

Kinetic Analysis of Systems Containing Aromatic Amine, Phenol, and Hydroperoxide

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Abstract—Processes and phenomena in three-component systems containing a secondary aromatic amine, a sterically hindered phenol, and a hydroperoxide are analyzed from the standpoint of kinetics. The following three phenomena, which are well known, are related to each other: (1) simultaneous phenol and hydroperoxide consumption during the generation of amyl radicals; (2) consecutive consumption of phenol and amine as antioxidants in the initiated oxidation of hydrocarbons; and (3) catalytic acceleration of phenoxyl radical reaction with hydroperoxide by aromatic amines. These three phenomena reflect the process behavior in the title systems in the generation or addition of the corresponding free radicals. It was shown that the main catalytic feature of the reactions in three-component systems is a trend toward their coupled nature. The requirements to the experimental conditions are formulated under which coupling either takes place in full measure or does not play any role at all.

The processes occurring in the systems containing a secondary aromatic amine (AmH), a hydroperoxide (ROOH), and a spatially hindered phenol (ArOH) are of great interest. Each of the components can be oxidized to yield a radical. Therefore, three types of radicals with different reactivities are present in a solution: diarylaminyl (Am^\cdot), sterically hindered phenoxyl (ArO^\cdot), and peroxide (RO_2^\cdot) radicals. The presence of these radicals determines the mechanistic complexity of the processes and reveals itself in experiments in the form of the hard-to-explain and sometimes unpredictable behavior of the systems under certain conditions.

Kinetic studies of reactions in the $\text{AmH} + \text{ArOH} + \text{ROOH}$ system is of practical importance due to close relations between the mechanisms of the processes and the mechanism of antioxidative action of aromatic amines and phenols in the oxidation reactions of organic compounds RH.

This work is devoted to the elucidation of the main specific features of radical reaction kinetics in the $\text{AmH} + \text{ArOH} + \text{ROOH}$ systems, which were analyzed under the conditions when radicals Am^\cdot , RO_2^\cdot , and ArO^\cdot are generated. The results of this analysis are compared to available experimental data.

1. Am^\cdot radicals are generated in the $\text{AmH} + \text{ArOH} + \text{ROOH}$ system. At comparable ArOH and ROOH concentrations, Am^\cdot radicals formed by the reaction



first attack mostly ArOH:



Another reaction,



is very slow because $k_1 \gg k_2$ (at $T \approx 350 \text{ K}$ $k_1 \approx 10^7$ [1], and $k_2 \approx 10^4\text{--}10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ [2]). AmH and ArO^\cdot radicals are formed by reaction (I) at the rate v_i . Phenoxyl radicals ArO^\cdot do not react with Am^\cdot [3]. Therefore, ArO^\cdot is consumed by the reactions



At $T \approx 350 \text{ K}$, the values k_{-1} are within the limits $10^3\text{--}10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ [4]. The values $2k_3$ for 4-substituted 2,6-di-*t*-butylphenoxyls change over wide ranges: from zero for stable 2,4,6-di-*t*-butylphenoxyl radical to $\sim 5 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ [5]. In connection with this, reaction (III) plays a key role in the overall process kinetics. At high values of k_3 , the stationary concentration of ArO^\cdot is very low ($[\text{ArO}^\cdot] \sim (v_i/2k_3)^{1/2}$). Therefore, reaction coupling can be excluded and ArOH and ROOH consumption is consecutive.

ROOH can enter the transformations via two reactions



The Am^\cdot radicals are much more active in reaction with ROOH than the ArO^\cdot radicals. Thus, at $T \approx 350$ K, $k_2 \approx 10^4$ – 10^5 [2], and $k_4 \leq 10$ l mol $^{-1}$ s $^{-1}$ [6]. Therefore, if the experimental conditions are favorable for the intensive occurrence of reaction (–I) between ArO^\cdot and AmH resulting in a growth of Am^\cdot concentration (at a given value of k_3 this can be due to the presence of AmH as an additive and/or AmH accumulation during the process), then ROOH may become a participant of the transformations long before ArOH consumption (ROOH enters the transformations via the reactions with Am^\cdot).

As noted above, at the early stages, the AmH + ArOH + ROOH system can be considered pseudobinary (AmH + ArOH) in which Am^\cdot radicals are generated. The ArO^\cdot radicals are consumed by reaction (III). As AmH radicals are accumulated in the system, the concentration of Am^\cdot grows according to the law

$$[\text{Am}^\cdot] \approx \frac{v_i + k_{-1}(v_i/2k_3)^{1/2}([\text{AmH}]_0 + v_i t)}{k_1([\text{ArOH}]_0 - v_i t)}.$$

As a consequence, reactions of these radicals become more intensive. For instance, the rate v_1 of reaction (I) may become higher than v_i

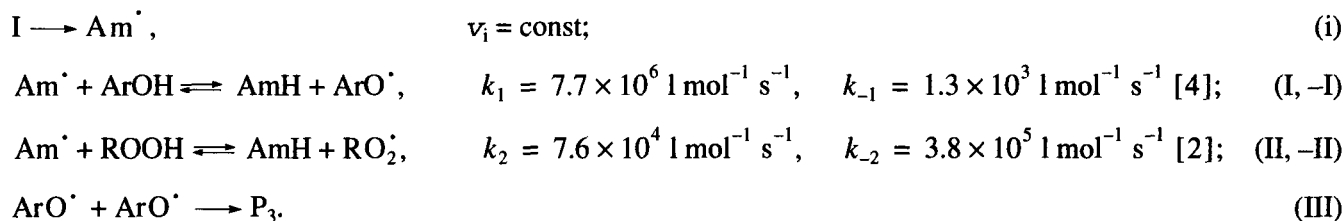
$$\begin{aligned} \frac{v_1}{v_i} &= \frac{k_1[\text{Am}^\cdot][\text{ArOH}]}{v_i} \\ &= 1 + k_{-1}(2k_3 v_i)^{-1/2}([\text{AmH}]_0 + v_i t). \end{aligned}$$

If one adds ROOH to the AmH + ArOH system after a period t upon the start of a run, the rate v_2 of the reaction between Am^\cdot and ROOH depends on the concentration of unreacted phenol $[\text{ArOH}]_t = [\text{ArOH}]_0 - v_i t$. The value v_2 will be equal to a certain value $v_2 = \alpha v_i$ if the residual concentration of $[\text{ArOH}]_t$ at the instant of ROOH addition is

$$[\text{ArOH}]_t = \frac{1 + k_{-1}(2k_3 v_i)^{-1/2}([\text{AmH}]_0 + [\text{ArOH}]_0)}{\frac{\alpha k_1}{k_2[\text{ROOH}]_0} + \frac{k_{-1}}{(2k_3 v_i)^{1/2}}}. \quad (1)$$

Equation (1) shows that the absolute value of k_3 is the main factor that affects the consecutive and simultaneous consumption of ArOH and ROOH. The higher the value of k_3 , the more rapid a switch from one reaction regime to another (less time is needed for the growth of α in a given range, for instance from 0.1 to 0.3) and the more complete is the phenol consumption (in which case the $[\text{ArOH}]_t/[\text{ArOH}]_0$ ratio is lower) by the time ROOH is involved in the reaction. Formula (1) enables one to obtain acceptable estimates even if ROOH is present in the system from the start rather than added during a run.

Based on the above arguments, we may propose the mechanism of the process and formulate the requirements to reactant concentrations at which ArOH and ROOH will consecutively be consumed



Scheme 1.

The numerical values of constants in scheme 1 refer to the well-studied diphenylamine + 2,4,6-tri-*tert*-butylphenol + cumyl hydroperoxide (DPA + TTBP + CHP) system at $T \approx 350$ K. To draw more general conclusions, let us consider that the value of k_3 is case-dependent; that is, reaction (III) is not associated with any specific phenoxyl radical. The DPA + TTBP + CHP mixture will further be considered as a model system.

According to scheme 1, in the steady-state reaction, the concentrations of radicals are

$$\begin{aligned} [\text{ArO}^\cdot] &= (v_i/2k_3)^{1/2}, \\ [\text{Am}^\cdot] &= \frac{v_i + k_{-1}(v_i/2k_3)^{1/2}[\text{AmH}]}{k_1[\text{ArOH}]}, \\ [\text{RO}_2^\cdot] &= \frac{k_2}{k_1 k_{-2}} \frac{[\text{ROOH}]}{[\text{AmH}][\text{ArOH}]} \{v_i + k_{-1}(v_i/2k_3)^{1/2}[\text{AmH}]\}. \end{aligned}$$

Obviously, at specified values of rate constants, the consecutive consumption of ArOH and ROOH is

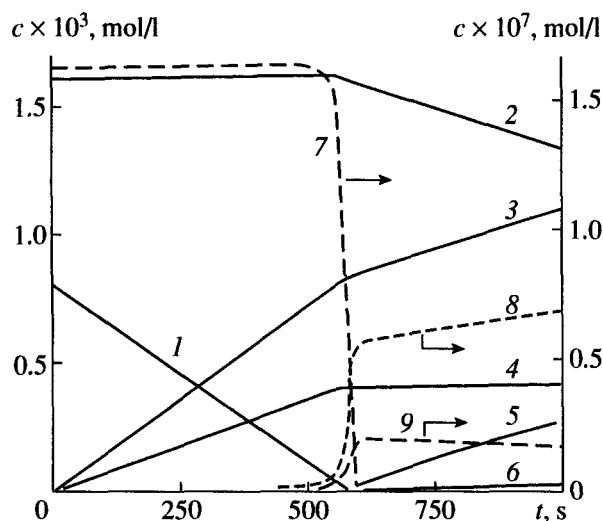
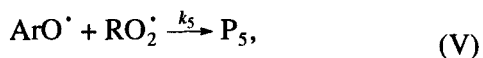
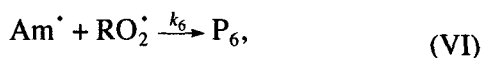


Fig. 1. Calculated curves of initial species consumption and reaction product accumulation in the experiment on the decomposition of compound I ($v_{Am^*} = 1.4 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1} = \text{const}$) in the presence of ArOH ($8 \times 10^{-4} \text{ mol/l}$) and ROOH ($1.6 \times 10^{-3} \text{ mol/l}$) in the case of rapidly recombining ArO^* radicals ($2k_3 = 5 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$): (1) ArOH; (2) ROOH; (3) AmH; (4) P_3 ; (5) P_6 ; (6) P_7 ; (7) ArO^* ; (8) Am^* ; and (9) RO_2^* .

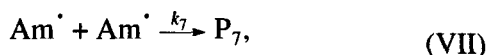
observed if radicals decay only via reaction (III). That is, the rates of the following steps are negligible:



$$k_5 = 2 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1} [7, 8];$$



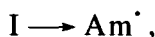
$$k_6 = 6 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1} [9];$$



$$2k_7 = 3.6 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1} [9].$$

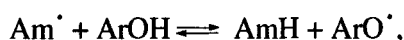
The inequality $v_3 \gg v_5$ is true if

$$\frac{[\text{AmH}][\text{ArOH}]}{[\text{ROOH}]} \gg \frac{k_2 k_5}{k_1 k_{-2}} \left(\frac{2v_i}{k_3} \right)^{1/2} + \frac{k_{-1} k_2 k_5}{k_1 k_{-2} k_3} [\text{AmH}]. \quad (2)$$

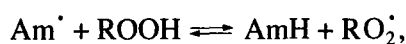


$$v_i = \text{const};$$

(i)



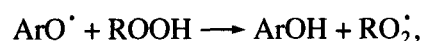
$$k_1 = 7.7 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}, \quad k_{-1} = 1.3 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}; \quad (\text{I}, -\text{I})$$



$$k_2 = 7.6 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}, \quad k_{-2} = 3.8 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}; \quad (\text{II}, -\text{II})$$



$$k_5 = 2 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}; \quad (\text{V})$$



$$k_4 = 2.67 \text{ l mol}^{-1} \text{ s}^{-1} (\text{CCl}_4 [10]). \quad (\text{IV})$$

Scheme 2.

The necessity of the fulfillment of inequalities $v_3 \gg v_6$ and $v_3 \gg v_7$ results in the respective formulas

$$[\text{ArOH}] \left(\frac{[\text{AmH}]}{[\text{ROOH}]} \right)^{1/2} \gg \frac{1}{k_1} \left(\frac{2k_2 k_6 v_i}{k_{-2}} \right)^{1/2} + \frac{k_{-1}}{k_1} \left(\frac{k_2 k_6}{k_{-2} k_3} \right)^{1/2} [\text{AmH}], \quad (3)$$

$$[\text{ArOH}] \gg \frac{(2k_7 v_i)^{1/2}}{k_1} + \frac{k_{-1}}{k_1} \left(\frac{k_7}{k_3} \right)^{1/2} [\text{AmH}]. \quad (4)$$

Using expressions (2)–(4), we may determine the requirements to v_i and k_3 for which the consumption of TTBP and CHP in the DPA + TTBP + CHP system is consecutive at the initial concentrations $[\text{DPA}] = [\text{TTBP}] = [\text{CHP}] = 1 \times 10^{-3} \text{ mol/l}$:

$$1 \gg 7.35 \times 10^3 (v_i / 2k_3)^{1/2} + 6.75 \times 10^3 / k_{-3}, \quad (2a)$$

$$1 \gg 2.01 v_i^{1/2} + 1.85 k_3^{-1/2}, \quad (3a)$$

$$1 \gg 0.78 v_i^{1/2} + 0.72 k_3^{-1/2}. \quad (4a)$$

The inequality (2a) suggests that $k_3 \gg 6.75 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$. If this condition is fulfilled, then the requirements to v_i can be found from (3a). Thus, if $k_3 = 2.5 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$, then the consecutive consumption of ArOH and ROOH will be observed at $v_i \ll 0.25 \text{ mol l}^{-1} \text{ s}^{-1}$.

The above case of consecutive consumption of phenol and hydroperoxide at high values of k_3 illustrates the data shown in Fig. 1. The curves were obtained within the framework of the mechanism shown in scheme 1 supplemented with steps (V)–(VII). Simulations were performed with the Kinetika program package and a set of rate constants for the model DPA + TTBP + CHP system. Comparison with the experimental data is impossible because there are no such data.

Let us consider a more complicated limiting case when the ArO^* radicals formed from ArOH are stable ($k_3 = 0$). To describe the processes, we can use the following reaction scheme:

At the initial stage, the Am^\cdot radical is only consumed by reaction (I). Because of AmH and ArO^\cdot accumulation, the rate of reaction $(-I)$ continuously increases. After the period t , the rates of the forward and backward reactions become equal v_i :

$$v_i \approx k_1[\text{Am}^\cdot]_t[\text{ArOH}]_t \approx k_{-1}[\text{AmH}]_t[\text{ArO}^\cdot]_t.$$

Let us estimate t . In the absence of the AmH additive, we may assume that $[\text{AmH}]_t \approx [\text{ArO}^\cdot]_t \approx (v_i/k_{-1})^{1/2}$ and $t \approx [\text{ArO}^\cdot]_t/v_i = (v_i/k_{-1})^{-1/2}$. Thus, at $v_i = 1.4 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$, $t \approx 20 \text{ s}$. In the presence of AmH , t is much shorter. For instance, at $[\text{AmH}]_0 = 2.15 \times 10^{-3} \text{ mol/l}$, $t \approx (k_{-1}[\text{AmH}])^{-1} \approx 0.4 \text{ s}$. The concentrations of ArO^\cdot and Am^\cdot at this moment differ substantially. At $v_i = 1.4 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$, $[\text{ArOH}]_0 = 8 \times 10^{-4} \text{ mol/l}$, and $[\text{AmH}]_0 = 0$, the radical concentrations are as follows: $[\text{ArO}^\cdot]_t = 3.3 \times 10^{-5} \text{ mol/l}$ and $[\text{Am}^\cdot]_t = v_i/k_1([\text{ArOH}]_0 - [\text{ArO}^\cdot]_t) = 2.4 \times 10^{-10} \text{ mol/l}$.

At the time t , ArO^\cdot and AmH do not stop accumulating. To a first approximation, the concentration grows in proportion to t . The rates of reactions (I) and $(-I)$ increase more rapidly, approximately in proportion to t^2 . The values v_i and v_{-1} remain approximately equal to each other but become higher than v_i because reactions (I) and $(-I)$ approach a quasiequilibrium state.

As ArO^\cdot and Am^\cdot are accumulated, ROOH reacts more and more intensively. To elucidate the role of each radical, let us make necessary estimates assuming that the either reaction (II) or (IV) can be neglected. Suppose, for instance, that reaction (IV) can be neglected and ROOH enters the process only via the interaction with the radicals Am^\cdot in reaction (II). Then, after the time τ , the system will start operating in the regime when half of the Am^\cdot radicals is replaced by the ArO^\cdot radicals by reaction (I) and the others are replaced by RO_2^\cdot via reaction (II). The ArO^\cdot and RO_2^\cdot radicals then recombine by reaction (V). Let us estimate $[\text{ArO}^\cdot]_\tau$ at, say, $v_i = 1.4 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$, $[\text{AmH}]_0 = 0$, and $[\text{ArOH}]_0 = 8 \times 10^{-4}$ and $[\text{ROOH}]_0 = 1.6 \times 10^{-3} \text{ mol/l}$. Using the stoichiometric relations

$$\begin{aligned} [\text{ROOH}]_\tau &\approx [\text{ROOH}]_0, \\ [\text{AmH}]_\tau &\approx [\text{ArO}^\cdot]_\tau \approx v_i\tau, \\ [\text{ArOH}]_\tau &\approx [\text{ArOH}]_0 - [\text{ArO}^\cdot]_\tau \end{aligned} \quad (5)$$

and assuming that reactions (I) and $(-I)$ are quasiequilibrated, we arrive at

$$\begin{aligned} &[\text{ArO}^\cdot]_\tau \\ &\approx \frac{(K_1^2 v_i^2 + 8K_1 k_2 v_i [\text{ROOH}][\text{ArOH}]_0)^{1/2} - K_1 v_i}{4k_2 [\text{ROOH}]}, \end{aligned}$$

where $K_1 = k_1/k_{-1}$. Upon substituting numerical values, we find that $[\text{ArO}^\cdot]_\tau \approx 1.48 \times 10^{-4} \text{ mol/l}$, $\tau' \approx [\text{ArO}^\cdot]_\tau/v_i \approx 105 \text{ s}$, and $[\text{Am}^\cdot]_\tau \approx v_i/2k_2[\text{ROOH}]_0 = 6 \times 10^{-9} \text{ mol/l}$.

Although the above estimates are rough, they allow us to draw several reliable conclusions. First, because the value of $[\text{ArO}^\cdot]_\tau$ is high, reaction (IV) cannot be neglected. That is, ROOH enters the transformations largely via the reaction with ArO^\cdot , especially in the experiments without AmH additives (in the above example, $v_{4(\tau)} \approx 5.14 \times 10^{-7} \text{ mol l}^{-1} \text{ s}^{-1}$). Second, reaction $(-II)$ can be neglected. This is explainable by the fact that ROOH initially does not participate in the process, and the concentration of RO_2^\cdot radicals is negligible. When ROOH starts reacting, the concentration of ArO^\cdot is so high that the inequality is fulfilled; that is, $v_5 \gg v_{-2}$, i.e., $k_5[\text{ArO}^\cdot] \gg k_{-2}[\text{AmH}]$. Third, a very high concentration of $[\text{ArO}^\cdot]_\tau$ (~20% of $[\text{ArOH}]_0$) raises doubt about whether ArO^\cdot is a fast species (to which the pseudo-steady-state approximation is applicable) under experimental conditions.

It follows from the above that

$$\frac{d[\text{Am}^\cdot]}{dt} = v_i - k_1[\text{Am}^\cdot][\text{ArOH}] \quad (6)$$

$$+ k_{-1}[\text{ArO}^\cdot][\text{AmH}] - k_2[\text{Am}^\cdot][\text{ROOH}] = 0,$$

$$\frac{d[\text{RO}_2^\cdot]}{dt} = k_2[\text{Am}^\cdot][\text{ROOH}] \quad (7)$$

$$+ k_4[\text{ArO}^\cdot][\text{ROOH}] - k_5[\text{ArO}^\cdot][\text{RO}_2^\cdot] = 0,$$

$$\frac{d[\text{ArO}^\cdot]}{dt} = k_1[\text{Am}^\cdot][\text{ArOH}] - k_{-1}[\text{ArO}^\cdot][\text{AmH}] \quad (8)$$

$$- k_4[\text{ArO}^\cdot][\text{ROOH}] - k_5[\text{ArO}^\cdot][\text{RO}_2^\cdot].$$

Equation (8) suggests that the concentration of ArO^\cdot under the experimental conditions passes through a maximum with the coordinates τ' and $[\text{ArO}^\cdot]_\tau$. To estimate these coordinates, let us use expression (5) for $[\text{ROOH}]_\tau$ and $[\text{ArOH}]_\tau$ and assume that $[\text{AmH}]_\tau \approx [\text{AmH}]_0 + [\text{ArO}^\cdot]_\tau$. The expression for $[\text{Am}^\cdot]_\tau$ can be

found from equation (6). By equating derivative (8) to zero, we obtain

$$[\text{ArO}^\cdot]_\tau = \frac{b - (b^2 - 4ac)^{1/2}}{2a},$$

where $a = 2[\text{ROOH}]_0(k_1k_4 - k_{-1}k_2)$; $b = k_1v_i + 2k_{-1}k_2[\text{AmH}]_0[\text{ROOH}]_0 + 2k_1k_4[\text{ArOH}]_0[\text{ROOH}]_0 + 2k_2k_4[\text{ROOH}]_0^2$; and $c = v_i(k_1[\text{ArOH}]_0 - k_2[\text{ROOH}]_0)$.

In the above example ($v_i = 1.4 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$, $[\text{AmH}]_0 = 0$, $[\text{ArOH}]_0 = 8 \times 10^{-4} \text{ mol/l}$, and $[\text{ROOH}]_0 = 1.6 \times 10^{-3} \text{ mol/l}$), the concentration $[\text{ArO}^\cdot]_\tau$ is 1.5 times lower than $[\text{ArO}^\cdot]_\tau = 9.56 \times 10^{-5} \text{ mol/l}$, and $\tau \approx 68 \text{ s}$. If this experiment were carried out in the presence of AmH with a concentration of $2.15 \times 10^{-3} \text{ mol/l}$ added from the start, then $[\text{ArO}^\cdot]_\tau = 1.13 \times 10^{-5} \text{ mol/l}$.

Adding up equations (6)–(8), we obtain

$$\frac{d[\text{ArO}^\cdot]}{dt} = v_i - 2k_5[\text{ArO}^\cdot][\text{RO}_2^\cdot]. \quad (9)$$

At $t > \tau'$, derivative (9) is negative. Obviously, this is only possible if the concentration of RO_2^\cdot radicals increases at a higher rate than the concentration of ArO^\cdot decreases. However, equation (7) shows that an increase in the concentration of RO_2^\cdot is possible provided that the concentration of Am^\cdot increases. Thus, the concentration of ArO^\cdot decreases at $t > \tau'$ and, simultaneously the concentrations of RO_2^\cdot and Am^\cdot radicals increase. Therefore, ROOH is initially consumed by the reactions with both radicals Am^\cdot and ArO^\cdot (especially in the experiments without AmH additives). At later stages, the concentration of ArO^\cdot decreases, and the concentration of Am^\cdot increases, and the latter play a more and more important role in inveigling ROOH into transformations.

Let us compare the values of terms in equation (8) at $t = \tau'$. For the sake of certainty, let us consider the above examples using equation (6) to calculate $[\text{Am}^\cdot]_\tau$.

(a) Suppose $v_i = 1.4 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$, $[\text{ArOH}]_0 = 8 \times 10^{-4}$ and $[\text{ROOH}]_0 = 1.6 \times 10^{-3} \text{ mol/l}$, and there are no AmH additive ($[\text{AmH}]_0 = 0$). In this case, $[\text{ArO}^\cdot]_\tau = 9.56 \times 10^{-5}$ and $[\text{Am}^\cdot]_\tau = 2.40 \times 10^{-9} \text{ mol/l}$. Then,

$$\begin{aligned} \frac{d[\text{ArO}^\cdot]}{dt} &= v_i - v_{-1} - v_4 - v_5 = 1.30 \times 10^{-5} \\ &- 1.19 \times 10^{-5} - 4.1 \times 10^{-7} - 7.0 \times 10^{-7} = 0. \end{aligned} \quad (8a)$$

In this case, $v_2 = k_2[\text{Am}^\cdot][\text{ROOH}] = 2.91 \times 10^{-7} \text{ mol l}^{-1} \text{ s}^{-1}$ and $[\text{RO}_2^\cdot]_\tau = 3.66 \times 10^{-11} \text{ mol/l}$.

(b) Suppose the conditions are met, but $[\text{AmH}]_0 = 2.15 \times 10^{-3} \text{ mol/l}$. In this case, $[\text{ArO}^\cdot]_\tau = 1.13 \times 10^{-5}$ and $[\text{Am}^\cdot]_\tau = 5.35 \times 10^{-9} \text{ mol/l}$

$$\begin{aligned} \frac{d[\text{ArO}^\cdot]}{dt} &= v_i - v_{-1} - v_4 - v_5 = 3.25 \times 10^{-5} \\ &- 3.18 \times 10^{-5} - 4.83 \times 10^{-8} - 7.0 \times 10^{-7} = 0, \end{aligned} \quad (8b)$$

$v_2 = 6.51 \times 10^{-7} \text{ mol l}^{-1} \text{ s}^{-1}$ and $[\text{RO}_2^\cdot]_\tau = 3.10 \times 10^{-10} \text{ mol/l}$.

It can be seen that in the run without an AmH additive, the values v_i and v_{-1} are by almost an order of magnitude higher than v_i and much higher than the rates of other steps. The difference between v_i and v_{-1} is only ~10%. This means that reactions (I) and (–I) may roughly be considered as quasiequilibrated even at $t = \tau'$. This is true of later reaction stages to a greater extent, as is evident from the v_2 value, which at $t = \tau'$ is almost 2.5 times lower than its maximal value $0.5v_i$ achieved at later stages. For such a pronounced increase in v_2 , $[\text{Am}^\cdot]$ should also increase by a factor of ~2.5. This would cause a similar increase in v_i , and the difference $v_i - v_{-1}$ would become equal to $0.5v_i = 7 \times 10^{-7} \text{ mol l}^{-1} \text{ s}^{-1}$ (~2% of the increased values v_i and v_{-1}) with an increase in the reaction conversion. In the presence of AmH, the quasiequilibrium approximation is applicable at even $t = \tau'$, as is clear from the above estimates of $[\text{ArO}^\cdot]_\tau$, v_i , and v_{-1} .

Let us turn to equation (9). Because radicals decay only in reaction (V), equation (9) reflect the balance of the rates of radical generation and decay (v_{dec}),

$$\frac{d[\text{ArO}^\cdot]}{dt} = v_i - 2v_5 = v_i - v_{\text{dec}}. \quad (9a)$$

If we consider $v_{\text{dec}} = 2v_5$ as a figurative point, the above process can be viewed as the movement of this point in the rate–time plane. This movement is not an approach of $v_{\text{dec}} = v_i$ to the horizontal asymptote. Rather, this is a semioscillation around v_i at deep depths. The movement begins at $t = 0$ when $v_{\text{dec}} = 0$, that is, with an amplitude equal to $\Delta = v_{\text{dec}} - v_i = -v_i < 0$. Then, at $t = \tau'$, the v_{dec} point passes through the equilibrium state $v_{\text{dec}} = v_i$ to the region of positive amplitudes. The maximal deviation is achieved at $\tau'_1 > \tau'$ when the point changes the direction of its movement and starts to approach v_i asymptotically. Equation (9a) shows that during relaxation, the concentration of ArO^\cdot decreases. As noted above, the absolute values of v_i and v_{-1} also increase because they are the terms of equation (8). Therefore, as v_{dec} approaches v_i during relaxation when the process enters the steady-state mode, the approximation of the steady-state ArO^\cdot concentration becomes more accurate.

Suppose the process is stationary within a certain accuracy starting from the time θ (Fig. 2). The areas of figures AOB and BCD contoured by the point v_{dec} during its movement below and above the v_i axis are equal to each other and accurate to an infinitesimal, because the concentrations of radicals (including ArO^\bullet) become negligible when the process becomes stationary. Let us also take into account that the nature of reaction (V) resulting in radical decay does not change during the whole process. Therefore, starting from the time θ , the state of the system (i.e., the rates of elementary steps and the concentrations of reactants and products) becomes the same as if the process occurred in the stationary mode at earlier stages. This means that, because the concentrations of initial reactants, intermediate radicals, and final products are "self-tuned," for the time θ , the process that is clearly unsteady can conventionally be considered stationary. Derivatives (9) and (9a) for the least active radical ArO^\bullet can be considered equal to zero during the whole process.

Figure 2 shows that the duration of the unsteady period θ depends on experimental conditions. In the presence of AmH, the time θ' is shorter than θ so that the unsteady period can be neglected. In this case, the concentrations are stationary from the process start. With an increase in the ArOH concentration (or a decrease in the ROOH concentration), the duration of the unsteady period increases; that is, $\theta'' > \theta$.

The above consideration provides physical grounds for the applicability of the steady-state approximation to the concentrations of all radicals (including the least active radical ArO^\bullet) even at early stages of the reaction. Note that kinetic simulations in several relevant cases lead to the same conclusions. Obviously, within the framework of steady-state approximation, kinetics is adequately described only at $t \geq \theta$. Nevertheless, conventional applicability simplifies the detection and analysis of the main regularities even when θ cannot be neglected on a run duration scale.

The steady-state approximation and scheme 2 suggest the following relations for the rates of consumption v_{cons} and accumulation v_{accum} of various species:

$$v_{\text{cons}}^{\text{ArOH}} = v_{\text{cons}}^{\text{ROOH}} = v_{\text{accum}}^{\text{P}_5} = 0.5 v_{\text{accum}}^{\text{AmH}} = 0.5 v_i. \quad (10)$$

According to (10), during the generation of Am^\bullet radicals in the presence of ROOH and ArOH, whose phenoxyl radicals are stable, ROOH and ArOH are consumed simultaneously at the same rate equal to $0.5 v_i$. Quinolide peroxide P_5 is accumulated at the same rate $0.5 v_i$, and amine AmH is accumulated at the rate v_i . Relations (10) do not depend on the nature of ArOH and ROOH, the presence or absence AmH, and v_i .

The above behavior is well known as a phenomenon of the simultaneous consumption of ArOH and ROOH during Am^\bullet generation [11].

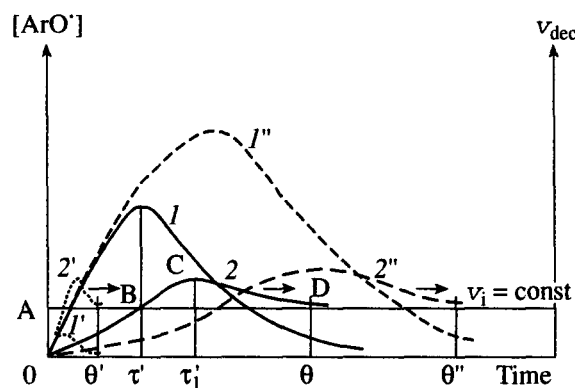


Fig. 2. Kinetic curves of (I , I' , and I'') ArO^\bullet accumulation and (2 , $2'$, and $2''$) changes in the rates of radical decay during the unsteady period θ . See text for explanation.

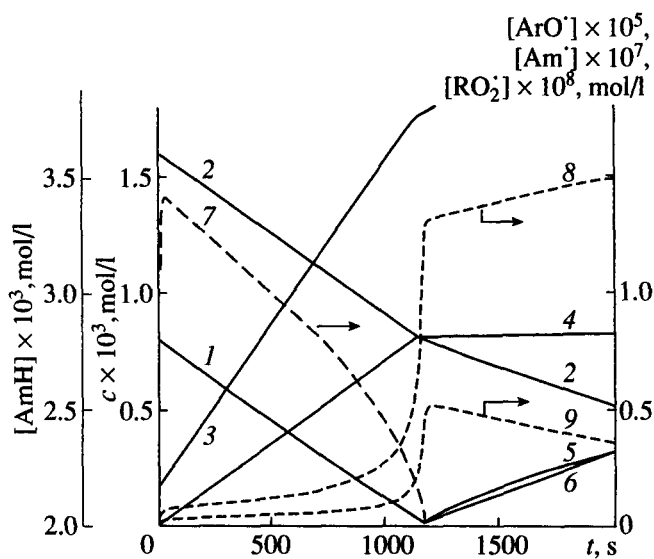


Fig. 3. Consumption of initial species and product accumulation in the generation of Am^\bullet ($v_{\text{Am}^\bullet} = 1.4 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$) in the three-component system ArOH ($8 \times 10^{-4} \text{ mol/l}$) + ROOH ($1.6 \times 10^{-3} \text{ mol/l}$) + AmH ($2.15 \times 10^{-3} \text{ mol/l}$) under the condition that the ArO^\bullet radicals are stable ($k_3 = 0$) and the unsteady period θ' is negligible: (1) ArOH ; (2) ROOH ; (3) AmH ; (4) P_5 ; (5) P_6 ; (6) P_7 ; (7) ArO^\bullet ; (8) Am^\bullet ; and (9) RO_2^\bullet .

Figure 3 shows simulated kinetic curves corresponding to the run with the AmH additive discussed above. In this simulation, scheme 2 was supplemented by "nondetailed" reactions (VI) and (VII) (in fact, these reactions are not elementary [12–15]). These reactions should be taken into account after the complete consumption of deficient ArOH. In this case, if the unsteady period θ' is very short, the kinetics of initial species consumption and product accumulation during the run is quantitatively described within the frame-

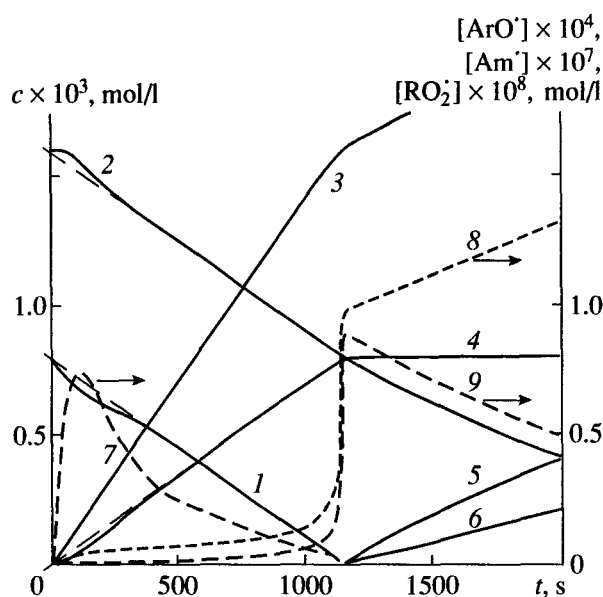


Fig. 4. Consumption of initial species and product accumulation in the generation of $\text{Am}\cdot$ ($v_{\text{Am}\cdot} = 1.4 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$) in the mixture ArOH ($8 \times 10^{-4} \text{ mol/l}$) + ROOH ($1.6 \times 10^{-3} \text{ mol/l}$) under the condition that the $\text{ArO}\cdot$ radicals are stable ($k_3 = 0$), and the unsteady period θ is moderately long: (1) ArOH ; (2) ROOH ; (3) AmH ; (4) P_5 ; (5) P_6 ; (6) P_7 ; (7) $\text{ArO}\cdot$; (8) $\text{Am}\cdot$; and (9) $\text{RO}_2\cdot$.

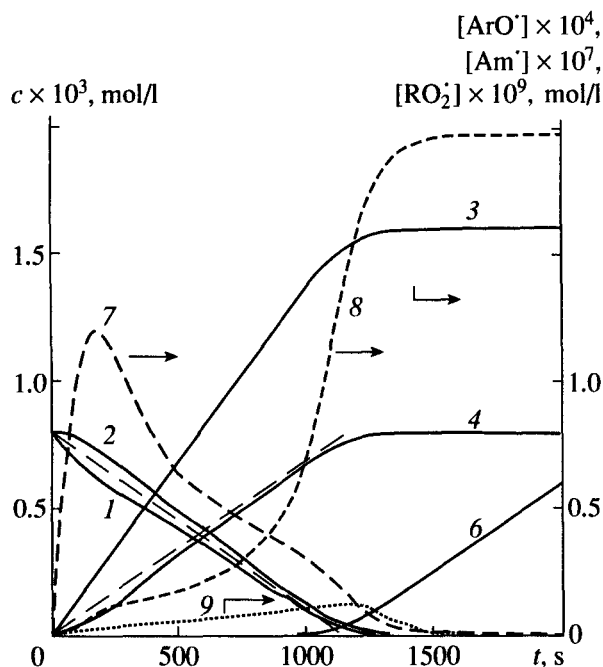


Fig. 5. Consumption of initial species and product accumulation in the generation of $\text{Am}\cdot$ ($v_{\text{Am}\cdot} = 1.4 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$) in the equimolar mixture ArOH ($8 \times 10^{-4} \text{ mol/l}$) + ROOH ($8 \times 10^{-3} \text{ mol/l}$) under the condition that the $\text{ArO}\cdot$ radicals are stable ($k_3 = 0$) and the unsteady period θ'' is long: (1) ArOH ; (2) ROOH ; (3) AmH ; (4) P_5 ; (5) P_6 ; (6) P_7 ; (7) $\text{ArO}\cdot$; (8) $\text{Am}\cdot$, and (9) $\text{RO}_2\cdot$.

work of steady-state approximation applied to the concentrations of all radicals. Figure 3 supports the relations (10).

Figure 4 shows the results of the run without the AmH additive discussed above. In this case, the unsteady period θ is long ($\sim 20\%$ of the run duration), and the value $[\text{ArO}\cdot]_r$ reaches $\sim 10\%$ of $[\text{ArOH}]_0$. In complete agreement with the stationary mode of reaction during the time θ , the duration of runs (the time of complete ArOH consumption) is completely the same in Figs. 3 and 4, and the curves for the accumulation and consumption of nonradical species during the main period of reaction in Fig. 4 are identical to the corresponding curves in Fig. 3. The values of $[\text{ArOH}]_0$, $[\text{ROOH}]_0$, and $[\text{P}_5]_0 = 0$ can be obtained by extrapolating the curves of ArOH and ROOH consumption and P_5 accumulation at their main segments to the time $t = 0$. They agree with the experimental data reported in [11] showing the absence of induction periods on the curves of $\text{ArO}\cdot$, ROOH , and P_5 consumption.

Figure 5 shows that if an unsteady period θ'' is comparable to the duration of a run, the curves of ArOH and ROOH consumption and P_5 accumulation start to approach the corresponding asymptotic values (10) at relatively early stages of the reaction, but they may fail to merge with them with an acceptable accuracy.

Let us formulate the requirements to the simultaneous consumption of ArOH and ROOH . When deriving expressions for the concentrations of radicals, we will assume that reactions (I) and (–I) are at quasiequilibrium:

$$[\text{ArO}\cdot] \approx K_1 [\text{ArOH}] [\text{Am}\cdot] / [\text{AmH}].$$

Then,

$$[\text{RO}_2\cdot] = \frac{k_2 [\text{Am}\cdot]}{k_5 [\text{ArO}\cdot]} [\text{ROOH}]$$

$$\approx \frac{k_2 [\text{AmH}] [\text{ROOH}]}{K_1 k_5 [\text{ArOH}]},$$

$$[\text{ArO}\cdot] = \frac{v_i}{2k_5 [\text{RO}_2\cdot]}$$

$$\approx \frac{K_1 [\text{ArOH}]}{2k_2 [\text{AmH}] [\text{ROOH}]} v_i,$$

$$[\text{Am}\cdot] \approx \frac{[\text{AmH}] [\text{ArO}\cdot]}{K_1 [\text{ArOH}]} = \frac{v_i}{2k_2 [\text{ROOH}]}.$$

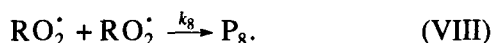
Simultaneous consumption of ArOH and ROOH is observed if reaction (V) between $\text{ArO}\cdot$ and $\text{RO}_2\cdot$ is the only reaction of irreversible radical decay. In the inequalities shown below, the numerical values in parentheses refer to the DPA + TTBP + CHP system for which the rate constants were considered above:

$$(a) v_5 = 0.5v_i = k_5[RO_2^*][ArO^*] \gg v_7 = 2k_7[Am^*]^2;$$

$$\text{therefore, } [ROOH] \gg (k_7v_{-1})^{1/2}/k_2 \quad (\gg 5.6 \times 10^{-2} v_{-1}^{1/2});$$

$$(b) v_5 \gg v_6 = 2k_6[Am^*][RO_2^*]; \text{ therefore, } [ArOH]/[AmH] \gg 2k_6/K_1k_5 \quad (\gg 1.0 \times 10^{-3});$$

$$(c) v_5 \gg v_8 = 2k_8[RO_2^*]^2, \text{ where } v_8 \text{ is the rate of reaction}$$



The necessity of the fulfillment of this condition leads to the following inequality

$$\frac{[ArOH]}{[AmH]} \gg \frac{2k_2}{K_1k_5} \left(\frac{k_8}{v_i} \right)^{1/2} [ROOH] \\ (\gg 1.1 \times 10^{-5} [ROOH]/v_i^{1/2}).$$

The above inequalities are consistent with each other. They are fulfilled in the case of the DPA + TTBP + CHP system over broad ranges of reactant concentrations and v_i .

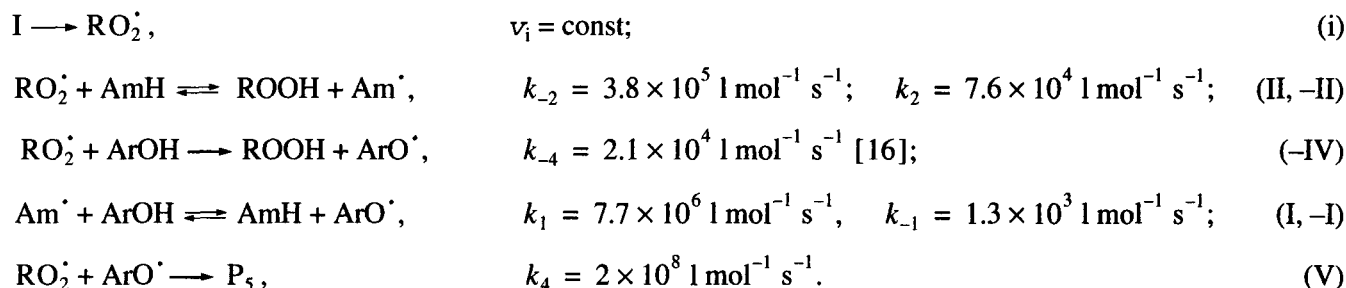
Thus, the above analysis shows that the consumption of ArOH and ROOH may either be consecutive or simultaneous depending on the conditions and the stability of ArO^* (the value of k_3). In the presence of ArOH and ROOH, the Am^* radicals are almost completely reduced to form AmH. In the case of the consecutive consumption of ArOH and ROOH, ArOH is the

only reducing agent. In the case of consecutive consumption, half of Am^* is reduced by ArOH and the other portion is reduced by ROOH. That is, ArOH and ROOH have the same reducing abilities with respect to Am^* independently of the ratio between the concentrations of ArOH and ROOH. This is a consequence of process coupling, for which the reversibility of reaction (I) is favorable. The Am^* radicals are the main initiators of ROOH participation in the transformations. The role of these radicals becomes more important in the course of the process.

2. RO_2^* radicals are generated in the $AmH + ArOH + ROOH$ system. This situation takes place in the decomposition of azo-bis-isobutyronitrile in solutions of AmH, ArOH, and ROOH saturated with O_2 .

Peroxide radicals intensively react with ArOH and especially with AmH. When the concentrations of ArOH and AmH are comparable, RO_2^* reacts mostly with AmH, and RO_2^* radicals are replaced by Am^* . The situation resembles that considered above, but ROOH participation in the process is not necessary for the generation of RO_2^* .

To describe the process when ArOH generates stable ArO^* radicals ($k_3 = 0$), the following reaction scheme can be proposed (the numerical values of constants refer to the DPA + TTBP + CHP system at 350 K):



Scheme 3.

The RO_2^* radicals are replaced by Am^* at early stages by reaction (–II). These in turn are replaced by ArO^* by reaction (I). Along with these reactions leading to the accumulation of ArO^* , reaction (V) consumes them together with RO_2^* , and this consumption is intensified during the reaction.

At the moment τ' , the rates of these processes become equal to each other: $v_{-2} = v_5 = 0.5v_i$. From this point on, half of the RO_2^* radicals generated in the system are replaced by ArO^* via the consecutive reactions (–II) and (I), and the others decay by reaction (V) together

with the ArO^* radicals. As this takes place, the concentration reaches the value $[ArO^*]_r = (k_{-2}/k_5)[AmH]$. At a specified set of rate constants and $1 \times 10^{-3} \text{ mol/l}$, $[ArO^*]_r = 1 \times 10^{-6} \text{ mol/l}$. The time τ' depends on v_i . At $v_i = 10^{-7} - 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$, $\tau' \approx [ArO^*]_r/v_i$ is 20–2 s, which is very short. The rate of reaction (–I) between ArO^* and AmH can be very high. For instance, at the specified concentration of AmH, $v_{-1} = k_{-1}[ArO^*]_r[AmH] \approx 2.5 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$. At $v_i \ll 2.5 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$, reactions (I) and (–I) at $t > \tau'$ can be considered quasiequilibrium. The concentration $[ArO^*]$ approaches $[ArO^*]_r$, and

the rate of radical decay v_{dec} asymptotically approaches v_i . The values of $[\text{ArO}^\cdot]_\tau$ and τ are small because pseudo-steady-state approximation is applicable to all radicals. Taking all of the above into account, scheme 3 leads to the following equalities:

$$v_{\text{cons}}^{\text{ArOH}} = v_{\text{accum}}^{\text{ROOH}} = v_{\text{accum}}^{\text{P}_3} = 0.5 v_i \text{ and } v_{\text{cons}}^{\text{AmH}} = 0. \quad (11)$$

Equalities (11) show that, when the RO_2^\cdot radicals are generated in the $\text{AmH} + \text{ArOH} + \text{ROOH}$ system, AmH is not consumed while ArOH is present, although the RO_2^\cdot radicals react with AmH much faster than with ArOH (recall the requirements to experimental conditions). Only the consumption of ArOH at the rate $0.5v_i$ and the accumulation of ROOH and P_3 at the same rates should be observed. The simultaneous consumption of ArOH and ROOH in the generation of Am^\cdot is independent of the presence of AmH . Similarly, the consecutive consumption of ArOH and AmH in the generation of RO_2^\cdot radicals is independent of the ROOH concentration.

No special study of RO_2^\cdot radical generation in the $\text{AmH} + \text{ArOH} + \text{ROOH}$ system in an inert medium was carried out. However, the fulfillment of equalities (11) was experimentally confirmed by the kinetics of antioxidant consumption in the oxidation of hydrocarbons RH in the presence of the $\text{AmH} + \text{ArOH}$ mixtures. Indeed, in the generation of RO_2^\cdot radicals in the mixture of a moderately oxidizable hydrocarbon with $\text{AmH} + \text{ArOH}$ saturated with oxygen, the oxidation of RH can be neglected to a first approximation because the RO_2^\cdot radicals immediately react with AmH and ArOH , which are strong antioxidants [17]. The Am^\cdot and ArO^\cdot radicals are less active than RO_2^\cdot in the reaction with RH . Under the experimental conditions, the hydrocarbon RH can conventionally be considered as an inert solvent in which reactions of scheme 3 occur. Then, according to equalities (11), during the induction period of the initiated oxidation of RH in the presence of the $\text{AmH} + \text{ArOH}$ mixture, ArOH is oxidized at the rate of $0.5v_i$ before AmH .

The phenomenon of the consecutive consumption of the ArOH and AmH antioxidant in the initiated oxidation of hydrocarbons has long been known [18].

Indeed, the inhibitors are consumed in the above-mentioned order at the rates close to those expected from equalities (11).

Let us formulate the requirements to the experimental conditions. Scheme 3 suggests that

$$[\text{ArO}^\cdot] = \frac{k_{-2}}{k_5} [\text{AmH}],$$

$$[\text{RO}_2^\cdot] = \frac{v_i}{2k_{-2}[\text{AmH}]}.$$

The pseudo-steady-state equation for Am^\cdot without account of (II), which has a very low rate, and the expressions for $[\text{ArO}^\cdot]$ and $[\text{RO}_2^\cdot]$ lead to the equation

$$[\text{Am}^\cdot] = \frac{k_5 v_i + 2k_{-1}k_{-2}[\text{AmH}]^2}{2k_1 k_5 [\text{ArOH}]}.$$

For the consecutive consumption of ArOH and AmH , reaction (V) should be the only reaction of radical decay. The inequality $v_3 \gg v_7$ or $k_5[\text{RO}_2^\cdot][\text{ArO}^\cdot] \gg k_7[\text{Am}^\cdot]^2$ is fulfilled if

$$[\text{ArOH}] \gg \left(\frac{2k_7}{v_i}\right)^{1/2} \frac{k_5 v_i + 2k_{-1}k_{-2}[\text{AmH}]^2}{2k_1 k_5}.$$

Using the set of constants for the $\text{DPA} + \text{TTBP} + \text{CHP}$ system, we find that at $v_i = 10^{-7}$ – $10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$ and $[\text{AmH}] = 10^{-3}$ – 10^{-4} mol/l , this inequality is fulfilled at $[\text{ArOH}] 6.2 \times 10^{-6} \text{ mol/l}$.

For the fulfillment of the requirement $v_5 \gg v_6$, it is necessary that

$$[\text{ArOH}] \gg \frac{k_6}{k_{-2}[\text{AmH}]} \frac{k_5 v_i + 2k_{-1}k_{-2}[\text{AmH}]^2}{2k_1 k_5}.$$

By varying v_i and $[\text{AmH}]$ within the limits mentioned above, the inequality is true if $[\text{ArOH}] \gg 1.1 \times 10^{-6} \text{ mol/l}$.

The following inequality is necessary for the condition $v_3 \gg v_3$:

$$k_3 \ll \frac{k_5^2 v_i}{2k_{-2}^2 [\text{AmH}]^2}.$$

Upon substituting the values $k_{-2} = 3.8 \times 10^5$ and $k_5 = 2 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$, we obtain

$v_i, \text{ mol l}^{-1} \text{ s}^{-1}$	1×10^{-7}		1×10^{-6}	
$[\text{AmH}], \text{ mol/l}$	1×10^{-4}	1×10^{-3}	1×10^{-4}	1×10^{-3}
$k_3, \text{ l mol}^{-1} \text{ s}^{-1}$	$\ll 1.4 \times 10^6$	$\ll 1.4 \times 10^4$	$\ll 1.4 \times 10^7$	$\ll 1.4 \times 10^5$

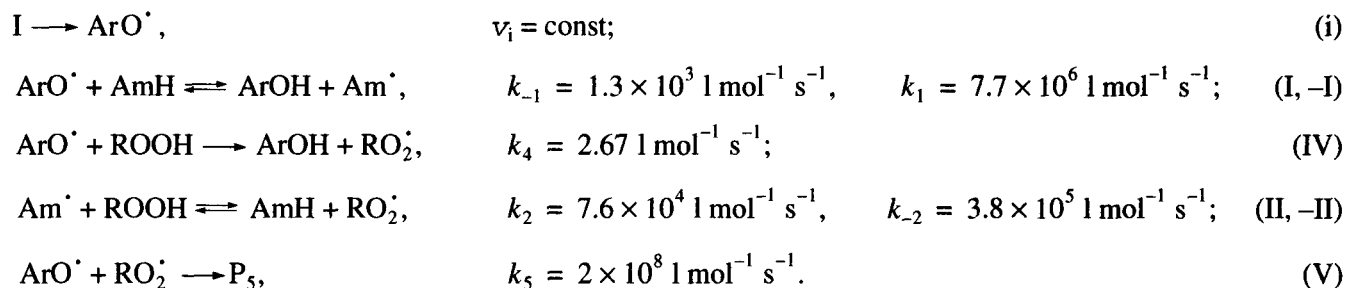
Figure 6 shows how the value of k_3 affects the curves of ArOH and AmH consumption. In the systems under

consideration, the Am^\cdot -radical-induced participation of ArOH in the overall process does not depend on the

numerical value of k_3 , but this constant determines the kinetics of ArOH and AmH consumption. As can be seen from Fig. 6, with an increase in k_3 from 0 to its maximal value, the time of ArOH consumption and the induction period of AmH consumption are almost doubled. The data shown in Fig. 6 were obtained in scheme 3 supplemented with nondetailed reactions (VI)–(VIII). The numerical values of rate constants are given in the text. In calculations, we assumed that the products of radical recombination do not participate in further transformations.

3. *ArO \cdot radicals are generated in the AmH + ArOH + ROOH system.* This case was not tested experimentally because no acceptable sources of phenoxyl radicals was found.

Based on previous findings, we may assume that when the concentrations of components are comparable and phenoxyl radicals ArO \cdot are stable ($k_3 = 0$), the following scheme can be used for the process description (the numerical values of rate constants refer to the DPA + TTBP + CHP system):



Scheme 4

Initially, the attack of ArO \cdot radicals is mostly directed toward AmH because $k_{-1} \gg k_4$. The Am \cdot radicals are formed at a rate close to v_i , and the situation begins to resemble the case of Am \cdot generation in the AmH + ArOH + ROOH system considered above. Because the values of k_{-1} and k_1 and the concentrations of AmH and ArOH are high, reactions (I) and (–I) are rapidly quasiequilibrated. An increase in the concentrations of ArO \cdot and Am \cdot result in inveigling ROOH into the overall process basically via the interaction with Am \cdot in reaction (II). The RO $_2\cdot$ radicals formed by reaction (II) decay in reaction (V). In the steady-state regime after the period τ' , half of the ArO \cdot radicals generated in the system are replaced by Am \cdot by reaction (–I), and the others recombine with RO $_2\cdot$ in reaction (V). The pseudo-steady-state concentrations of radicals are

$$\begin{aligned}
 [\text{Am}] &\approx \frac{v_i}{2k_2[\text{ROOH}]}, \\
 [\text{ArO}\cdot] &\approx \frac{v_i(k_1[\text{ArOH}] + k_2[\text{ROOH}])}{2k_{-1}k_2[\text{AmH}][\text{ROOH}]}, \\
 [\text{RO}_2\cdot] &\approx \frac{k_{-1}k_2[\text{AmH}][\text{ROOH}]}{k_5(k_1[\text{ArOH}] + k_2[\text{ROOH}])}.
 \end{aligned}$$

The concentration of ArO \cdot can be rather high. Thus, at $v_i = 1 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$ and concentrations of the components equal to $1 \times 10^{-3} \text{ mol/l}$, $[\text{ArO}\cdot] \approx 4 \times$

10^{-5} mol/l . The rate of reaction (IV) is $v_4 \approx 1 \times 10^{-7} \text{ mol l}^{-1} \text{ s}^{-1}$, which is $\sim 10\%$ of v_i . The time of transition to the pseudo-steady-state regime largely depends on the concentration of phenol; at $[\text{ArOH}]_0 = 1 \times 10^{-3} \text{ mol/l}$, $\tau' \approx [\text{ArO}\cdot]/v_i \approx 40 \text{ s}$.

Within the framework of the steady-state approximation with respect to the concentrations of all inter-

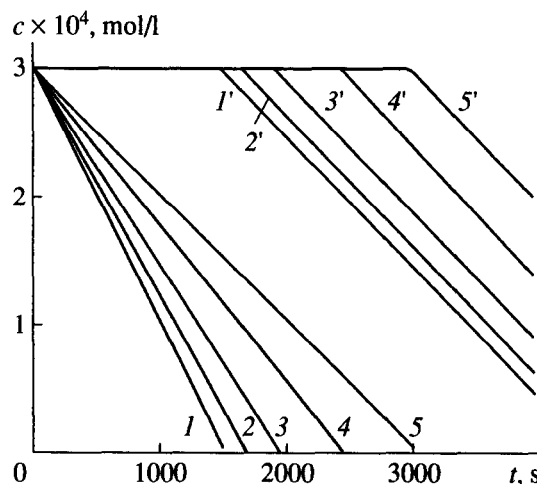


Fig. 6. Transformation of kinetic curves of (1–5) ArOH and (1'–5') AmH consumption depending on the stability of phenoxyl ArO \cdot radicals, that is, on $2k_3$, $\text{l mol}^{-1} \text{ s}^{-1}$: (1, 1') 4×10^9 , (2, 2') 4×10^7 , (3, 3') 4×10^6 , (4, 4') 4×10^5 , and (5, 5') 0. The rate of RO $_2\cdot$ radical generation is $v_{\text{RO}_2\cdot} = 2 \times 10^{-7} \text{ mol l}^{-1} \text{ s}^{-1}$ and $[\text{ArOH}]_0 = [\text{AmH}]_0 = 3 \times 10^{-4} \text{ mol/l}$.

mediates from scheme 4, we have

$$v_{\text{cons}}^{\text{ROOH}} = v_{\text{accum}}^{\text{ArOH}} = v_{\text{accum}}^{\text{P}_5} = 0.5 v_i \text{ and } v_{\text{cons}}^{\text{AmH}} = 0. \quad (12)$$

According to (12), in the generation of stable phenoxyl radicals in the AmH + ArOH + ROOH system, only ROOH is consumed at the rate of $0.5 v_i$. Phenol ArOH and quinolide peroxides P_5 are accumulated at the same rate. Amine AmH is not to be consumed while ROOH is present in the system, although the rate constant k_{-1} of the reaction between ArO^\bullet and AmH is by almost three orders of magnitude higher than the rate constant k_4 of the reaction between ArO^\bullet and ROOH. The same regularities should be observed independently of the concentrations of reactants and v_i . From the formal standpoint, the reducing agent for half of the ArO^\bullet radicals is ROOH rather than AmH.

The most important condition for relations (12) is the stability of the ArO^\bullet radicals ($k_3 \rightarrow 0$). The requirement of $v_5 \gg v_3$ leads to the following inequality:

$$k_3 \ll \frac{2}{v_i} \left(\frac{k_{-1} k_2 [\text{AmH}] [\text{ROOH}]}{k_1 [\text{ArOH}] + k_2 [\text{ROOH}]} \right)^2.$$

At $[\text{ArOH}] = [\text{AmH}] = [\text{ROOH}] = 1 \times 10^{-3} \text{ mol/l}$ and $v_i = 1 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$, it is necessary that $k_3 \ll 3.2 \times 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$.

Although these conclusions have not yet found experimental support, the experimentally observed catalytic acceleration of the reaction of the stable phenoxyl radicals ArO^\bullet with the hydroperoxide ROOH under the action of AmH [19] is indirect evidence.

Within the framework of ideas developed in this work, this phenomenon can be predicted. Let us assume that we have the AmH + ArOH + ROOH + ArO^\bullet system for the formation of which the ArO^\bullet should be added to the three-component AmH + ArOH + ROOH system. To describe the processes in this system, we can use scheme 4 without steps (i) and (–II) (because $k_5 [\text{ArO}^\bullet] \gg k_{-2} [\text{AmH}]$).

When adding the ArO^\bullet radical to the AmH + ArOH + ROOH system, reactions (–I) and (I) almost immediately transfer to the quasiequilibrium mode. The characteristic time is

$$\tau' = \left\{ k_{-1} \left([\text{ArO}^\bullet]_\infty + [\text{AmH}]_\infty \right) + k_1 \left([\text{ArOH}]_\infty + [\text{Am}^\bullet]_\infty \right) \right\}^{-1} \approx (k_1 [\text{ArOH}]_0)^{-1},$$

which is equal to only 10^{-3} – 10^{-4} s at $[\text{ArOH}]_0 \sim 10^{-4}$ – 10^{-3} mol/l .

Assuming the steady-state concentrations for all radicals, we have

$$v_{\text{cons}}^{\text{ArH}} = 0, \quad (13)$$

$$v_{\text{cons}}^{\text{ROOH}} = v_{\text{accum}}^{\text{ArOH}} = v_{\text{accum}}^{\text{P}_5} = 0.5 v_{\text{cons}}^{\text{ArO}^\bullet}.$$

ROOH participates in the process under the action of the Am^\bullet and ArO^\bullet radicals, and

$$v_{\text{cons}}^{\text{ArO}^\bullet} = 2 v_{\text{cons}}^{\text{ROOH}} = 2 k_2 [\text{Am}^\bullet] [\text{ROOH}] + 2 k_4 [\text{ArO}^\bullet] [\text{ROOH}]. \quad (14)$$

In the absence of AmH, that is in the new three-component system ArOH + ROOH + ArO^\bullet , phenoxyl radicals are slowly consumed by reactions (IV) and (V), and step (IV) is rate-determining. Therefore,

$$v_{\text{cons}}^{\text{ROOH}} = v_{\text{accum}}^{\text{ArOH}} = v_{\text{accum}}^{\text{P}_5} = 0.5 v_{\text{cons}}^{\text{ArO}^\bullet}, \quad (13a)$$

and the rate of the process is

$$v_{\text{cons}}^{\text{ArO}^\bullet} = 2 v_{\text{cons}}^{\text{ROOH}} = 2 k_4 [\text{ArO}^\bullet] [\text{ROOH}]. \quad (14a)$$

If one adds AmH to the three-component ArOH + ROOH + ArO^\bullet system, the four-component catalytic system AmH + ArOH + ROOH + ArO^\bullet is created for which, as noted above, expressions (13) and (14) are true. Comparison of (13) and (13a) shows that the composition of products does not change when AmH is added. AmH is not consumed during the reaction. Comparison of (14) and (14a) suggests that the reaction rate increases in the presence of AmH by a value of v_{cat} (the rate of a catalytic component):

$$v_\Sigma = v_{\text{noncat}} + v_{\text{cat}} = 2 k_4 [\text{ArO}^\bullet] [\text{ROOH}] + 2 K_{-1} k_2 \frac{[\text{AmH}]}{[\text{ArOH}]} [\text{ArO}^\bullet] [\text{ROOH}]. \quad (15)$$

Therefore, AmH is a catalyst for the reaction of ArO^\bullet with ROOH, *quod erat demonstrandum*.

Analogous consideration of the hypothetical system consisting of AmH, ArOH, ROOH, and a stable peroxy radical RO_2^\bullet led us to the conclusion that the catalytic effect of AmH on the reaction of RO_2^\bullet with ArOH will be very small because of the fast irreversible decay of Am^\bullet by reactions (VI) and (VII) of recombination with RO_2^\bullet and Am^\bullet .

As we see, the main kinetic feature of the reactions considered in this article is that they are coupled. In all cases, the least active (with respect to the radicals generated in the systems) of the initial reactants is involved in the coupled transformations due to the Am^\bullet radi-

cals. Because of coupling, a change in the form of generated radicals leads to serious changes in the role of separate elementary steps. Therefore, in one case, a step with a high rate constant can be neglected, but in another case, this step should be taken into account to describe the kinetics. For instance, reaction (–II) plays an important role in the generation of RO_2^\cdot radicals with AmH, and reaction (II) of Am^\cdot with ROOH is unimportant. If the Am^\cdot radicals are generated, reaction (–II) becomes unimportant and reaction (II) becomes important.

The above kinetic analysis allowed us to determine the main kinetic regularities in the $\text{AmH} + \text{ArOH} + \text{ROOH}$ systems under different conditions, including those not studied experimentally. Note that available experimental data agree well with the conclusions drawn in this work. Three phenomena, which seemed independent before this analysis ((1) simultaneous phenol and hydroperoxide consumption during the generation of amyl radicals; (2) consecutive consumption of phenol and amine as antioxidants in the initiated oxidation of hydrocarbons; and (3) catalytic acceleration of phenoxyl radical reaction with hydroperoxide by aromatic amines) can now be considered within the framework of a unified model reflecting the main features of the processes in the $\text{AmH} + \text{ArOH} + \text{ROOH}$ systems when the corresponding radicals are generated or added to these systems.

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