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Formation of Radicals in the Reactions of Tetralin, 2-Cyanopropane, and Ethylbenzene Hydroperoxides with Styrene

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Abstract—The formation of free radicals in the reactions of structurally different hydroperoxides with styrene is investigated. The free-radical chain oxidation of styrene initiated by hydroperoxides has been studied volumetrically by measuring O_2 consumption during the reaction. The bimolecular rate constants of radical initiation in the reactions of styrene with tetralin, 2-cyanopropane, and ethylbenzene hydroperoxides are 1.5×10^{-8}, 2.6×10^{-7}, and 6.5×10^{-9} l mol^{-1} s^{-1} (323 K), respectively. The reactivity of a hydroperoxide increases with increasing electron-acceptor properties of the substituent in its molecule.

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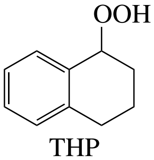
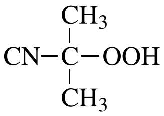
INTRODUCTION

Peroxides and hydroperoxides are widely used as initiators in the oxidation and polymerization of organic compounds [1]. The results concerning the reactions of hydroperoxides (ROOH, HPs) with various substrates have been generalized and analyzed by Denisova and Denisov [2, 3]. The study of the reactions of vinyl monomers, including styrene, with hydroperoxides has been limited to tertiary hydroperoxides, such as cumyl hydroperoxide (CHP) and *tert*-butyl hydroperoxide (TBHP) [2–4]. In the present work, we studied the formation of free radicals in the reactions between styrene and structurally different hydroperoxides, namely, tetralin hydroperoxide (THP), 2-cyanopropane hydroperoxide (CPHP), and ethylbenzene hydroperoxide (EBHP) and measured the rate constants of these reactions for the first time.

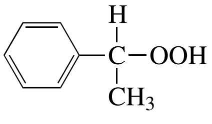


THP



$$CN-\overset{CH_3}{\underset{CH_3}{C}}-OOH$$

CPHP



EBHP

EXPERIMENTAL

The oxidation rates of styrene (M) and styrene–chlorobenzene mixtures were measured using a manometric setup with an automatic pressure control system or a capillary burette filled with *n*-decane (Warburg technique) at 323 K and atmospheric O_2 pressure. The above hydroperoxides were used as initiators of styrene oxidation. They were purified by standard procedures (THP was recrystallized from petroleum ether and its mixtures with chlorobenzene, and EBHP was distilled in vacuo). Cyanopropane hydroperoxide was synthesized according to a known procedure [5, 6] but with some changes: 0.05 mol of hydroquinone and 0.07 mol of benzoquinone were taken per 0.1 mol of azodiisobutyronitrile (AIBN). The compounds were dissolved in isopropanol (150 ml), and toluene (600 ml) was then added. The synthesis was carried out in a tall water-jacketed vessel with a Schott filter sealed into the bottom. Oxygen, fed through this filter, was vigorously bubbled through the liquid. After 3-h-long heating of the mixture under moderate reflux of isopropanol, hydroquinone (0.1 mol) was added, a reflux condenser was replaced with a descending condenser, and the alcohol was distilled off for 2 h. After a temperature of 96°C was reached, the contents were held at this temperature for 30 min and cooled. Our procedure differed from the standard procedure [5, 6] in that the main CPHP fraction, which was distilled at 45°C, was transferred into a narrow tall tube. The top half of the tube was wrapped up in a heat insulator, and the tube was placed into a freezer operated at –20°C. The bluish liquid over the crystals and the upper, molten part of the crystals were removed. The active O_2 content of the middle fraction of distilled CPHP was 98.8%, and that of THP and EBHP was 99.8 and 94.6%, respectively (according to iodometric analysis). The products and ROOH were analyzed by TLC on Silufol UV-254 plates using a binary mixture of benzene with chloroform, dichloromethane, tetrahydrofuran, or ethyl acetate as the eluant.

The products of AIBN decomposition in the absence of O_2 were obtained in benzene. For this purpose, a pumped and sealed tube containing AIBN was heated in boiling water for 90 min. After benzene was removed in vacuo at 20°C, the unseparated products were used as additives to CPHP.

RESULTS AND DISCUSSION

Styrene purified from admixtures resulting in linear chain termination [7] is oxidized via the following classical mechanism [4] (with AIBN as the initiator):

$$\mathrm{AIBN} \xrightarrow{(\mathrm{O_2,\,M})k_{\mathrm{AIBN}}} \mathrm{M}^{\bullet}, \tag{I}$$

$$\mathrm{M}^{\bullet} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{MOO}^{\bullet}, \tag{II}$$

$$\mathrm{MOO}^{\bullet} + \mathrm{M} \xrightarrow{k_2} \mathrm{MOOM}^{\bullet} \equiv \mathrm{M}^{\bullet}, \tag{III}$$

$$2\mathrm{MOO}^{\bullet} \xrightarrow{k_6} \text{Products.} \tag{IV}$$

The styrene peroxy radical $\mathrm{MOO}^{\bullet}$, unlike the $\mathrm{ROO}^{\bullet}$ radicals of hydrocarbons being oxidized, does not abstract an H atom from the substrate to form a hydroperoxide. It adds to the double bond of the monomer to form polyperoxides. This facilitates the processing of experimental data, making it unnecessary to take into account chain generation from ROOH forming during the experiment. The polyperoxides are thermally stable and do not react with M [4].

In the general case, the rate of styrene oxidation ($W_{\mathrm{O_2}}$) is

$$W_{\mathrm{O_2}} = k_2 k_6^{-1/2}[\mathrm{M}]W_{\mathrm{in}}^{1/2}, \tag{1}$$

where W_{in} is the initiation rate and k_2 and k_6 are the rate constants of chain propagation and termination, which are equal to 110.0 and 6.2×10^7 l mol^{-1} s^{-1} (323 K), respectively [8]. For the initiation of M oxidation by azodiisobutyronitrile,

$$W_{\mathrm{in}} = W_{\mathrm{AIBN}} = k_{\mathrm{AIBN}}[\mathrm{AIBN}],$$

where k_{AIBN} is the initiation rate constant equal to 2.2×10^{-6} s^{-1}. The rate constant ratio $k_2/k_6^{1/2}$ (323 K) is $(1.40 \pm 0.04) \times 10^{-2}$ (l mol^{-1} s^{-1})$^{1/2}$ and remains unchanged even at very low W_{AIBN} values (Fig. 1).

The chain length in our experiments exceeded 100 units, and, for this reason, no correction for changes in the gas balance was applied [1].

When studying the initiating ability of ROOH, the rate of radical formation was derived from the experimental oxidation rate (Eq. (1)). In the general case,

$$W_{\mathrm{in},\,\Sigma} = W_{\mathrm{AIBN}} + W_{\mathrm{HP}} + W_{\mathrm{X}} + W_{\mathrm{aut}}, \tag{2}$$

where the last three terms are the initiation rates due to ROOH, due to the admixtures X in ROOH, and in autooxidation in the absence of an initiator or hydroperoxide ([AIBN] = [ROOH] = 0).

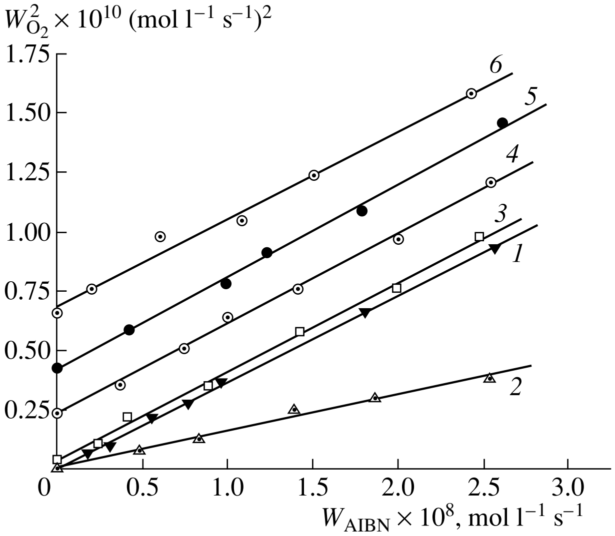


Fig. 1. Dependence of the squared styrene (M) oxidation rate on the rate of initiation with AIBN at [M] = 4.35 mol/l and T = 323 K: (*1*) $[\mathrm{EBHP}]_0 = 1.02 \times 10^{-2}$ mol/l; (*2*) [ROOH] = 0; (*3*) $[\mathrm{THP}]_0 = 1.34 \times 10^{-2}$ mol/l; (*4–6*) $[\mathrm{CPHP}]_0 = 5.71 \times 10^{-3}$, 1.03×10^{-2}, and 1.57×10^{-2} mol/l, respectively. For the linear plots *2–6*, $W_{\mathrm{O_2}} = W_\Sigma$.

In the absence of AIBN,

$$W_{\mathrm{in}} = W_{\mathrm{HP}} + W_{\mathrm{X}} + W_{\mathrm{aut}}. \tag{3}$$

The oxidation rates $W_{\mathrm{O_2}} \equiv W_\Sigma$ and $W_{\mathrm{O_2}} \equiv W$ correspond to the initiation rates $W_{\mathrm{in},\,\Sigma}$ and W_{in}.

The introduction of HP into styrene results in radical exchange by the reaction

$$\mathrm{MOO}^{\bullet} + \mathrm{ROOH} \longrightarrow \mathrm{MOOH} + \mathrm{ROO}^{\bullet}, \tag{V}$$

whose rate constant in nonpolar solvents is ~1×10^3 l mol^{-1} s^{-1} [9]. Given that the $\mathrm{MOO}^{\bullet}$ and $\mathrm{ROO}^{\bullet}$ radicals differ in reactivity, the experimentally measured $k_2/k_6^{1/2}$ ratio (steps (III) and (IV)) depends on [ROOH] [10]. This should be taken into account when using formula (1). This dependence was studied by the mixed initiation method [11]. In the case of AIBN + THP or AIBN + CPHP mixed initiation, $k_2/k_6^{1/2}$ remained unchanged and the experimental parameter $k_2/k_6^{1/2}$ decreased only in the presence of EBHP. The experimental results obtained by the mixed initiation method are presented in Fig. 1: the $k_2/k_6^{1/2}$ ratio is determined by the slope of the straight line, and the ordinate intercept is primarily determined by the rate of radical formation involving HP (this value is significant only for CPHP).

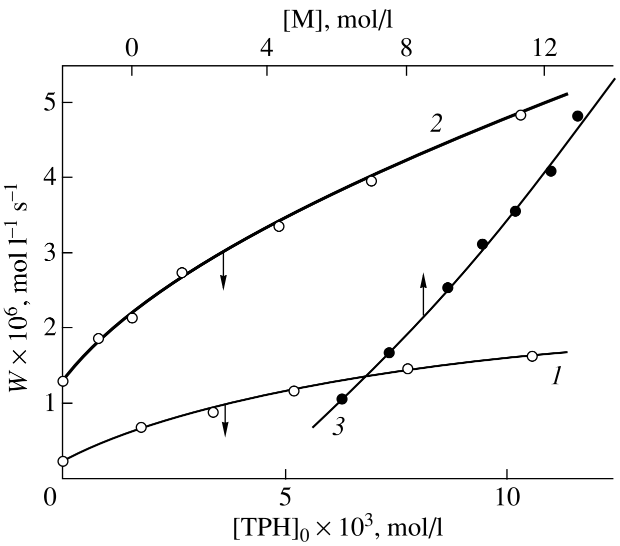


Fig. 2. Experimental data for styrene oxidation with tetralin hydroperoxide (THP) at 323 K: [M] = (*1*) 4.35 and (*2*) 8.70 mol/l, and (*3*) $[THP]_0 = 1.02 \times 10^{-2}$ mol/l.

Tetralin Hydroperoxide

The dependences of the styrene oxidation rate W on $[THP]_0$ and [M] are shown in Fig. 2. From the W_{THP} values calculated using formula (1) and from the linear plots of $\ln W_{THP}$ as a function of $\ln[THP]_0$ and $\ln[M]$, we deduced that the reaction is first-order with respect to the reactants: $[THP]_0^{1.0 \pm 0.1}$ and $[M]_0^{1.1 \pm 0.1}$; that is,

$$W_{THP} = k_{THP}[THP][M].$$

The following reaction is energetically most favorable [2]:

$$RO–OH + CH_2 = CHPh \xrightarrow{k_{THP}} RO^{\bullet} + HOCH_2–C^{\bullet}HPh.$$

Here, the preliminary formation of an intermediate complex between the reactants is assumed. Therefore, k_{THP} is the product of the equilibrium constant of complex formation and the rate constant of complex decomposition to radicals.

In the absence of AIBN and THP, radicals are formed slowly. For instance, at [M] = 8.42, 6.51 and 4.35 mol/l, $W_{aut} = 11.4 \times 10^{-11}$, 5.2×10^{-11}, and 2.1×10^{-11} mol l^{-1} s^{-1}, respectively. Taking into account these values does not change significantly the value of $k_{THP} = (1.5 \pm 0.3) \times 10^{-8}$ l mol^{-1} s^{-1} derived from the data presented in Fig. 2. The k_{THP} value is lower than the same constants for the tertiary hydroperoxides CHP and TBHP, for which $k_{HP} = 5.5 \times 10^{-8}$ and 2.2×10^{-8} l mol^{-1} s^{-1}, respectively [4].

The slight difference between the k_{in} values for these hydroperoxides can be due to the difference between the respective values of bond strength ($D_{O–O}$), which is one of the main factors in reactivity [2, 3].

2-Cyanopropane Hydroperoxide

The experiments involving CPHP were carried out both in the presence and in the absence of AIBN. The dependences of the oxidation rate on the reactant concentrations observed in these experiments are presented in Tables 1 and 2 and in Fig. 1. The processing of these data in terms of Eqs. (1)–(3) leads to first orders (±0.1) with respect to [CPHP] and [M] and to $k_{CPHP} = (2.6 \pm 0.2) \times 10^{-7}$ l mol^{-1} s^{-1}. This constant is much higher than the same constants for CHP and TBHP (see above) in spite of the fact that CPHP, $Me_2C(CN)OOH$, also has a tertiary structure.

For this reason, it was necessary to see whether admixtures can cause intensive chain initiation. Alcohols and ketones, which are the main products of the thermal decomposition of HPs, considerably accelerate HP decomposition to radicals [2, 12, 13]. However, only traces of acetyl cyanide were found in CPHP and the 2-hydroxy-*iso*-butyronitrile content of CPHP was <0.2 wt %. The introduction of this alcohol (≤0.4 wt %) did not change the rate of styrene oxidation. We studied the effect of the AIBN decomposition products (see Experimental) on the formation of radicals from CPHP. The main AIBN decomposition product is the dinitrile of tetramethylsuccinic acid [5]. These studies have demonstrated that the products of the anaerobic decomposition of AIBN as additives exert no effect on this reaction. This result confirms the conclusion that the CN group does not react with ROOH [4].

Along with the above compounds, which have no effect on CPHP decomposition, H_2O_2 was also detected. During the synthesis of CPHP, H_2O_2 is formed via the fast interaction of semiquinone radicals with O_2 [8] (r is the cyanoisopropyl radical):

$$rOO^{\bullet} + HOPhOH \longrightarrow rOOH + HOPhO^{\bullet},$$

$$HOPhO^{\bullet} + O_2 \longleftrightarrow C_6H_4O_2 + HOO^{\bullet},$$

$$HOO^{\bullet} + HOPhOH \longrightarrow H_2O_2 + HOPhO^{\bullet}$$

When a secondary alcohol is used, H_2O_2 is additionally formed by the reactions

$$rOO^{\bullet} + Me_2C(OH)H \longrightarrow rOOH + Me_2C^{\bullet}(OH)$$

$$\xrightarrow{O_2} Me_2C(OH)OO^{\bullet},$$

$$Me_2C(OH)OO^{\bullet} \xrightarrow{HOPhOH} Me_2C(OH)OOH$$

$$\longleftrightarrow Me_2CO + H_2O_2.$$

We failed to experimentally study the influence of H_2O_2 on CPHP decomposition, because H_2O_2 added to CPHP ≤2% does not increase but even retards the rate of styrene oxidation even in the absence of CPHP. According to our observations, this is due to H_2O_2 decomposition with O_2 evolution, which was detected

Table 1. Dependence of the styrene oxidation rate constant on the 2-cyano-2-hydroperoxypropane concentration at 323 K

$[ROOH]_0 \times 10^3$, mol/l	$W_\Sigma \times 10^6$	$W^*_{in,\Sigma} \times 10^9$	$W_{in} \times 10^9$
	$mol\ l^{-1}\ s^{-1}$		
$[AIBN] = 2.97 \times 10^{-3}$, $[M] = 4.35$ mol/l			
0	4.92	6.53	0.02
1.98	5.73	8.85	2.32
2.61	5.88	9.32	7.79
5.40	6.84	12.6	6.08
7.97	7.48	15.1	8.55
10.3	8.12	17.8	11.2
15.2	9.35	23.6	12.0
$[AIBN] = 0$, $[M] = 8.70$ mol/l			
0	1.28	–	0.11
0.98	6.10	–	2.51
2.02	8.21	–	4.54
3.16	10.3	–	7.15
4.53	12.5	–	10.5
5.40	13.6	–	12.5
6.17	14.3	–	13.8
7.27	15.5	–	16.2
10.3	18.7	–	23.6

* $W_{in,\Sigma}$ and W_{in} are defined by Eqs. (2) and (3).

at $[M] \leq 1.7$ mol/l in chlorobenzene in the absence of initiators ([AIBN] = [CPHP] = 0).

It is well known that H_2O_2 reacts with styrene at a rate approximately two orders of magnitude lower than THP [3]. In turn, the experimental k_{CPHP} value exceeds k_{TBHP} by more than one order of magnitude (see above). Since the H_2O_2 concentration in CPHP is ≤2%, it cannot be responsible for the observed rapid formation of radicals.

The observed kinetics and the first orders of the reaction with respect to the reactants also indicate the insignificant role of the admixtures (X) in the formation of radicals. Indeed, for the admixture fraction $\alpha = [X]/[ROOH]$, the formation rate of radicals in the bimolecular reaction between X and ROOH is $W_X = k_X\alpha[ROOH]^2$; for the monomolecular decomposition of X, $W_X = k_X\alpha[ROOH]$. If these reactions took place, both would be zero-order with respect to [M] and the former would be second-order with respect to [CPHP]. However, this was not observed in our experiments. First-order kinetics with respect to both reactants could be observed only for $X \equiv H_2O_2$; however, it has been shown above that the contribution from H_2O_2 to chain initiation is very small.

Thus, our results concerning possible radical formation routes other than the reaction between styrene and a hydroperoxide, the data obtained for cumene oxidation with CPHP or CHP as the initiator, and the ratio $k_{CPHP}/k_{CHP} = 3.1$ at 363 K [6] (under our conditions, this ratio is 4.7 at 323 K) suggest that the high reactivity of CPHP is due to the influence of the CN group. For the reactions of styrene with the tertiary hydroperoxides TBHP, CHP, and CPHP, $k_{HP} = 2.2 \times 10^{-8}$, 5.5×10^{-8} [4], and $26.0 \times 10^{-8}\ l\ mol^{-1}\ s^{-1}$, respectively. The electronegativity of the substituents increases in the same order: $CH_3 < C_6H_5 < CN$. Accordingly, this order is also followed by the electrophilic substituent (Hammett) constants: $\sigma^+_P = -0.256$, -0.085, and 0.674 [14]. These changes in the properties of the substituent must result in changes both in D_{O-O} and in the equilibrium constants of complex formation and complex decomposition to radicals. The D_{O-O} value for CPHP is unknown, and, therefore, the effect of a substituent on the bond dissociation energy and the polar effect of the substituent on the reactivity of the molecule cannot be estimated separately.

Ethylbenzene Hydroperoxide

The introduction of EBHP into styrene containing a constant AIBN concentration retards the oxidation process (Fig. 3): the experimentally measured $k_2/k_6^{1/2}$ ratio decreases with increasing [EBHP]. The $k_2/k_6^{1/2}$ ratio for THP and CPHP remains unchanged in the same hydroperoxide concentration range under the same conditions (Fig. 1), although radicals structurally different

Table 2. Dependence of the styrene oxidation rate on the styrene concentration in chlorobenzene at a constant 2-cyano-2-hydroperoxypropane concentration ($[ROOH] = 7.8 \times 10^{-3}$ mol/l, $T = 323$ K)

[M], mol/l	2.11	3.26	4.35	5.38	6.47	8.70
$W \times 10^6$, $mol\ l^{-1}\ s^{-1}$	1.96	3.62	5.70	8.03	10.02	16.2
$W_{in} \times 10^6$, $mol\ l^{-1}\ s^{-1}$	4.45	6.29	8.76	11.4	12.7	17.7

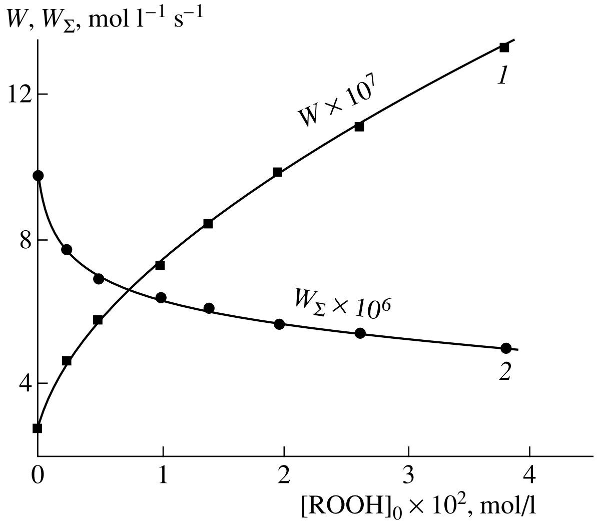


Fig. 3. Styrene oxidation rate as a function of the ethylbenzene hydroperoxide concentration at $T = 323$ K and $[\mathrm{M}] = 4.35$ mol/l. W_{AIBN} = (*1*) 0 and (*2*) 2.58×10^{-8} mol l^{-1} s^{-1}.

from $\mathrm{MOO}^\bullet$ are formed in the exchange reaction (V). Since the $\mathrm{MOO}^\bullet$ radical ($\sim\mathrm{CH_2CH(OO^\bullet)Ph}$) and the $\mathrm{ROO}^\bullet$ radical of ethylbenzene ($\mathrm{CH_3CH(OO^\bullet)Ph}$) are structurally similar, their reactivities in steps (III) and (IV) are very likely to be nearly equal. Therefore, the retardation is most likely caused by an admixture in EBHP rather than by the radical exchange reaction (V). The main admixtures may be methyl phenyl carbinol, acetophenone, and small amounts of phenol [15]. If phenol were involved in the retardation of oxidation, $k_2/k_6^{1/2}$ would be invariable and the order of the oxidation rate with respect to W_{AIBN} would be >0.5 (for strong inhibitors in the absence of "side" reactions, this order is ~1 [3]). It follows from our experimental data that $W_\Sigma \sim W_{\mathrm{AIBN}}^{1/2}$ (Fig. 1) and that $k_2/k_6^{1/2}$ decreases with increasing EBHP concentration at [AIBN] = const (Fig. 3). These regularities are characteristic of conjugated oxidation processes. Oxidation is retarded by low concentrations of secondary alcohols and is slightly accelerated by ketones [16]. The dependence of the cooxidation rate on the reactant concentrations is complicated [16]. For this reason, the kinetic experiments were carried out at [M] = const and different EBHP concentrations. In two comparative runs at $[\mathrm{ROOH}]_j$ = const (Fig. 3), one in the presence and the other in the absence of AIBN, the effective $k_2/k_6^{1/2}$ ratio is the same because it is independent of the initiation rate (see [16] and Fig. 1). At [AIBN] = const,

$$W_\Sigma = (k_2/k_6^{1/2})_j[\mathrm{M}]\,W_{\mathrm{in},\,\Sigma}^{1/2}, \tag{4}$$

where $k_2/k_6^{1/2}$ stands for the oxidizability of styrene at the *j*th concentration of ROOH. At [AIBN] = 0,

$$W = (k_2/k_6^{1/2})_j[\mathrm{M}]\,W_{\mathrm{in}}^{1/2}, \tag{5}$$

where $W_{\mathrm{in},\,\Sigma}$ and W_{in} are defined by expressions (2) and (3), respectively.

It follows from Eqs. (4) and (5) that

$$W_\Sigma^2 - W^2 = (k_2^2/k_6)_j[\mathrm{M}]^2 W_{\mathrm{AIBN}}.$$

This expression allows one to determine the ratio of the constants as functions of $[\mathrm{ROOH}]_j$. Using $(k_2/k_6^{1/2})_j$ and Eq. (5), we derived W_{in} from the dependence of W on $[\mathrm{ROOH}]_j$ for [AIBN] = 0 (Fig. 3, curve *1*). It follows from equality (3) that

$$(W_{\mathrm{in}} - W_{\mathrm{aut}})/[\mathrm{ROOH}] = k_{\mathrm{EBHP}}[\mathrm{M}] + k_{\mathrm{X}}\alpha[\mathrm{ROOH}]. \tag{6}$$

Processing the experimental data (Fig. 3, Table 3) in the coordinates of Eq. (6) led to $k_{\mathrm{EBHP}}[\mathrm{M}] = (2.8 \pm 0.4) \times 10^{-8}$ and $(5.3 \pm 0.5) \times 10^{-8}$ s^{-1} at [M] = 4.35 and 7.81 mol/l, respectively. Hence, $k_{\mathrm{EBHP}} = (6.5 \pm 0.9) \times 10^{-9}$ l mol^{-1} s^{-1}, which is ~2.3 times lower than the same constant for THP. Therefore, the reactivity of the secondary hydroperoxides depends on their molecular structure.

Thus, the secondary and tertiary hydroperoxides examined here differ in terms of reactivity toward styrene. The bimolecular rate constants of radical initiation in the reactions of styrene with tetralin, 2-cyanopropane, and ethylbenzene hydroperoxides at 323 K are equal to 1.5×10^{-8}, 2.6×10^{-7}, and 6.5×10^{-9} l mol^{-1} s^{-1}, respectively. The nature of the substituent R in the molecule of the tertiary hydroperoxide $\mathrm{RMe_2COOH}$ is the factor determining the rate of the reaction between the hydroperoxide and styrene. The reactivity of the hydroperoxide increases as the properties of the substituent change from electron-donor to electron-acceptor. For example, for R = $\mathrm{CH_3}$, $\mathrm{C_6H_5}$, and CN, the initiation rate constant is $k_{\mathrm{HP}} = 2.2 \times 10^{-8}$, 5.5×10^{-8}, and 26.0×10^{-8} l mol^{-1} s^{-1}, respectively; that is, it increases as the Hammett constants σ_{P}^{+} grows.

Table 3. Dependence of the styrene oxidation rates (W_Σ) at [AIBN] = const ($W_{\mathrm{AIBN}} = 1.06 \times 10^{8}$ mol l^{-1} s^{-1}) and [AIBN] = 0 (W) on the ethylbenzene hydroperoxide concentration (T = 323 K, [M] = 7.81 mol/l)

$[\mathrm{ROOH}]_0$, mol/l	0	0.52	1.05	1.44	2.08	2.66
$W_\Sigma \times 10^6$, mol l^{-1} s^{-1}	11.3	8.43	7.88	7.36	7.12	6.83
$W \times 10^6$, mol l^{-1} s^{-1}	1.03	1.57	1.96	2.15	2.46	2.65

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