependence for the inhibited process (Fig. 2). The temperature dependence expressed as

$$k_1 = 10^{11 \cdot 3} \exp(-30000/RT)\,(\mathrm{s}^{-1})\,, \tag{1}$$

can be calculated from analogous measurements carried out at another two different temperatures (Table. 1). The value is practically identical with that already published[1]. The values of constants k_1 employed for calculation of relationship (*1*) are presented in Table II.

The rate constant of the induced decomposition reaction (k_i) is, with regard to the above mentioned facts, expressed as a difference between the overall rate constant (k) and inhibited decomposition rate constant ($k_i = k - k_1$). Numerical values of k_i calculated on this basis using results from Figs 1 and 2 and those in Table I for temperatures 140·0 and 154·4°C resp. (corresponding values of k being $2 \cdot 3 \,.\, 10^{-5}\,\mathrm{s}^{-1}$ and $8 \cdot 5 \,.\, 10^{-5}\,\mathrm{s}^{-1}$, resp.) are presented also in Table II.

Since in the case of induced decomposition one is not dealing with an elementary process it is necessary to define the rate constant, in another words to define the mechanism of this chain reaction. For this purpose we carried out an experiment where the chain decomposition of cumene hydroperoxide was tested separately,

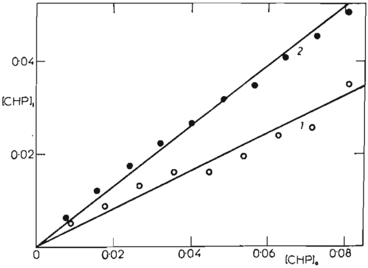

FIG. 2

Concentration of Cumene Hydroperoxide after 3 h Decomposition ($[\mathrm{CHP}]_t$ in mol/l) in n-Heptane at 154·5°C *vs* Initial Concentration of Peroxide ($[\mathrm{CHP}]_0$ in mol/l)

1 In the presence of $4 \,.\, 10^{-2}$ mol/l N-phenyl-β-naphthylamine, *2* without N-phenyl-β-naphthylamine.

the initiation being effected by cumyl peroxide. Under this condition of experiment the spontaneous decomposition of cumene hydroperoxide is excluded from the overall

TABLE I

Decomposition of Cumene Hydroperoxide in n-Heptane in the Presence of 4 . 10^{-2} mol/l of N-Phenyl-β-naphthylamine at Two Temperatures

$[CHP]_0$ and $[CHP]_t$ stand for the initial and final concentration of peroxide, respectively.

$[CHP]_0$ mol/l	$[CHP]_t$ mol/l	$[CHP_0]$ mol/l	$[CHP]_t$ mol/l
140°C, 7·5 h		169·3°C, 1 h	
0·0162	0·0125	0·0087	0·0033
0·0243	0·0177	0·0175	0·0087
0·0324	0·0223	0·0262	0·0145
0·0405	0·0296	0·0350	0·0191
0·0486	0·0359	0·0437	0·0266
0·0567	0·0408	0·0524	0·0294
0·0648	0·0412	0·0611	0·0327
0·0729	0·0477	0·0699	0·0364
0·0809	0·0530	0·0786	0·0424
		0·0873	0·0462

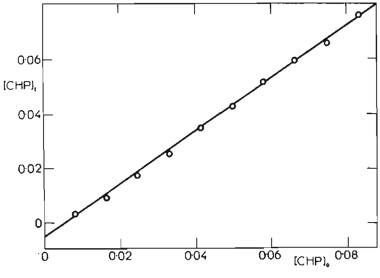

FIG. 3

Concentration Change of Cumene Hydroperoxide ($[CHP]_t$ in mol/l) after 2 h Decomposition at 120·4°C in n-Heptane in the Presence of 2·6 . 10^{-2} mol/l Cumyl Peroxide Initiator in Dependence on the Initial Concentration of Cumene Hydroperoxide ($[CHP]_0$ in mol/l) reaction and the hydroperoxide loss through the induced decomposition which is generally of n-th order, can thus be described by an integral equation

$$[\mathrm{CHP}]_t^{-(n-1)} = [\mathrm{CHP}]_0^{-(n-1)} + (n-1)\,k_i't\,. \tag{2}$$

The observed results obey the straight line relationship (*2*) only in the case when $n = 0$. In accordance with equation (*2*) the slope is equal to one and the intercept has a negative value (Fig. 3). We are thus coming to another conclusion, *i.e.* that under conditions of initiation of cumene hydroperoxide chain decomposition by cumyl peroxide the induced decomposition is of zero kinetic order with regard to cumene hydroperoxide concentration. It follows from the results in Figs 1 and 2 that the experimentally found first order of this reaction with regard to peroxide concentration is in this particular case applicable to cumyl peroxide concentration. As this is constant it will become a part of the constant k_i'.

Following kinetic scheme of chain decomposition of cumene hydroperoxide complies with the presented solution:

$$\mathrm{i} \xrightarrow{k_1} 2\,\mathrm{RO}^\cdot(\mathrm{RO}^\cdot + {}^\cdot\mathrm{OH})\,, \tag{A}$$

$$\mathrm{RO}^\cdot({}^\cdot\mathrm{OH}) + \mathrm{SH} \xrightarrow{k_2} \mathrm{ROH}(\mathrm{H_2O}) + \mathrm{S}^\cdot\,, \tag{B}$$

$$\mathrm{RO}^\cdot \xrightarrow{k_3} {}^\cdot\mathrm{CH_3} + \mathrm{C_6H_5COCH_3}\,, \tag{C}$$

$${}^\cdot\mathrm{CH_3} + \mathrm{CHP} \xrightarrow{k_4} \mathrm{CH_3OH} + \mathrm{RO}^\cdot\,, \tag{D}$$

$${}^\cdot\mathrm{CH_3} + \mathrm{SH} \xrightarrow{k_5} \mathrm{CH_4} + \mathrm{S}^\cdot\,, \tag{E}$$

$$\mathrm{S}^\cdot + \mathrm{S}^\cdot \xrightarrow{k_6} \text{products}\,, \tag{F}$$

where i denotes the peroxide initiating the chain decomposition process (either cumene hydroperoxide or cumyl peroxide), SH hydrocarbon medium, ROH cumyl alcohol, $\mathrm{RO}^\cdot$ and $\mathrm{S}^\cdot$ cumyloxy and n-heptane radical, resp. When $k_4 \gg k_5$ the disappearance of cumene hydroperoxide by the induced decomposition is on the basis of the above mentioned mechanism expressed by equation

$$-\,\mathrm{d}[\mathrm{CHP}]_i/\mathrm{d}t = k_1k_3[\mathrm{i}]/k_2[\mathrm{SH}]\,. \tag{3}$$

The relationship is in accordance with both conditions *i.e.* zero order with regard to cumene hydroperoxide concentration in the case of cumyl peroxide initiation and first order when cumene hydroperoxide itself acts as initiator.

The induced decomposition thus proceeds *via* hydroxyl abstraction from cumene hydroperoxide by an alkyl radical. The $\cdot\mathrm{CH_3}$ radicals are here preferred to n-heptyl

TABLE II

Values of Rate Constants for Spontaneous (k_1) and Induced (k_i) Decomposition of Cumene Hydroperoxide in n-Heptane at Various Temperatures

Temperature, °C	$k_1 \cdot 10^5$, s^{-1}	$k_i \cdot 10^5$, s^{-1}	
		experimental	calcul.
140·0	1·4	0·96	1·2
154·5	4·1	4·4	5·1
169·3	17	—	—

radicals whereas other analogous reactions of more reactive (cumyloxy and hydroxy) radicals present in the system do not actually decompose the peroxy bond. Cumyloxy radicals formed in process (*D*) yield $\cdot CH_3$ radicals through their fragmentation. These $\cdot CH_3$ radicals attack another peroxide molecule, the reaction is repeated and it becomes a chain reaction.

The rate constant of the induced decomposition is then, with regard to Eq. (*3*), expressed as

$$k_i = k_1 k_3 / k_2[\text{SH}] \tag{4}$$

and it is determined by the rate of cumyloxy radicals formation and their fragmentation.

On the basis of described scheme of radical processes k_i can be expressed as a product of k_1 and the ratio of acetophenone to cumyl alcohol formed ($k_3/k_2[\text{SH}] = [C_6H_5COCH_3]/[\text{ROH}]$). Since this ratio was, for the case of cumyl peroxide decomposition in n-heptane, determined previously[9] it is possible to verify the presented scheme also by the conformation of experimental and theoretical values for k_i. The value of k'_1 determined from the kinetics of peroxide decomposition (Fig. 3) was found to be $9 \cdot 10^{-7}$ mol l^{-1} s^{-1}; the corresponding value calculated according to equation (*4*) is then $6 \cdot 10^{-7}$ mol l^{-1} s^{-1} taking $k_1 = 4{\cdot}2 \cdot 10^{-5}$ s^{-1} [ref.[7]], $[C_6H_5COCH_3]/[\text{ROH}] = 0{\cdot}51$ [ref.[9]] and $[\text{i}] = 2{\cdot}6 \cdot 10^{-2}$ mol/l. A similar very good agreement between found and theoretical values of k'_i is observed also in the case of other two temperatures (Table II).

A more general expression for k_i can be obtained using Eq. (*1*) and the Arrhenius relationship for ($k_3/k_2[\text{SH}]$) computed from temperature dependence of acetophenone/cumyl alcohol ratio[9]:

$$k_3/k_2[\text{SH}] = 10^{4\cdot3} \exp\left(-8000/\boldsymbol{R}T\right), \tag{5}$$

so that

$$k_i = 10^{15.6} \exp(-38000/RT)\,(\mathrm{s}^{-1})\,. \tag{6}$$

Since there is a good agreement between theoretical and experimental values for k_i also the value for activation energy of the induced decomposition calculated from equation (6) (38 kcal/mol) fits well with that determined from experimental data for k_i (Table II) (37 kcal/mol).

The decomposition of hydroperoxides is generally accompanied by bimolecular reactions which are considered also in the case of cumene hydroperoxide decomposition[5].

$$2\,\mathrm{CHP} \longrightarrow \mathrm{RO^{\cdot}} + \mathrm{ROO^{\cdot}} + \mathrm{H_2O}\,, \tag{G}$$

$$\mathrm{CHP} + \mathrm{SH} \longrightarrow \mathrm{ROH} + \mathrm{SOH}\,. \tag{H}$$

These reactions, however, were not detected in our kinetic analysis. This is possibly due to their relatively lesser importance or due to their being obscured by other parallel reactions.

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Translated by J. Sedlář.