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Abstract

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FORMATION OF RADICALS IN THE REACTION OF HYDROPEROXIDE WITH THE DOUBLE BOND OF STYRENE

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In the oxidation of olefins and the polymerization of unsaturated compounds using hydroperoxides as initiators, one has to deal with the system: hydroperoxide–compound with a double bond. The high reactivity of both double bonds and hydroperoxide groups is well known. It is therefore natural to raise the question of the possibility of a reaction between hydroperoxide and an olefinic double bond with formation of free radicals. Indirect evidence for such a reaction is contained in the fact of the rapid decomposition of hydroperoxide in the presence of styrene ([1]).

In the present work, the formation of radicals from tert-butyl hydroperoxide in the presence of styrene in heptane solution was studied. The rate of radical formation was measured from the consumption of α-naphthylamine (by the inhibitor method). The procedure for carrying out the experiments and for analysis for inhibitor was the same as in ([2]). The results of the experiments are shown in Figs. 1–3. Styrene accelerates the formation of radicals from tert-butyl hydroperoxide; at constant hydroperoxide concentration, the rate of radical formation increases linearly with increasing styrene concentration (Fig. 1). In the presence of a sufficiently high concentration of styrene (2.6 mol/l), when practically all radicals are formed by the reaction of styrene with hydroperoxide, $W_i \sim$ [ROOH] (Fig. 2). This indicates the formation of radicals by a bimolecular reaction between hydroperoxide and styrene, alongside a very slow monomolecular decomposition of hydroperoxide into radicals:

$$W_i = k_1[\text{ROOH}] + k_2[\text{ROOH}][\text{styrene}].$$

At 90° $k_1 = 6 \cdot 10^{-8}$, $k_2 = 5.9 \pm 0.2 \cdot 10^{-7}$ l/mol • sec. At a sufficiently high concentration of styrene,

$$W_i = k_2[\text{ROOH}][\text{styrene}]$$

and from the temperature dependence of W_i (at constant concentrations of hydroperoxide and styrene) the activation energy was determined (Fig. 3): $E_2 = 17.2 \pm 0.5$ kcal/mol.

$$k_2 = 1.2 \cdot 10^4 \exp(-17200/RT) \text{ l/mol} \bullet \text{sec.}$$

In ([3]) a reaction of the type was demonstrated:

$$\mathrm{ROOH} + \mathrm{R'H} \rightarrow \mathrm{RO} + \mathrm{H_2O} + \mathrm{R'}$$

with participation of the C—H bond of the solvent. It may be assumed that the reaction between hydroperoxide and styrene also proceeds with participation of the C—H bond of styrene. To check this, an experiment was carried out with tert-butyl hydroperoxide and ethylbenzene, which is structurally analogous to styrene but has no double bond. At 95° for ethylbenzene $k_i = 8.8 \cdot 10^{-8}$ l/mol • sec, and for styrene $k_i = 8.7 \cdot 10^{-7}$ l/mol • sec, i.e., an order of magnitude higher. Moreover, it must be taken into account that in styrene the weakest C—H bond is stronger than in ethylbenzene, and therefore the reaction of hydroperoxide with the C—H bond of styrene is still less probable than for ethylbenzene. Consequently, in the case of styrene the formation of radicals occurs by the reaction of hydroperoxide with the double bond of styrene.

In work ([1]) an assumption was made concerning the following reaction between hydroperoxide and styrene:

$$\mathrm{ROOH} + \mathrm{C_6H_5CH{=}CH_2} \rightarrow \mathrm{ROO} \cdot + \mathrm{C_6H_5\dot{C}HCH_3}.$$

In order to calculate the heat of this reaction, it is necessary to know the heat content of the radical $\mathrm{C_6H_5\dot{C}HCH_3}$ ($\mathrm{R_1}\cdot$). For ethylbenzene ($\mathrm{R_1H}$) $\Delta H = 7.1$ kcal/mol, $Q_{\mathrm{R_1-H}} = 79$ kcal/mol (4 kcal less than in toluene, where $Q_{\mathrm{R-H}} = 83$ ([4])). We find $\Delta H_{\mathrm{R_1}\cdot}$:

$$\mathrm{R_1 - H \rightarrow R_1 \cdot + H \cdot} -79; \qquad \Delta H_{\mathrm{R_1-H}} = \Delta H_{\mathrm{R_1}\cdot} + \Delta H_{\mathrm{H}\cdot} - 79;$$

$$\Delta H_{\mathrm{R_1}\cdot} = 7.1 - 52 + 79 = 34.1; \qquad q = \Delta H_{\mathrm{ROOH}} - \Delta H_{\mathrm{ROO}\cdot} + \Delta H_{\mathrm{styrene}}$$

$$-\Delta H_{\mathrm{R_1}} = (\Delta H_{\mathrm{ROOH}} - \Delta H_{\mathrm{RO\cdot 2}} - \Delta H_{\mathrm{H}}) + \Delta H_{\mathrm{H}} + \Delta H_{\mathrm{styrene}} - \Delta H_{\mathrm{R_1}}$$

$$= -90 + 52 + 35.2 - 34.1 = -36.9 \text{ kcal/mol.}$$

Fig. 1-3: kinetic plots

Figure 1: Fig. 1-3: kinetic plots

Since simple decomposition of hydroperoxide at the O–O bond requires 35 kcal/mol and is a monomolecular reaction, this decomposition will proceed much faster than the bimolecular reaction considered above.

Fig. 1

Fig. 2

Fig. 3

Fig. 1. Dependence of the rate of formation of radicals from tert-butyl hydroperoxide (0.16 mol/l, 90°) on the concentration of styrene. Solvent–heptane

Fig. 2. Dependence of the rate of formation of radicals on the concentration of tert-butyl hydroperoxide (styrene concentration 2.62 mol/l, 90°)

Fig. 3. Temperature dependence of the constant k_2 of the reaction between styrene and tert-butyl hydroperoxide

The most energetically favorable bimolecular reaction between hydroperoxide and styrene is the reaction:

$$\mathrm{ROOH} + \mathrm{C_6H_5CH{=}CH_2} \rightarrow \mathrm{RO}\cdot + \mathrm{C_6H_5\dot{C}HCH_2OH} + q.$$

Let us calculate the heat of this reaction:

$$\mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \cdot\mathrm{OH} - 35,$$

$$\mathrm{C_6H_5CH{=}CH_2} + \cdot\mathrm{OH} \rightarrow \mathrm{C_6H_5\dot{C}HCH_2OH(R_2\cdot)} + q_1, \quad (1')$$

$$\mathrm{C_6H_5\dot{C}HCH_2OH} + \mathrm{H_2} \rightarrow \mathrm{C_6H_5\dot{C}HCH_3(R_1\cdot)} + \mathrm{H_2O} + q_2. \quad (2')$$

In reaction 2′, the C–OH bond ($Q = 90$ kcal/mol) and the H–H bond ($Q = 104$ kcal/mol) are broken, and a CH_2–H bond (94) and an H–OH bond (118) are formed; hence $q_2 = 94 + 118 - 104 - 90 = 18$. On the other hand,

$$q_2 = \Delta H_{\mathrm{R_2}} - \Delta H_{\mathrm{R_1}} - \Delta H_{\mathrm{H_2O(g)}},$$

and

$$\Delta H_{\mathrm{R_2}} = q_2 + \Delta H_{\mathrm{R_1}} + \Delta H_{\mathrm{H_2O}} = 18 + 34.1 - 57.8 = -5.7.$$

$$q_1 = \Delta H_{\text{styrene}} + \Delta H_{\text{HO}} - \Delta H_{\text{R}_2} = 35.2 + 9.3 + 5.7 = 50.2,$$

$$q = 50.2 - 35 = 15.2 \text{ kcal/mol}.$$

Other possible bimolecular reactions in which the O—O bond of the peroxide is broken

and the double bond of styrene, will be energetically less favorable. The bimolecular reaction considered above is in good agreement with the experimental data —the high rate of radical formation in the hydroperoxide–styrene system and the low activation energy of this reaction (17 kcal/mol).

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Note: Figure translations are in progress. See original paper for figures.