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The Role of Labile Products of Styrene Epoxide Conversion in Its Oxidation in Polar Acid Medium

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Abstract—Phenylacetaldehyde (PAA) and benzyl alcohol (BAl) are formed in oxygen atmosphere from styrene epoxide in the presence of *p*- toluenesulfonic acid (TSA) in a solution of 90 vol % *tert*-butanol with 10 vol % chlorobenzene (BUC). The ratio of the propagation (k_2) to the termination (k_6) rate constants has been measured to be $k_2/\sqrt{k_6} = 8.6 \times \times 10^{-3}$ (L/(mol s))$^{1/2}$ at 343 K by the method of initiated oxidation of PAA in a BUC solution. One of the products of the radical chain PAA oxidation is BA. This reaction leads to BAl accumulation during the conjugated oxidation of PAA with the epoxide in an acid alcohol medium. The contribution of BAl formed to the oxidation is almost unnoticeable.

Keywords: styrene epoxide, *p*-toluenesulfonic acid, phenylacetaldehyde, benzaldehyde, benzyl alcohol, oxidation by molecular oxygen

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Having once revealed the competition of heterolysis and homolysis in the complex process of styrene epoxide (SE) conversion in a polar medium in the presence of acid, we began to distinguish between conventionally binary and ternary systems [1]. The ability of the SE + toluenesulfonic acid (TSA) binary system (BS) in an isopropanol medium or in the presence of styrene in a BUC solution to absorb molecular oxygen was established by studying the SE + TSA + substrate ternary system (TS), where the substrate is a compound easily oxidized via the radical chain mechanism [1]. The specific feature of $BS_{(SE + TSA)}$ oxidation is that the reactant epoxide in the absence of acid is very stable to radical chain oxidation even at 413 K [2]. In an acidified alcohol or acetonitrile solution of the epoxide, oxygen absorption proceeds spontaneously without extrinsic initiation and is accompanied by accumulation of benzaldehyde (BA) and hydrogen peroxide (H_2O_2) in the oxidation product (oxidate). It was shown that benzaldehyde does not increase the rated of oxidation under the operating conditions of BS oxidation [3].

An improvement in the chromatographic procedures used in this work allowed us to identify and quantify another two labile organic compounds phenylacetaldehyde (PAA) and BAl in BS oxidates. The phenomenon of PAA formation in acid alcohol solutions is not new [4]; however, no information about BA formation under the same conditions has been reported. The easy oxidizability of BAl to yield BA and H_2O_2 is known [5, 6]. The purpose of the work was to investigate the contribution of this reaction to oxygen uptake during the oxidation of $BS_{(SE + TSA)}$.

EXPERIMENTAL

The BUC solvent blend composed of 90 vol % *tert*-butanol and 10 vol % chlorobenzene was prepared from the analytical grade alcohol and chlorobenzene purified according to the standard sulfuric acid procedure. A common glass bubbling cell with a reflux condenser was used for experiments. The samples were analyzed for organic compounds by techniques of liquid (LC) and gas–liquid chromatography (GLC), and the hydrogen peroxide concentration was determined by iodometry. The rates of oxygen uptake were determined according to the previously developed procedure on a manometric setup at a constant O_2 pressure with the use of fused silica reactors of 7–15 mL capacity [1, 7]. Deviations from the standard sequence of operations in special sets of experimental runs a and b (Fig. 2) are given accordingly in the text.

Benzyl alcohol was identified with the use of a standard in modes *a*, *b*, and *c* of GLC analysis: (*a*) a steel column of 1200 × 3 mm, 15% polyethylene glycol adipate on Chromaton N-AW, analysis temperature423 K; (*b*) a glass column of 1200 × 3 mm, 15% Silicon DC-550 on Inerton, 373K; and (*c*) a steel column of 1200 × 3 mm, 15% Carbowax-6000 on Chromaton N-AW, 433K. Routine analyses of the oxidates for BA during the study of kinetics were performed in the *c* mode. The PAA content in oxidates was determined

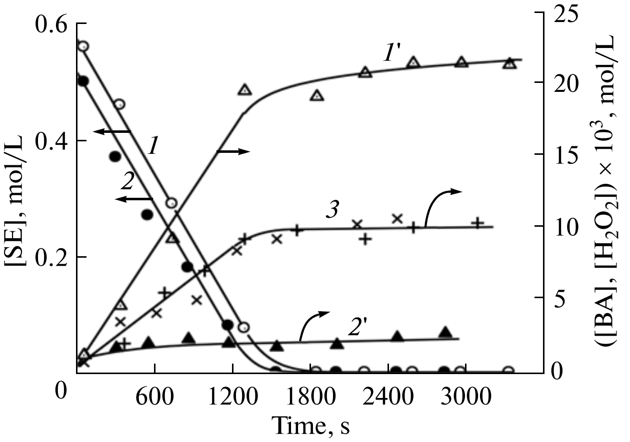


Fig. 1. Rate curves for styrene epoxide consumption of in (*1*) an oxygen and (*2*) an argon atmosphere and (*1'* and *2'*) the corresponding benzaldehyde buildup curves . Curve *3* to the kinetics of H_2O_2 buildup in two identical oxidation runs. $[SE]_0 = 0.54$, $[TSA] = 0.013$ mol/L, BUC, 343 K.

by high-performance liquid chromatography (HPLC). The aldehyde was preliminary identified by GLC in the *c* mode and LC on a Separon SGX-CN column (*n*-heptane + 0.1 vol.% isopropanol, UV-254).

RESULTS AND DISCUSSION

Figure 1 shows SE consumption and BA and H_2O_2 buildup rate curves. Neither the aldehyde nor hydrogen peroxide is formed in an argon atmosphere, with the epoxide being consumed at the same rate as in an oxygen atmosphere. As SE is consumed in the O_2 atmosphere, the BA and H_2O_2 buildup ceases. But the absorption of oxygen does not cease, although it slows down (Fig. 2). The data in Figs. 2a and 2b show a complex time dependence of oxygen uptake by SE + TSA system. Curve *1* in Fig. 2a illustrates this situation: after SE exhaustion by the 15th min, the O_2 uptake curve bends and the oxidation rate decreases by a factor of ~3 times, but it does not fall to zero.

Let us explain the special technique used from running the experiments relevant to Fig. 2a. The reactor of the manometric setup prepared for the experiment and charged with 5 mL of solution of 0.013 mol/L TSA in BUC and 0.27 mol/L (0.15 mL) of pure SE was purged with oxygen to displace air; the reactor was mounted into setup and placed in a thermostat; and the initial rate of oxidation (V_0) was measured after reactor heating (8 min). After the break on the rate curve with a drop in of uptake rate because of total consumption of SE, the measurement of the final rate of oxygen uptake (V_f) was continued (Fig. 2a, curve *1*). After completion of the run, the reactor was withdrawn, another 0.15 mL of SE was introduced into oxidate, the system was blown with oxygen, and V_0 and V_f were measured again (Fig. 2a, curve *2*). Similarly, having repeated twice the sequence of operations: introducing 0.15 mL of SE, purging the reactor with O_2, and measuring V_0 and V_f, we obtained curves *3a* and *4a*. A comparison of curves *1–4* in Fig. 2a shows that the value of V_0 in this set slightly changes, increasing from run to run by ~3–4 %, whereas the values of V_f unambiguously increase with each repeated oxygen uptake (compare the slopes of the end parts of curves *1–4* in Fig. 2a).

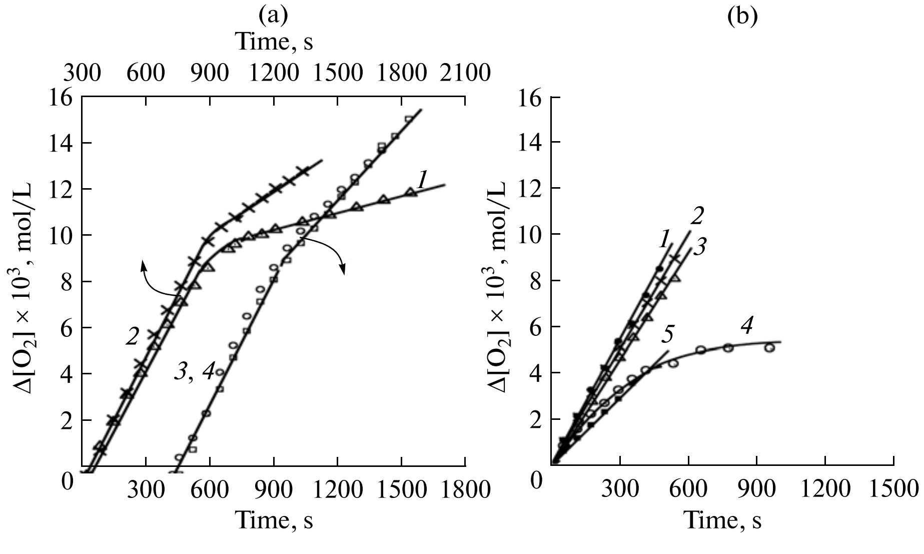


Fig. 2. Oxygen uptake rate curves: (a) (*1–4*) set of experiments on the oxidation of $BS_{(SE + TSA)}$ with the repeated introduction of 0.27 mol/L of SE and purging with O_2 at the end of the runs 1–3 (curves *1*, *2* and *3*, *4* are conditionally spaced by the *t* axis). $[SE]_0 = 0.27$, $[TSA] = 0.013$ mol/L, BUC, 343 K; (b) (*1–4*) long-term experiment without refreshing the oxygen atmosphere (conditional division into four portions through the run), (*5*) oxidation after run 4 and blowing out with O_2. $[SE]_0 = 1.05$, $[TSA] = 0.013$ mol/L, BUC, 343 K.

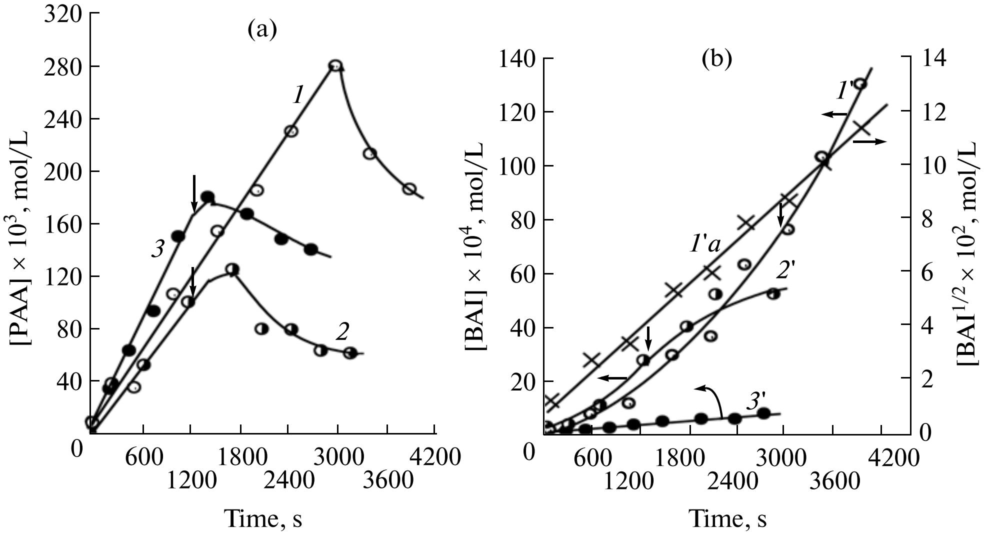


Fig. 3. (*1*–*3*) Phenylacetaldehyde and (*1'*–*3'*) benzyl alcohol buildup curves in the $BS_{(SE + TSA)}$ system in a BUC solution; [TSA] = 0.013 mol/L, 343 K: (*1*, *1'*) oxygen, $[SE]_0 = 1.16$ mol/L; (*1'a*) approximation of curve *1'* in the $[BAl]^{1/2}$–*t* coordinates; (*2*, *2'*) oxygen, $[SE]_0 = 0.58$ mol/L; (*3*, *3'*) argon, $[SE]_0 = 0.58$ mol/L. The vertical arrows mark the concentrations of the compounds at the time of complete consumption of styrene epoxide.

Rate curves *1*–*5* of Fig. 2b were obtained by altering the experimental procedure. The initial solution from the beginning contained 0.6 mL (1.05 mol/L) of SE and 0.013 mol/L of TSA. After the first measurement of the uptake rate (curve *1*, Fig. 2b), without demounting, cooling, and oxygen-purging the reactor, mercury in the measuring burette was brought down to the initial level by filling it with oxygen; and the measurements were repeated three times in the same way. Resulting rate curves *1*–*4* (in fact, these are four pieces cut from the rate curve of the long run) are set in Fig. 2b to the origin of coordinates for clarity. In the sequence of curves *1*–*4* in Fig. 2b, V_0 does not increase, unlike the case of runs *1*–*4* illustrated in Fig. 2a, rather, it drops during the long experimental run. The uptake ceases by the to 40th min; and the epoxide in solution is nearly consumed by that time. After completion of run *4* (Fig. 2b), the reactor was demounted, purged with oxygen flow, and mounted back in the setup and the rate of resumed O_2 uptake WAS measured (Fig. 2b, curve *5*). The final rate V_f measured as the slope of curve *5* in Fig. 2b was close to the value of V_f found for curve *4* in Fig. 2a. The data in Figs. 2a and 2b lead to two conclusions, one is that a certain labile product (products) is formed by oxidation of $BS_{(SE + TSA)}$ and oxidation of this product in the solution slightly increases V_0 and significantly increases V_f (Fig. 2a, curves *1*–*4*), and the other is that a heavy inert gas that terminate the absorption of O_2 uptake is accumulates during the oxidation of the secondary products of SE conversion in the reactor of the manometric setup. The elimination of the "blanket" of this gas by purging the reactor with an O_2 flow resumes the oxygen uptake (Fig. 2b, curve *5*). The additional $BS_{(SE + TSA)}$ oxidation runs in the cell equipped with a$Ba(OH)_2$ solution trap at the exit of the bubbling gas confirmed the formation of carbon dioxide. To determine the source of CO_2 during BS oxidation and reveal the cause of the growth in V_f rise in the runs (Fig. 2a, curves *1*–*4*), the accumulation of benzyl alcohol (BAl) and phenylacetaldehyde (PAA) was studied and the possibility of their participation in oxygen absorption during the oxidation of $BS_{(SE + TSA)}$ was assessed.

The BAl and PAA buildup rate curves during the conversion of $BS_{(SE + TSA)}$ are exemplified in Fig. 3. Phenylacetaldehyde is formed and in both oxygen and argon at comparable rates; i.e., PAA is not a specific product of the oxidative conversion of the epoxide. It is not inconceivable that a slightly higher rate of PAA buildup and a somewhat lower rate of its consumption after reaching a maximum in argon (Fig. 3, curve *3*) in comparison with the same parameters of curves *1* and *2* in Fig. 3 are due to a high oxidizability of PAA and its noticeable consumption in the oxygen atmosphere.

Benzyl alcohol accumulates at approximately an order of magnitude lower rate in the argon atmosphere than during oxidation, as follows from comparison of curves *1'*, *2'*, and *3'* in Fig. 3. It is cannot be ruled out that its buildup in the inert atmosphere is simply a consequence of the presence of impurity oxygen in the argon used. The BAl buildup curve in oxygen is S-shaped (Fig. 3, curve *2'*), the buildup continues for a while after the complete consumption of SE (Fig. 3; curves *1'*, *2'*). The acceleration of BAl buildup is especially clearly seen in the long run with a high initial SE concentration (Fig. 3, curve *1'*): rate curve *1'* is linearized in the $\sqrt{[BAl]} - t$ coordinates, a transform that is equivalent to linearity in the $[BAl] - t^2$ coordinates and will be commented below. The PAA to BAl concentration ratio for curves *1*, *2* and *1'*, *2'* in Fig. 3 at the time of the complete consumption of SE in these runs (marked by vertical arrows) is [PAA]/[BAl] ≈ 30.

It is possible to estimate the relative contributions of these labile compounds to the O_2 uptake in their joint oxidation with $BS_{(SE + TSA)}$ if the ratio between PAA and BAl oxidizabilities is known. In a first approximation, the values of $(k_2/\sqrt{k_6})_{PAA}$ and $(k_2/\sqrt{k_6})_{BAl}$ can be used for this purpose, where k_2 is the propagation rate constant and k_6 is the termination rate constant of the radical chain oxidation of the relevant individual compound. Experiments on the radical chain oxidation of benzyl alcohol and PAA in BUC solutions were performed in the presence of the initiator azobisisobutyronitrile (AIBN). The classical expression of the rate of radical chain oxidation in the case of quadratic termination is $V = (k_2/\sqrt{k_6}))$ [RH] $\sqrt{V_i}$, RH is PAA or BAl in our case. The rate of initiation is $V_i = k_i$[AIBN], and the initiation rate constant is $k_{iAIBN} = 4 \times 10^{-5}$ s^{-1} (343 K) [8]. The data obtained by measuring the rates of the radical chain oxidation of PAA and BAl in the presence of AIBN (Fig. 4) suggest the chain character of oxidation of both substrates with the quadratic chain termination: the Bal oxidation rate is proportional to $\sqrt{V_i}$ and the chain lengths are 15–38 units. The same is true for the oxidation of PAA, except that $(k_2/\sqrt{k_6})_{PAA})$ was calculated by the method and equation for the case of mixed initiation [9], since the aldehyde dissolved in BUC was oxidized at a significant rate without AIBN. The chain length in the runs with PAA ranged from 5 to 11 units. The characteristic feature of the experiments on the PAA oxidation initiated by AIBN was a fast drop in V_{O_2} during the run until the complete cessation of O_2 absorption. The aforementioned method of reactor purging with O_2 resumed the absorption. A separate run in the bubbling reactor with $Ba(OH)_2$ solution at the exit of the gas showed that the AIBN-initiated radical chain oxidation of individual PAA leads to the formation of CO_2. Therefore, the values of V_{O_2} for curve *1* (Fig. 4) were calculated from the slopes of the initial portions of the PAA oxidation rate curves. The $k_2/\sqrt{k_6}$ ratios calculated from the slope of curves *1* and *2* in Fig. 4 are $(k_2/\sqrt{k_6})_{PAA} = 8.6 \times 10^{-3}$ (L/(mol s))$^{1/2}$ and $(k_2/\sqrt{k_6})_{BAl} = 2.0 \times 10^{-3}$ (L/(mol s))$^{1/2}$, respectively. The above value of $(k_2/\sqrt{k_6})_{BAl}$ is ~1.7 times below that reported in [5]. It is likely that this difference is simply due to different values of k_{iAIBN} used in our study [8] and by Opeida et al. [5] as the basis for calculation of $k_2/\sqrt{k_6}$. The value of k_{iAIBN} was not reported in [5], but even if we take the least of the two quantities, which is our value $(k_2/\sqrt{k_6})_{BAl} = 2.0 \times 10^{-3}$, and compare it with the parameter for the secondary alcohol isopropanol $(k_2/\sqrt{k_6})_{IPA} = 6.4 \times 10^{-4}$ (L/(mol s))$^{1/2}$ [10], an interesting detail is revealed: primary benzyl alcohol is oxidized three times faster than the secondary alcohol isopropanol. The neighborhood of the phenyl ring of the alcohol with the C atom on which the C–H bond is subjected to radical attack has an effect. In turn, the reactivity of PAA is two to four times higher than that of BAl according to the $k_2/\sqrt{k_6}$ values presented above. From the data on the concentration ratio of PAA and BAl accumulated in the $BS_{(SE + TSA)}$ oxidate with allowance for the of oxidizability PAA, which is two times that of Bal, it follows that the relative contribution of PAA to O_2 uptake during BS oxidation is ~60 times that of benzyl alcohol, and the latter can be neglected. Direct experiments on the oxidation of $TS_{(BAl + SE + TSA)}$ confirmed the validity of this conclusion. The introduction of benzyl alcohol into oxidized $BS_{(SE + TSA)}$ at the beginning of the run to have $[BAl]_0 =$ 0.15 mol/L, which is approximately 30 times the actual concentration of BAl produced during oxidation, did not increase the oxygen uptake and benzaldehyde buildup rates and did not change significantly the BAl buildup kinetics Δ[BAl] = *f*(*t*), where Δ[BAl] = $[BAl]_t - [BAl]_0$. Hence, we come to the reasonable conclusion that co-oxidation of BAl with $BS_{(SE + TSA)}$ is not the prime cause of the hydrogen peroxide and benzaldehyde buildup (Fig. 1) and the increase in V_f in runs 1–4 (Fig. 2a). Benzyl alcohol accumulating dur-

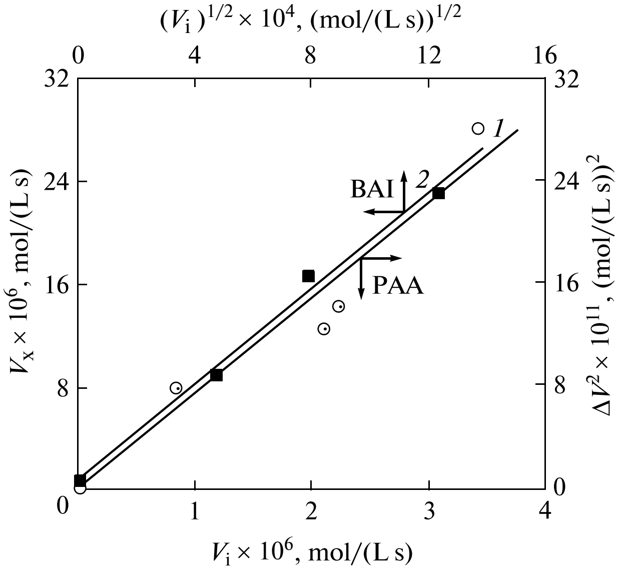


Fig. 4. Dependences of the oxidation rates on the rates of initiation with AIBN. Lines *1* and *2* refer to calculation of $k_2/\sqrt{k_6}$ at 343 K for phenylacetaldehyde in BUC solution with [PAA] = 0.99 mol/L and benzyl alcohol with [BAl] = 9.64 mol/L, respectively.

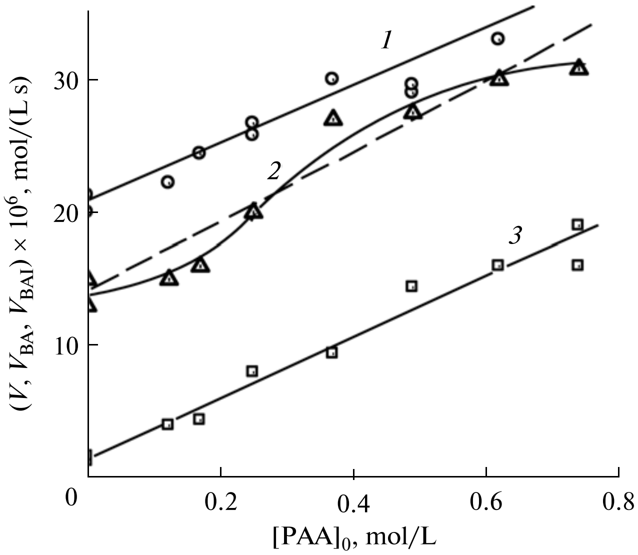


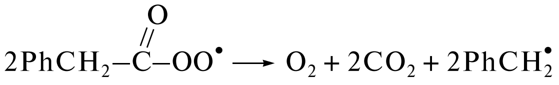
Fig. 5. Initial rates of (*1*) oxygen uptake and (*2*) benzaldehyde and (*3*) benzyl alcohol buildup depending on the initial phenylacetaldehyde concentration in the PAA + SE + TSA ternary system. $[SE]_0 = 0.44$, $[TSA] = 0.13$, BUC, 343 K.

ing BS oxidation is almost inert in oxidation. But PAA actively takes part in the joint oxidation of BS. The dependence plotted in Fig. 5 (curve *1*) clearly shows that the introduction of PAA into BS increases the oxygen uptake rate. In other words, PAA, SE, and TSA form a ternary system in their combined solution [1]. Note that the range of variation in $[PAA]_0$ in the runs relevant to Fig. 5 covers the actual interval of PAA buildup during SE oxidation: judging by curves *1*, *2*, and *3* in Fig. 3, $[PAA]_{max}$ values are 0.28, 0.12, and 0.17 mol/L, respectively. Of the data in Fig. 5, plot *3* is the most informative: straight line *3* curve emanates almost from the origin; i.e., $d[BAl]/dt = a[PAA]$. Consequently, the source of BAl in $BS_{(SE + TSA)}$ is accumulating PAA. Thus, the proportionality $[BAl]_t \sim t^2$ becomes understandable. Indeed, if $d[BAl]/dt = a[PAA]$ (Fig. 5, curve *3*) and $[PAA] = bt$ (linear time dependence of PAA buildup is obeyed until the complete consumption of SE (Fig. 3, curves *1*–*3*)), then $d[BAl]/dt = abt$ and $[BAl] = abt^2/2$ or $[BAl]^{1/2} = (\sqrt{ab/2})t$, which is the case observed in the experiment, see curve *1'a* in Fig. 3 (*a* and *b* are effective rate constants numerically equal to the slopes of curve *3* in Fig. 5 and curve *2'* in Fig. 3, respectively, $a = 2.5 \times 10^{-5}\,s^{-1}$, $b = 7.5 \times 10^{-5}$ mol $L^{-1}\,s^{-1}$). Now it is clear why the buildup of BAl continues after the complete consumption of the epoxide (see *1'*, *2'* in Fig. 3): the source of BAl is the oxidation of PAA, which is slowly consumed after the complete exhaustion of SE (Fig. 3, curves *1*– *3*).

Phenylacetaldehyde accumulates in the binary system at approximately an order of magnitude higher rate than BAl and is oxidized in the $TS_{(SE + TSA + PAA)}$ ternary system to yield BA, BAl, and carbon dioxide. However the pattern of the dependence of the BA buildup rate on $[PAA]_0$ (Fig. 5, curve *2*) suggests the presence of a route of SE oxidation immediately into BA.

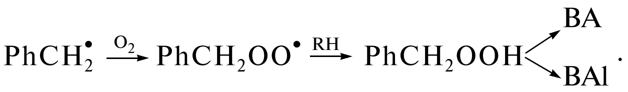
From the results of this study, it unambiguously follows that oxidation of benzyl alcohol does not play a significant role in the oxidation of the binary system. The source of H_2O_2 produced during oxidation of BS is unknown.

Finally, let us say a few words about the nature of formation of BAl, BA, and CO_2 from PAA. It is obvious that these products of radical chain oxidation of PAA in the $TS_{(PAA + SE + TSA)}$ system involving the formation of the phenylacetyl peroxide radical as the chain carrier, its possible fragmentation



$$2PhCH_2{-}\overset{\overset{\displaystyle O}{/\!/}}{C}{-}OO^{\bullet} \longrightarrow O_2 + 2CO_2 + 2PhCH_2^{\bullet}$$

and the subsequent conversion of the benzyl radical according to the conventional scheme:



$$PhCH_2^{\bullet} \xrightarrow{O_2} PhCH_2OO^{\bullet} \xrightarrow{RH} PhCH_2OOH \begin{matrix} \nearrow BA \\ \searrow BAl \end{matrix}.$$

An important issue of this aspect of the study for us is that the test for H_2O_2 [11] has shown no formation of hydrogen peroxide during the initiated oxidation of PAA in a BUC solution.

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