The kinetics of oxidation of 1-chloro-2-(4-isopropylphenyl)-2-methylpropane by molecular oxygen

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The kinetics of formation of 2-[4-(1-chloro-2-methylpropan-2-yl)phenyl]propan-2-yl hydroperoxide during the azobisisobutyronitrile-initiated oxidation of 1-chloro-2-(4-isopropylphenyl)-2-methylpropane by molecular oxygen at 70—100 °C was studied.

Key words: 1-chloro-2-(4-isopropylphenyl)-2-methylpropane, 2-[4-(1-chloro-2-methylpropan-2-yl)phenyl]propan-2-yl hydroperoxide, oxidation by molecular oxygen.

Among pyrethroids of the newest generation, 2-(*p*-ethoxyphenyl)-2-methylpropyl *m*-phenoxybenzyl ether (ethofenprox) has gained great practical significance. Available methods for the synthesis of ethofenprox are rather labor-consuming and based on the use of difficultly accessible reagents. Therefore, a search for alternative routes of its synthesis is urgent. We propose a new scheme for the preparation of ethofenprox.[1] The key stages in this scheme are the liquid-phase oxidation of 1-chloro-2-(4-isopropylphenyl)-2-methylpropane by molecular oxygen followed by the transformation of the obtained peroxide into the substituted phenol. In this work, we studied the kinetic regularities of liquid-phase oxidation of 1-chloro-2-(4-isopropylphenyl)-2-methylpropane (RH) by molecular oxygen to form 2-[4-(1-chloro-2-methylpropan-2-yl)phenyl]propan-2-yl hydroperoxide, which made it possible to optimize this process.

Experimental

1-Chloro-2-(4-isopropylphenyl)-2-methylpropane and 2-[4-(1-chloro-2-methylpropan-2-yl)phenyl]propan-2-yl hydroperoxide were synthesized and purified by previously described procedures.[1,2] Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol.

RH (4.7—47.0 mmol) was placed in a glass three-necked 15-mL thermostatted reactor with a reflux condenser and magnetic stirrer, and AIBN (0.07—1.2 mmol) was added. In experiments with additives of sodium stearate and CaO, $C_{17}H_{35}COONa$ (0.053 g) and/or CaO (0.356 g), respectively, were introduced into the reaction mixture. Dioxygen was fed with a flow rate of 1 L h^{-1} into the reactor through a bubbler with the Schott filter. Hydroperoxide was analyzed iodometrically.[3] The temperature was varied within 70—100 °C.

Decomposition of ROOH was studied in a glass reactor in an inert atmosphere in a medium of chlorobenzene, isopropylbenzene, and RH at 80—136 °C.

Results and Discussion

The character of the kinetic curves of ROOH accumulation (Fig. 1) indicates that hydroperoxide is con-

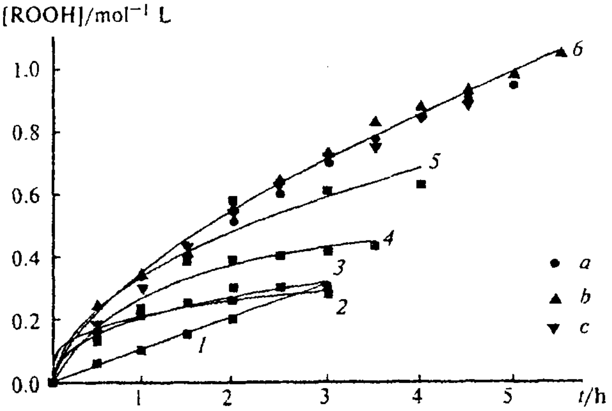

Fig. 1. Temperature effect on the accumulation of 2-[4-(1-chloro-2-methylpropan-2-yl)phenyl]propan-2-yl hydroperoxide ([AIBN] = 0.0143 mol L^{-1}) during the oxidation of 1-chloro-2-(4-isopropylphenyl)-2-methylpropane by molecular oxygen at T/°C = 70 (*1*), 90 (*2*), 100 (*3*), 80 (*4*), and 80 ([AIBN] = 0.053 mol L^{-1}) (*5*). Kinetics of hydroperoxide accumulation: *a*, in the presence of $C_{17}H_{35}COONa$ (0.017 mol L^{-1}); *b*, in the presence of CaO (0.64 mol L^{-1}); and *c*, in the presence of both $C_{17}H_{35}COONa$ and CaO (80 °C, [AIBN]$_0$ = 0.0143 mol L^{-1}) (*6*).

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sumed in parallel with its formation. The highest yield of hydroperoxide is observed at 80 °C and amounts to 10.53% (0.43 mol L^{-1}).

The dependences of the rate of ROOH accumulation on the concentrations of the initiator and RH were studied at 80 °C. The AIBN concentration was varied within 0.007—0.12 mol L^{-1}. The rates of oxidation and initiation (W_0 and W_i, respectively) were calculated from the data obtained. The following values of ek_d/s^{-1} were used for the calculation of W_i: $3.12 \cdot 10^{-4}$ (72 °C), $8.6 \cdot 10^{-4}$ (80 °C), $4.6 \cdot 10^{-3}$ (94 °C), and $1.1 \cdot 10^{-2}$ (102 °C). Here e is the probability of radical escape into the volume, and k_d is the rate constant of AIBN decomposition.[4] It was found that the initiator concentration of 0.057 mol L^{-1} is optimum. In this case, the yield of ROOH is 16% (0.6 mol L^{-1}). The dependences of the oxidation rate on the hydrocarbon concentration $[RH]_0$ and $W_i^{1/2}$ are linear (Fig. 2). Therefore, chain termination occurs by the recombination of peroxyl radicals ($RO^{\cdot}_2$), and the limiting stage of chain propagation is the reaction of $RO^{\cdot}_2$ with RH. The obtained kinetic regularities at the initial stages of hydroperoxide formation can be explained by the following reactions[5]:

$$\text{Initiator} \longrightarrow r^{\cdot} \xrightarrow{RH} R^{\cdot}$$

$$R^{\cdot} + O_2 \xrightarrow{k_1} RO^{\cdot}_2$$

$$RO^{\cdot}_2 + RH \xrightarrow{k_2} ROOH + R^{\cdot}$$

$$2\,RO^{\cdot}_2 \xrightarrow{k_6} \text{Molecular products} + O_2,$$

from which follows the oxidation rate

$$W_o = \frac{k_2}{\sqrt{k_6}} \cdot [RH] \cdot \sqrt{W_i}\,.$$

According to the data presented in Fig. 2, the parameter $k_2/\sqrt{k_6} = 5.1 \cdot 10^{-3}\ L^{1/2}\ (mol\ s)^{-1/2}$ and $5.7 \cdot 10^{-3}\ L^{1/2}\ (mol\ L)^{-1/2}$ (80 °C) from the dependences of W_0 on W_i and [RH], respectively. Note that in the case of cumene, $k_2/\sqrt{k_6} = 1.77 \cdot 10^{-2}\ L^{1/2}\ (mol\ s)^{-1/2}$ (80 °C).[4]

The limiting yield of hydroperoxide is 15—16 wt.%. The yield cannot be increased by either variation of the temperature or initiator concentration. Probably, the low yield of hydroperoxide is related to its decomposition, which prompted us to study the thermal decomposition of ROOH. The experiments at 80—120 °C showed that, under these conditions, the concentration of hydroperoxide remains almost unchanged for 10 h (Fig. 3). Appreciable decomposition of hydroperoxide is observed at higher temperatures. For example, at 136 °C the period of half-decomposition ($\tau_{1/2}$) amounts to 7 h (RH as the solvent). Comparison of the kinetic curves of ROOH decomposition and accumulation (see Figs. 1 and 3) suggests that the decomposition of hydroperoxide during RH oxidation is not related to thermal decomposition. It is most likely that ROOH decomposes by the action of the products formed during RH oxidation. To verify this assumption, we studied the decomposition of ROOH in the oxidate. The character of the kinetic curves of hydroperoxide accumulation and consumption (see Fig. 3) convincingly indicates that the influence of the oxidation by-products that accumulated in the oxidate is the reason for the hydroperoxide decomposition. Under the experimental conditions, ROOH is consumed in the oxidate according to a law of the pseudo-first order with the effective rate constant $k'_{eff} = 2.06 \cdot 10^{-4}\ s^{-1}$ (see Fig. 3). It is known[5] that organic acids (mainly, formic acid) formed by the oxidation of cumene catalyze

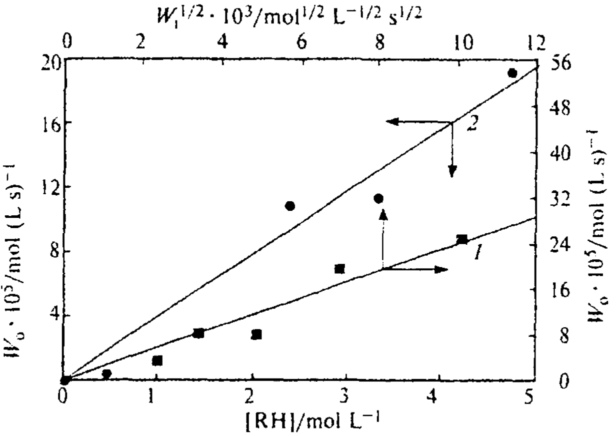

Fig. 2. Initial rate of accumulation of 2-[4-(1-chloro-2-methylpropan-2-yl)phenyl]propan-2-yl hydroperoxide as functions of the initiation rate (*1*) and concentration of 1-chloro-2-(4-isopropylphenyl)-2-methylpropane (*2*) at 80 °C.

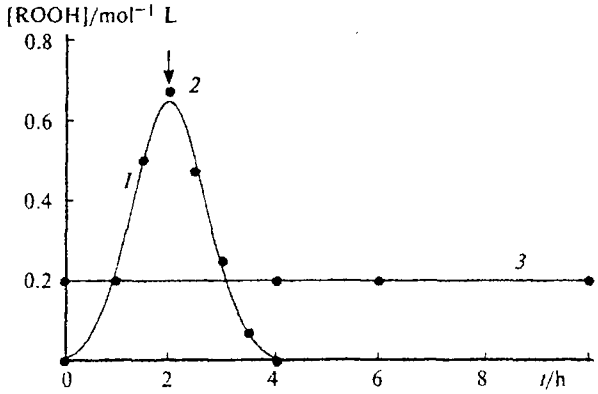

Fig. 3. Kinetic curves of accumulation of 2-[4-(1-chloro-2-methylpropan-2-yl)phenyl]propan-2-yl hydroperoxide in the oxidate (80 °C, [AIBN] = 0.057 mol L^{-1}) (*1*) and decomposition of 2-[4-(1-chloro-2-methylpropan-2-yl)phenyl]propan-2-yl hydroperoxide at 120 °C (the moment of cessation of oxygen supply is shown by arrow) (*2*). Kinetics of thermal decomposition of 2-[4-(1-chloro-2-methylpropan-2-yl)phenyl]propan-2-yl hydroperoxide at 120 °C (*3*).

the decomposition of cumene hydroperoxide. However, experiments with an additive of formic acid ([ROOH] : [HCOOH] = 1 : 1, 80 °C) showed that hydroperoxide decomposition is not accelerated in the presence of HCOOH. It has previously been found[6] that additives of a stronger (sulfuric) acid even in catalytic quantities result in ROOH decomposition. We observed the same effect for hydrochloric acid whose formation is possible during RH oxidation.[7]

The influence of acidic products on ROOH decomposition can be prevented by the addition of substances with basic properties, alkali or alkaline-earth metals or salts of these metals with weak acids, to the reaction mixture.[5] The kinetic curves of hydroperoxide accumulation in the presence of sodium stearate, CaO, and both of them are presented in Fig. 1. The results obtained show that basic additives increase the hydroperoxide yield to 1.5 mol L^{-1} (40 wt.%), which is almost threefold higher than that for standard oxidation.

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