# Acid-catalyzed formation of free radicals in the reaction of hydroperoxides with ketones

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The kinetics of formation of free radicals in the cyclohexanone (CH)—*tert*-butylhydroperoxide (TBHP)—*para*-toluenesulfonic acid (PTSA) system in acetonitrile was studied. The stoichiometry of the reaction corresponds to the consumption of two TBHP molecules per ketone molecule, whereas the yield of free radicals is ~20 % based on the TBHP reacted.

**Key words:** oxidation, acid catalysis, free radicals, acetonitrile, *p*-toluenesulfonic acid, *tert*-butyl hydroperoxide, cyclohexanone.

In one of the versions of the mechanism of acid-catalyzed decomposition of hydroperoxides,[1,2] the formation of free radicals

$$H_3O_2^+ + H_2O_2 \rightarrow H_3O^+ + HO^\cdot + HO_2^\cdot$$

is the result of the bimolecular reaction of two hydroperoxide molecules, one of which is protonated.

We have previously established that the introduction of the third component (ketone) into the initiating binary hydroperoxide—mineral acid system accelerates sharply overall consumption of hydroperoxide[3] and its radical decomposition. In this work, the kinetics of this reaction was studied.

## Experimental

The rate of formation of radicals (initiation rate $v_i$) was calculated by the aprobated procedure[2] from the rate of oxygen absorption by styrene oxidized in an acetonitrile solution in the presence of hydroperoxide and cocatalysts of its radical decomposition (ketone and acid) in a reactor of a manometric installation.

A two-section reactor[2] was used in order to heat separately an acetonitrile solution containing ketone, hydroperoxide, and styrene and a solution of acid. The separate heating was necessary to prevent decomposition of ROOH before the beginning of measurements of the oxidation rate. When reagents were heated, they were mixed by switching-on a shaker. Rectified ketones, cyclohexanone (CH), hydroperoxides, *tert*-butyl hydroperoxide (TBHP), styrene, and perchloric acid were used. Acetonitrile was purified by the known procedure.[2] *para*-Toluenesulfonic acid (PTSA) was recrystallized from chloroform and dried *in vacuo*. An initiator, azobisisobutyronitrile (AIBN) was recrystallized from ethanol, and the initiation rate for AIBN was calculated by the equation presented in the previous work.[4]

## Results and Discussion

The kinetic curves of oxygen absorption by styrene are presented in Fig. 1. A distinct effect of the combined presence of CH and PTSA in the solution is observed: according to kinetic curves *1*, *1'* and *2*, *2'*, the radical decomposition of TBHP is accelerated by approximately two orders of magnitude, and the rates of styrene chain oxidation increase ~10-fold when CH and PTSA are combined in a solution of TBHP. The fast formation of radicals is accompanied by the consumption of hydroperoxide (tested by iodometry), which results in the retardation of oxygen absorption (see Fig. 1, curves *1'* and *2'*). The addition of a fresh portion of TBHP again results in the fast oxidation (see Fig. 1, curve *3*).

The data on the rates of chain-radical oxidation of styrene in the presence of triple hydroperoxide—ketone—acid systems of various compositions and binary hydroperoxide—ketone and hydroperoxide—acid systems are presented in Table 1. No data for systems without hydroperoxides or with sole hydroperoxide are presented, because in these cases the oxidation rates are negligible. The analysis of the data presented in Table 1 allows one to draw the following conclusions: first, proton acids accelerate radical decomposition of secondary and ternary hydroperoxides in the presence of various ketones; second, synergism of the action of ketones (ket) and acids (ac) on the decomposition of hydroperoxides is pronounced, namely, in all cases $V_{ket} + V_{ac} \ll V_{ket+ac}$ (when all values are measured in the presence of the same [ROOH]). A substantial detail should also be mentioned: the well-known reaction of degenerate branching of ketones with hydroperoxides[5,6] does not virtually initiate oxidation under the conditions studied. For ex-

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**Table 1.** Oxidation rate of styrene ($\upsilon$/mol L$^{-1}$ s$^{-1}$) at various concentrations (mol L$^{-1}$) of the components of the initiating systems: ketone—acid—hydroperoxide in acetonitrile, [styrene] = 0.2 mol L$^{-1}$, 343 K

| [MEK] + [PTSA] + [CHHP] | $\upsilon \cdot 10^6$ | [CH] + [PTSA] + [TBHP] | $\upsilon \cdot 10^6$ | [AcAc] + [PTSA] + [TBHP] | $\upsilon \cdot 10^6$ |
|---|---|---|---|---|---|
| 1.14 + 0 + 0.025 | 0.1 | 0.97 + 0 + 0.003 | 0.3 | 0.39 + 0 + 0.003 | 0.2 |
| 0 + 0.011 + 0.025 | 10.6 | 0 + 0.011 + 0.003 | 3.0 | 0 + 0.011 + 0.003 | 3.0 |
| 1.14 + 0.011 + 0.025 | 22.0 | 0.97 + 0.011 + 0.003 | 31.0 | 0.39 + 0.011 + 0.003 | 5.2 |
| [CH] + [PTSA] + [CHP] | $\upsilon \cdot 10^6$ | [MEK] + [PTSA] + [TBHP] | $\upsilon \cdot 10^6$ | [AcAc] + [$HClO_4$] + [TBHP] | $\upsilon \cdot 10^6$ |
| 0.19 + 0 + 0.06 | 0.5 | 0.69 + 0 + 0.003 | 0.2 | 0.05 + 0 + 0.02 | 0.2 |
| 0 + 0.007 + 0.06 | 2.7 | 0 + 0.11 + 0.003 | 3.0 | 0 + 0.05 + 0.02 | 0.05 |
| 0.19 + 0.007 + 0.06 | 9.0 | 0.69 + 0.11 + 0.003 | 12.0 | 0.05 + 0.05 + 0.02 | 7.3 |

*Note.* PTSA, MEK, CH, AcAc, Ac are *para*-toluenesulfonic acid, methylethylketone, cyclohexanone, acetylacetone, and acetone, respectively; CHHP, TBHP, CHP are cyclohexyl hydroperoxide, *tert*-butyl hydroperoxide, and cumene hydroperoxide, respectively.

ample, for the CH—PTSA—CHP system, the ratio of the rates is the following: $V_{\text{CH—PTSA—CHP}} : V_{\text{PTSA—CHP}} : V_{\text{CH—CHP}} = 9 : 2.7 : 0.5$, which corresponds to the ratio of the initiation rates of 81 : 7.3 : 0.25 for square chain termination, *i.e.*, the contribution of the CH—CHP system to the overall initiation is negligible. Therefore, we will consider the ketone—acid—hydroperoxide (triple) and acid—hydroperoxide (binary) systems denoting the corresponding values by symbols "t" and "b."

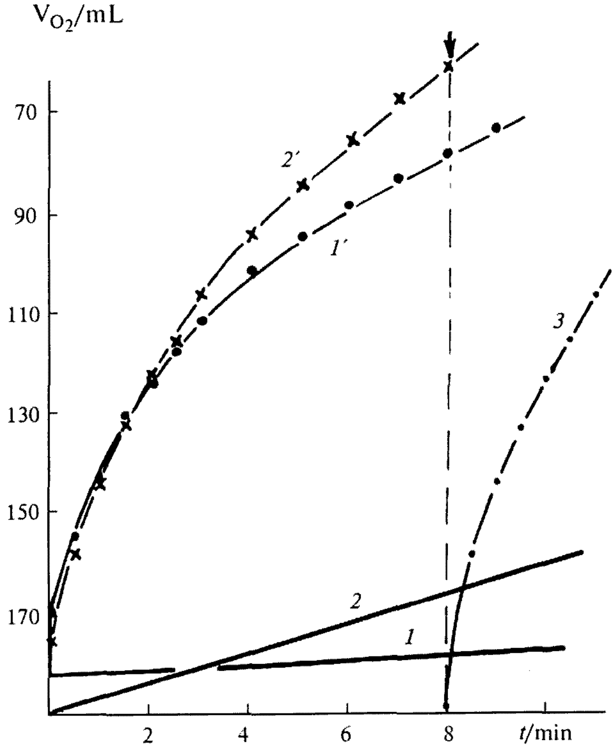


**Fig. 1.** Kinetics of oxidation of 0.2 mol L$^{-1}$ of styrene in acetonitrile, 343 K: *1*, in a solution of 0.97 mol L$^{-1}$ of CH + $3 \cdot 10^{-3}$ mol L$^{-1}$ of TBHP; *1'*, after addition of $1.1 \cdot 10^{-2}$ mol L$^{-1}$ of PTSA; *2*, in a solution of $1.1 \cdot 10^{-2}$ mol L$^{-1}$ of PTSA + $3 \cdot 10^{-3}$ mol L$^{-1}$ of TBHP; *2'*, after addition of 0.97 mol L$^{-1}$ of CH; *3*, addition of $3 \cdot 10^{-3}$ mol L$^{-1}$ of TBHP is indicated by the arrow on curve *2'*.

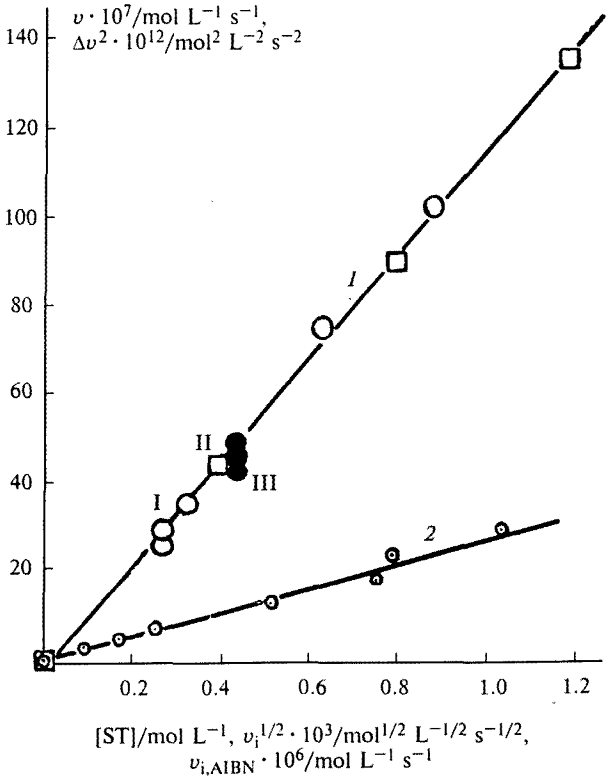


**Fig. 2.** *1*, Dependence of the rate of AIBN-initiated oxidation of 0.26 mol L$^{-1}$ of styrene (I) on $(\upsilon_i)^{1/2}$; II, experiments with 0.0025, 0.02, and 0.05 mol L$^{-1}$ of TBHP; III, experiments on oxidation of 0.2 mol L$^{-1}$ of styrene upon mixed initiation, dependence of $\Delta\upsilon^2$ on $\upsilon_{i,\text{AIBN}}$ in the presence of 0.005 mol L$^{-1}$ of TBHP, 0.0073 mol L$^{-1}$ of CH, and 0.0073 mol L$^{-1}$ of PTSA; *2*, dependence of oxidation rate $\upsilon$ on the concentration of styrene, initiator: 0.019 mol L$^{-1}$ of PTSA + 0.005 mol L$^{-1}$ of CH + 0.025 mol L$^{-1}$ of TBHP. Acetonitrile was used as a solvent, 343 K.

and acid—hydroperoxide (binary) systems denoting the corresponding values by symbols "t" and "b."

The rate of chain-radical oxidation ($v$) can be expressed by the formula

$$v = k_2/k_6^{-1/2}[\mathrm{RH}]v_i^{1/2}, \qquad (1)$$

where $k_2$ and $k_6$ are the rate constants of chain propagation and termination, $v_i$ is the rate of radical formation (initiation rate), and RH is styrene. When the TBHP—CH—PTSA t-system is an initiator, $v$ depends linearly on [RH] (Fig. 2, curve *2*).

When oxidation is initiated by AIBN, the dependence of $v$ on $(v_{i,\mathrm{AIBN}})^{1/2}$ is also expressed by the straight line (see Fig. 2, curve *1*). The value $(k_2 \cdot k_6^{-1/2})_{343\ \mathrm{K}} = 4.3 \cdot 10^{-2}$ L$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$ was determined from its slope, and the additives of TBHP were found to exert no effect on it (see Fig. 2, curve *1*, III). Since all components of the t-system can affect the chain length of styrene oxidation, the method of mixed initiation was used to determine the $k_2 \cdot k_6^{-1/2}$ value by the more reliable calculations of $v_i$ from $v$.[2] The t-system and AIBN were the components of the mixed initiator. The following value was determined from the slope of straight-line dependence $\Delta v^2 - f(v_{i,\mathrm{AIBN}})$, $\Delta v^2 = v_\Sigma^2 - v^2$ (see Fig. 2, line *1*), where $V_\Sigma$ is the oxidation rate in the presence of the t-system and AIBN[2]:

$$k_2 \cdot k_6^{-1/2} = 5.3 \cdot 10^{-2}\ \mathrm{L}^{1/2}\ \mathrm{mol}^{-1/2}\ \mathrm{s}^{-1/2}.$$

This value was used in calculations of $v_i$ from the $v_t$ values when the concentrations of components of the t-system (CH, PTSA, and TBHP) varied. The dependences of oxidation and initiation rates on the experimental conditions are presented in Figs. 3 and 4. The data presented in Fig. 3 testify to a complex mechanism of radical formation from TBHP in the acid medium: for the triple system, the reaction order with respect of PTSA $n = 0.5\pm0.1$, with respect to ketone $n = 1.5\pm0.15$, and the first reaction order with respect to hydroperoxide (Fig. 4, curves *1*, *1'*), *i.e.*, the initiation rate by the t-system is expressed as

$$v_{i,t} = k_{i,t}[\mathrm{PTSA}]^{1/2} \cdot [\mathrm{TBHP}]^1 \cdot [\mathrm{CH}]^{3/2}. \qquad (2)$$

The activation energy was measured within the 328 to 348 K range by two methods: from temperature dependences of initial oxidation rates and coefficients of transformation of kinetic curves.[7] According to Eq. (1), the overall activation energy determined by the temperature run of the oxidation rate is the following:

$$E = E_2 - (E_6/2) + (E_i/2) = 63.7\ \mathrm{kJ\ mol}^{-1}.$$

According to the literature data,[4] the $E_2 - (E_6/2)$ value is ~30 kJ mol$^{-1}$, whence $E_{i,t} = 67.3\pm8$ kJ mol$^{-1}$. Therefore, the Arrhenius form of the initiation constant is the following:

$$k_{i,t} = 1.87 \cdot 10^{10}\exp[-67.3(\mathrm{kJ\ mol}^{-1})/RT]\ (\mathrm{L}^2\ \mathrm{mol}^{-2}\ \mathrm{s}^{-1}),$$

$$k_{i,t} = 1.0\ \mathrm{L}^2\ \mathrm{mol}^{-2}\ \mathrm{s}^{-1}\ (343\ \mathrm{K}).$$

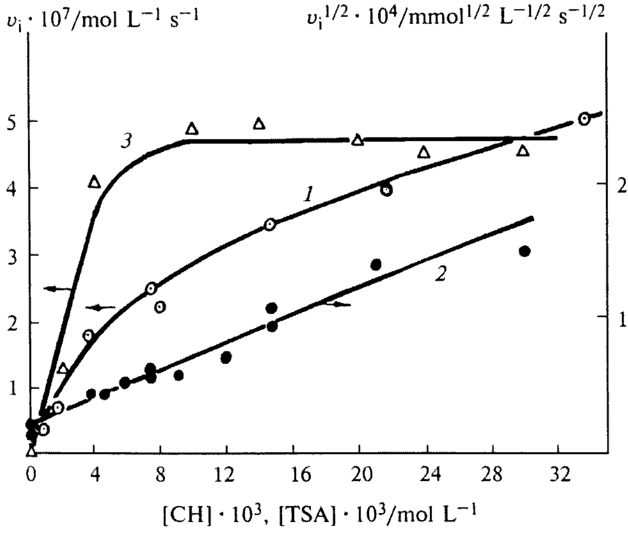


**Fig. 3.** *1* and *2*, Dependences for the triple system, 343 K: *1*, $v_i$ on [PTSA] at [TBHP] = $5 \cdot 10^{-3}$, [CH] = $7.3 \cdot 10^{-3}$ mol L$^{-1}$; *2*, $(v_i)^{1/2}$ on [CH] at [TBHP] = $5 \cdot 10^{-3}$, [PTSA] = $1.82 \cdot 10^{-2}$ mol L$^{-1}$; *3*, dependence of $v_i$ on [PTSA] for the binary system, [TBHP] = $1.1 \cdot 10^{-2}$ mol L$^{-1}$.

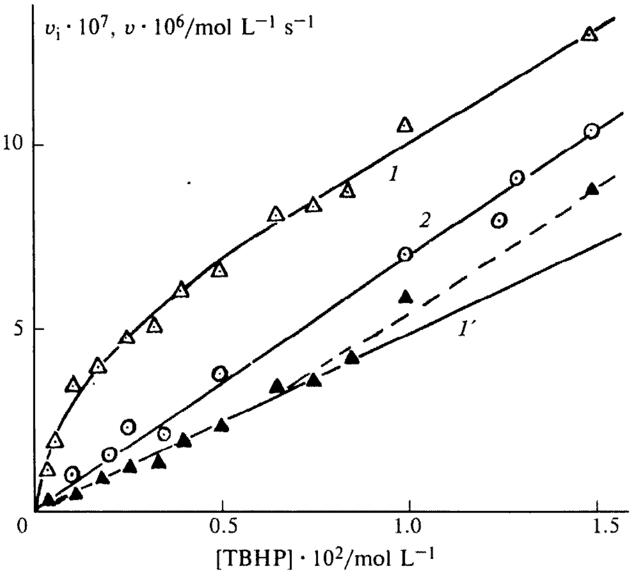


**Fig. 4.** Dependences of the oxidation rate on [TBHP] at [styrene] = 0.26, [PTSA] = $1.92 \cdot 10^{-2}$ mol L$^{-1}$, 343 K: *1*, triple system, [CH] = $5 \cdot 10^{-3}$ mol L$^{-1}$; *2*, binary system, [CH] = 0; *1'*, dependence of $v_i$ on [TBHP], calculated from the data in curve *1*.

The kinetic parameters of the binary system were obtained from the dependences of $v_i$ and $v$ on [TBHP] and [PTSA] (see Figs. 3 and 4). Proportionality $v \sim$ [TBHP] testifies to the second order of the reaction of the radical formation with respect to TBHP as well as for the other hydroperoxide—acid pairs.[2] When [PTSA] ≥ [TBHP], the $v_{i,b}$ value reaches a limit and changes slightly as [PTSA] increases (see Fig. 3, curve *3*), *i.e.*, at [PTSA] ≥ [TBHP] the reaction order with respect to acid is zero and $v_{i,b} = k_{i,b}\cdot[\mathrm{ROOH}]$.[2] Therefore, according to the data in Fig. 3, at [PTSA] ≥ [ROOH]

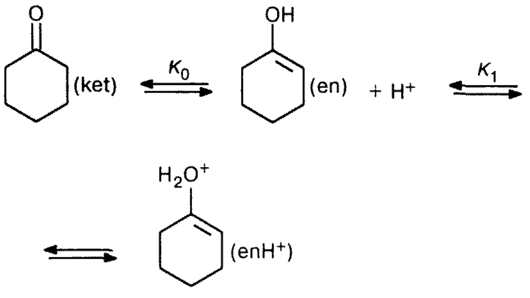
$$k_{i,b} = (v_{i,b}/[\mathrm{TBHP}]) = 3.9\cdot10^{-3}\ \mathrm{L\ mol^{-1}\ s^{-1}}\ (343\ \mathrm{K}).$$

At [PTSA] ≥ [ROOH] the ratio of $v_i$ values for the t- and b-systems is the following:

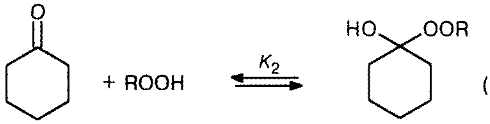
$$(v_{i,t}/v_{i,b}) = (k_{it}[\mathrm{PTSA}]^{1/2}\cdot[\mathrm{CH}]^{3/2}\cdot[\mathrm{TBHP}]/(k_{i,b}[\mathrm{TBHP}]^2) = (k_{i,t}[\mathrm{PTSA}]^{1/2}\cdot[\mathrm{CH}]^{3/2})/(k_{i,b}[\mathrm{TBHP}]^2).$$

Inserting the $k_{i,t}$ and $k_{i,b}$ values at [PTSA] = [TBHP] = 0.01 mol L$^{-1}$, we find that even at [CH] = $6\cdot10^{-3}$ mol L$^{-1}$, $v_{i,t} > v_{i,b}$, *i.e.*, ketone exerts an extremely strong effect on the radical formation. At TBHP > 0.6 mol L$^{-1}$ the curve of the dependence bends upward (Fig. 4, curve *1*), *i.e.*, the initiation reaction of the order higher than unity is manifested. It is likely that a new form of peroxide, which transforms rapidly into free radicals *via* the first-order reaction, forms in the presence of CH and TBHP. When [TBHP] becomes considerably higher than [CH], free hydroperoxide decomposes to radicals under the action of acid, and the contribution of the b-system becomes noticeable against the background of the t-system (see Fig. 4, curve *1*). The question concerning the ratio of radical and nonradical channels of transformation is usually central in studies of catalytic decomposition of hydroperoxides. The fraction of the radical channel (*e*) was determined by the graphic differentiation of the kinetic curve of styrene oxidation at [CH] = 0.04, [TBHP] = 0.04, and [PTSA] = $5.5\cdot10^{-3}$ mol L$^{-1}$ at 343 K from the formula $e = \Sigma v_i\Delta t/2\Delta[\mathrm{ROOH}]$. The $v_i$ values at each period $\Delta t$ were calculated from Eq. (1), the concentration of hydroperoxide decomposed in the experiment ($\Delta$[ROOH]) was determined by titration with a correction for formation of styrene hydroperoxide ROOH$_s$, $\Delta[\mathrm{ROOH}] = [\mathrm{ROOH}]_0 - [\mathrm{ROOH}]_t - [\mathrm{ROOH}]_s$; and the latter value was determined in a special experiment with AIBN. The value $e = 0.22$, *i.e.*, the contribution of the radical channel to the overall decomposition of TBHP is ~22 %, which is considerably higher than the similar value for binary systems.[1,2] Chromatographic analysis of the cyclohexanone oxidates (column with poly(ethylene glycol) adipate on Chromaton N—AW, 365 K, dodecane as an external standard) in experiments with the triple system shows that the consumption of TBHP is accompanied by the consumption of CH with the stoichiometry $\Delta$[CH] : $\Delta$[TBHP] = 0.4 ± 0.1, *i.e.*, one molecule of CH is approximately consumed per two TBHP molecules.

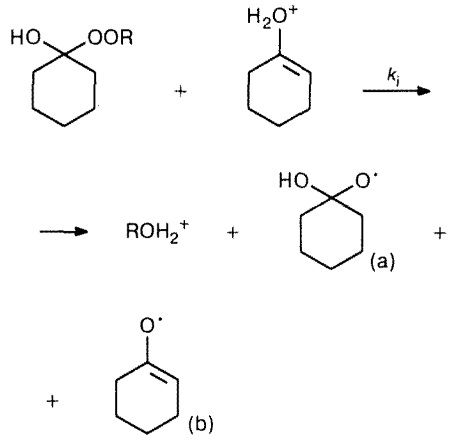
The experimental data obtained can be explained by the following simplified scheme of the mechanism of radical formation:



(1′)



(2′)

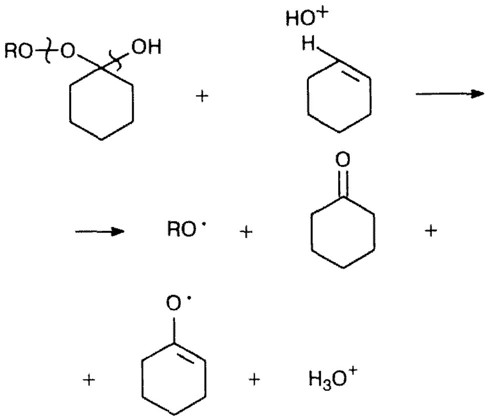


(3′)

The stage of radical formation (3′) can be written in another way, *via* the cleavage of the C—O bond and concerted cleavage of the O—O bond (Scheme 1).

The difference between variants (3′) and (3") is of no importance for the further discussion. The meaning of the scheme is the intermediate formation of semiperketal X$_1$ followed by its reaction with the protonated form of enol (enH$^+$). This scheme is based on our and the literature data: it follows from Table 1 that the formation of radicals in the triple ketone—ROOH—acid systems is not a particular case. Many substances can participate in this reaction, including ketones of different structures with different C—H bond strengths, for example, the acetone—cyclohexanone—acetylacetone series. If the lim-

**Scheme 1**



(3")

iting stage of the reaction studied involved the cleavage of the C—H bond of ketone in the redox act with hydroperoxide, the reaction rate would be the lowest with acetone and the highest with acetylacetone. The t-system involving cyclic ketone (CK), whose ability of forming semiperketals with hydroperoxides (reaction 2′) is well known[6] and exceeds those of aliphatic ketones, provides the highest rate of radical formation. The reaction order with respect to ketone $n < 1$ corresponds to the noncatalytic decomposition of semiperketal formed from CH and TBHP.[5] In the case of the acid-catalyzed radical decomposition in the t-system, $n > 1$ and an effect of CH on the decomposition of TBHP is considerably stronger than that in the noncatalytic reaction: according to the previously published data,[5] the rate of the TBHP radical decomposition is the highest in the CH medium, where the initiation constant is equal to $6 \cdot 10^{-7}$ s$^{-1}$ at 393 K. In our case, in the acid medium (see Fig. 3, curve *2*) when the temperature is 50° lower, the specific rate of radical formation from TBHP in the presence of only 0.02 mol L$^{-1}$ of CH is $3 \cdot 10^{-4}$ s$^{-1}$, *i.e.*, 500-fold higher. The difference in kinetic orders with respect to [CH] ($n < 1$ for the example cited[5] and is close to the second order in our case) is explained by reaction (3′) of the scheme suggested; this stage is similar to the scheme of acid-catalyzed radical formation from TBHP in the binary system[2]: the cleavage of the weak —O—O— bond is followed by the elimination of a protonated molecule of the strong base, alcohol. According to the scheme, the initiation rate is determined by reaction (3′), $v_i = k_i[X_1][enH^+]$ under the condition that [ket] > [ROOH], which corresponds to curve *2* in Fig. 3,

$$[X_1] = (K_2[ket]\,[ROOH]/(1 + K_2[ket]).$$

The concentration of enol can be expressed by the concentration of ketone as $[en] = K_0[ket]$, and the concentration of the protonated form is determined as

$$[enH^+] = K_1([en] - [enH^+]) \cdot [HAn],$$

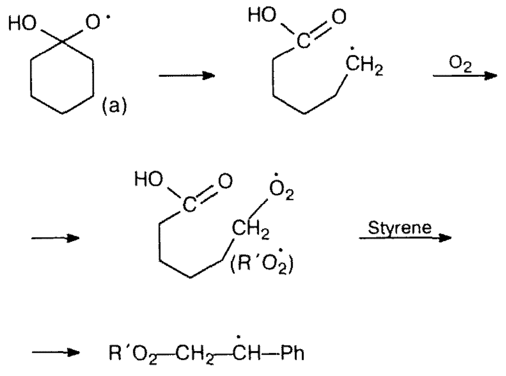
$$[enH^+] = (K_1[en] \cdot [HAn])/(1 + K_1[HAn]) = (K_0K_1[ket] \cdot [HAn])/(1 + K_1[HAn]),$$

whence the equation

$$v_i = (k_iK_0K_1K_2[ket]^2 \cdot [ROOH] \cdot [HAn])/(1 + K_1[HAn])(1 + K_2[ket]) \qquad (4)$$

follows that approximately corresponds to the experimental kinetic orders: the first order with respect of TBHP, $n_{TBHP} = 1$, $n_{ket} < 2$, and $n_{HAn} < 1$, *i.e.*, to the rational orders with respect of ketones and acid (**2**), which should be observed in the concentration ranges corresponding to the condition of commensurability of the $K_1$[HAn] and $K_2$[ket] values to unity (see the denominator of Eq. (4)).

Formation of two radicals per molecule of decomposed hydroperoxide in the form of semiperketal corresponds to the scheme of reactions 1′—3′, *i.e.*, the yield of radicals is equal to 100 %. The yield of radicals determined experimentally is equal to 22 %, and one ketone molecule is consumed per two reacting ROOH molecules. The supplement of the scheme by probable reactions (5) and (6) involving radicals (a) and (b) formed *via* reaction (3′) corresponds to the stoichiometry of consumption of one ketone molecule per two ROOH molecules with 50 % yield of radicals.



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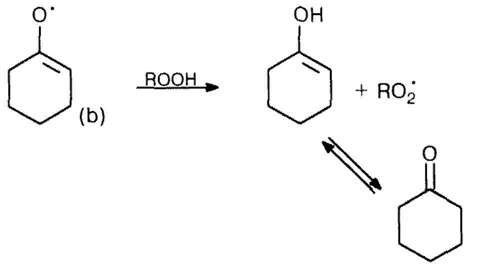

(6)

Since the 22 % yield of radicals was experimentally determined without special study of overall decomposition of TBHP in the triple PTSA—CH—TBHP system, this fact cannot be explained. It should be mentioned that our data on the stoichiometry of consumption of TBHP : CH in the presence of different acids (PTSA and $HClO_4$) are not contradictory: this value is close to 2 (Ref. 3) at the ratio of initial concentrations [TBHP] : [CH] ≈ 1 as in this work. The scheme of radical formation is not complete and final. The main result of the study is observation of the new catalytic reaction with high yield of free radicals.

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