Kinetics of the decomposition of cumene hydroperoxide

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Translation submitted by P. Curtis

For the synthesis of polymeric materials with a combination of specified properties it is necessary to understand the chemical processes leading to the formation of high molecular weight compounds. One of the most well-known methods for producing polymers is the process of radical polymerisation (ref. 1). During the polymerisation of monomers and oligomers, different compounds are used as initiators, including peroxides and hydroperoxides. For practical purposes it is important to know the change in the initiator concentration with time, both during storage of compounds of this kind and during polymerisation of the monomer (oligomer), which would make it possible to judge the amount of initiator remaining in the polymerisate.

The aim of the present work was to study the kinetics of decomposition of cumene hydroperoxide under different conditions: temperatures, concentrations, pressures. The present investigation was carried out on this specific compound because cumene hydroperoxide has been widely used as an initiator for radical polymerisation in practice. It must be pointed out that this work is a continuation of a series of studies by the present authors on the kinetics of radical polymerisation of oligoester acrylates, filling a gap with respect to description of the first stage of the kinetic scheme of polymerisation – the stage of initiation (refs. 2 and 3).

Cumene hydroperoxide (CHP) has the following physicochemical characteristics: molecular weight $M$ 152.2 g/mol, density $d_4^2$ 1.0545 g/cm$^3$, viscosity $\eta$ 20.71 cP at 293 K, boiling point $T_b$ 316–317 K at 0.005 mmHg, dipole moment 1.8 debye. Calculation was carried out on an IBM PC-846 computer by a scheme proposed in ref. 4 for benzoyl peroxide.

The change in concentration of CHP with time (ref. 5) is described by the equation

\[ [I] = [I_0] e^{-k_d t} \]  
\[ k_d = 2.75 \times 10^{10} e^{-29930 / RT} \]  

where $[I]$ and $[I_0]$ are the current and initial CHP concentrations (mol/l), $k_d$ is the rate constant of decomposition of the CHP (s$^{-1}$), $R$ is the universal gas constant, equal to 1.987 cal/mol K, $T$ is the temperature (K), $t$ is the time (s), $E_a$ is the activation energy, equal to 29 930 cal/mol, and $k_0$ is a pre-exponential function, equal to $2.75 \times 10^{10}$ s$^{-1}$.

INFLUENCE OF TEMPERATURE

Figure 1 gives curves of the decomposition of CHP at different temperatures in the range 298–423 K. From an analysis of the curves it can be seen that, at $T = 298$ K, the CHP decomposes over the course of 10 years by less than 0.1%. After polymerisation of the oligomer at $T = 423$ K for 10 h, 72% of CHP remains in the polymerisate, and only after holding at this temperature for a further 100 h can a reduction of up to 5% be expected in the residual peroxide concentration. The fact that the remaining initiator may have an adverse influence during service of products manufactured from the polymers must be taken into account.

In the case of three-dimensional polymerisation of oligomers (oligoester (meth)acrylates, etc.), heat treatment of the polymerisate is carried out at $T = 400–440$ K for 1–3 days or more, which results in subsequent decomposition of the peroxide. From Fig. 1 it is clear that heat treatment for 3 days at $T = 423$ K lowers the residual content of initiator CHP to 10%.
We will assume that the induced decomposition of peroxide proceeds in accordance with the following equation (ref. 5):

$$k_{d,ind} = 1.28 \times 10^{11} \exp(-25000/RT)$$  \hspace{1cm} (3)$$

Then, at $T = 353$ K, the proportion of residual peroxide will amount to 2% during heat treatment for 24 h, and the decomposition of the CHP during storage for 1 year at $T = 298$ K will amount to 80%.

Figure 2 gives the temperature dependence of the decomposition rate of CHP for atmospheric pressure (0.1 MPa) and for a pressure of 500 MPa with an activation volume $\Delta V^\neq = 10 \text{ cm}^3/\text{mol}$ (ref. 5).

Knowledge of a dependence of this kind is important when carrying out anabatic polymerisation. As can be seen from the curves, the temperature of semidecomposition amounts to 525 K at a pressure of 0.1 MPa and to 550 K at a pressure of 500 MPa.

**INFLUENCE OF CONCENTRATION**

Figure 3 gives the kinetic curves of decomposition of CHP at $T = 353$ K and different initial concentrations: 0.25, 0.5, 0.75, and 1 mol/l. As can be seen, the curves change proportionally with reduction in concentration.

**INFLUENCE OF PRESSURE**

Decomposition of the initiator proceeds by the scheme

$$k_1 \quad \rightarrow \quad k_\beta$$

Initiator    cage    free radicals

$$k_{-1} \quad \downarrow \quad k_\beta$$

cage 2 + small molecule

where $k_1$ is the rate constant of homolysis of the bond, $k_{-1}$ is the rate constant of recombination of the first pair of primary radicals (internal recovery), $k_\beta$ is the rate constant of diffusional separation of the primary radicals, $k_\beta$ is the rate constant of $\beta$-decomposition, 'cage' indicates the location of the primary radicals, and 'cage 2' indicates the location of the pair of radicals after $\beta$-decomposition, if it has occurred.

In accordance with the given scheme, an increase in pressure $P$ was expected to slow down the homolysis of CHP, since, with increase in pressure, there is an increase in the viscosity of the medium in which the cage itself is located. Thus, with increase in $P$, given that the peroxide decomposes by a monomolecular mechanism with the rupture of one bond, i.e. normally $\Delta V^\neq > 0$, there is an increase in the cage effect (ref. 6). From Fig. 4a and b it can be seen that, with increase in $P$ at $\Delta V^\neq = 5$ and 10 $\text{ cm}^3/\text{mol}$, the rate of decomposition decreases. If the less probable case where the values of $\Delta V^\pm$ are taken to be equal to -5 and -10 $\text{ cm}^3/\text{mol}$ is examined, then the kinetic curves of decomposition of CHP are shifted towards shorter times (Fig. 4).
The rate constant of decomposition of the initiator at different P was found from the following expression:

\[ k_d = k_{0.1} \exp(-\Delta V^{\neq}(P - P_{0.1})/RT) \]  

(4)

where \( P \) is the current pressure, \( P_{0.1} = 0.1 \) MPa, \( k_{0.1} \) is the pre-exponential function at \( P = 0.1 \) MPa, and \( R = 8.31 \) J/mol K.

When the influence of \( \Delta V^{\neq} \) on the behaviour of the curves \([I] = f(t)\) (Fig. 5) is compared, it becomes obvious that, when \( \Delta V^{\neq} > 0 \), decomposition of the peroxide is slowed down, but when \( \Delta V^{\neq} < 0 \) it is accelerated, i.e. the influence of pressure increases with increasing \( |\Delta V^{\neq}| \).

The redox system is CHP–iron naphthenate (Fe\(^{2+}\)).

For polymerisation of the monomers and oligomers under milder conditions, i.e. at room temperature, it is necessary to use a redox system, of the CHP–iron naphthenate type and other types, as the initiator. For systems of this kind, the kinetic equation has the form (ref. 5)

\[ k_d = 1.07 \times 10^9 \exp(-12000/RT) \]  

(5)

The behaviour of the given initiating system at different temperatures is illustrated in Fig. 6. It was established that, even at \( T = 323 \) K, the amount of reduction in the concentration of the CHP–iron naphthenate system amounts to 50% within 0.1 s. The influence of pressure in the case of a redox system at \( \Delta V^{\neq} = -5 \) and 5 cm\(^3\)/mol for a temperature of 298 K does not differ from that described above (Fig. 7).

Having solved equations (1), (2), and (4) jointly, it is possible to obtain an equation enabling the kinetics of decomposition of CHP under different conditions to be calculated:

\[ [I] = [I_0] \exp(-2.75 \times 10^{10} t \exp(-29930 + \Delta V^{\neq}(P - P_{0.1})/RT)) \]  

(6)
Table 1 gives values of the period of semidecomposition $\tau_{0.5}$ of CHP for different conditions.

**SPECIAL CASES**

In practice, cases may be encountered where it is necessary to create polymerisation conditions for oligomers with a constant rate of generation of primary radicals $d[R]/dt$. Since

$$\frac{d[R]}{dt} = k_{o}[l]$$

from equations (1) and (2) we will obtain the following expression:

$$\frac{d[R]}{dt} = k_{o}[l_0]e^{\frac{-E_a}{RT}}e^{k_{o}t} \exp(-\frac{E_a}{RT})$$

(8)

Setting different values of $d[R]/dt$ and numerically solving equation (8), it is possible to obtain the dependence $T=f(t)$ for the specified conditions.

The given dependence can be obtained by a different method. Through the specified time intervals $t$ in which the boundary condition $d[R]/dt = \text{const}$ is fulfilled, we find the values of $[l]$, and, using transformed equation (7) in relation to $T$,

$$T = -\frac{E_a}{R \ln \frac{d[R][l]}{dk_0}}$$

(9)

we find the values of $T$ for the specified time $t$. Figure 8 gives the dependences $T=f(t)$ for the decomposition of CHP with the specified values of $d[R]/dt$ indicating how the values of temperature have to be varied with different polymerisation times. The upper horizontal axis in Fig. 8 corresponds to curve 1, the middle axis to curve 2, and the lower axis to curve 3. The figures by the curves indicate the temperatures of 50 and 99% decomposition of CHP respectively.

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**Table 1** Period of semidecomposition of CHP under different conditions

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<th>$P$, MPa</th>
<th>$\Delta V$, cm$^3$/mol</th>
<th>$T$, K</th>
<th>$\tau_{0.5}$, $x 10^{-11}$</th>
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**Fig. 8** Curves of dependence of CHP decomposition at constant rate at initial temperature of 293 (1) and 353 K (2); (3) - curve of CHP + iron naphthenate (Fe$^{2+}$), decomposition $T = 273 K$ (1) = 0.03 mole/ per litre
Thus, the work carried out has made it possible to establish the influence of various factors such as temperature, pressure, and initiator concentration on the nature of decomposition of cumene hydroperoxide in a redox initiating system consisting of CHP and iron naphthenate (Fe$^{2+}$). The influence of change in the conditions of decomposition (induced decomposition) on the nature of the obtained kinetic curves of decomposition of the initiator has been shown.

REFERENCES


(No date given)