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Mild Oxidation of Styrene Epoxide in the Presence of Trace Perchloric Acid

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Abstract—Perchloric acid in a *tert*-butanol solution with 10 vol % chlorobenzene exhibits an almost three orders of magnitude higher activity in comparison with *para*-toluenesulfonic acid (TSA) as a catalyst for the parallel styrene epoxide (SE) heterolysis and homolysis processes. There is a substantial difference between the reactions mediated by these catalysts: rate curves for the overall consumption in the presence of perchloric acid (SE heterolysis) yield straight lines in the log [SE]–time coordinates, but the first-order rate constant drops with an increase in [SE]. However, the oxygen uptake rate increases with [SE]. In the case of TSA, neither overall consumption nor oxidation rate depended on [SE] at [SE] > [TSA]; i.e., the reaction was zero-order in SE.

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This work is in continuation of the investigation into the mechanism of conversion of phenyl-substituted ethylene oxides in the presence of acids. Earlier, it has been shown that styrene epoxide (SE) is decomposed mainly in the heterolytic mode by the action of *para*-toluenesulfonic acid (TSA), but there is a simultaneous (parallel to heterolysis) generation of transient species reactive toward oxygen [1–3]. Their existence is confirmed by the ability of TSA to catalyze SE oxidation with oxygen at a low temperature (343 K). Generally, the radical chain oxidation of SE proceeds quite slowly even at a 60 K higher temperature in the presence of a radical initiator [4]. A detailed kinetic study has shown the parallel occurrence of the heterolytic and homolytic processes of SE conversion in the presence of TSA, the rates of both processes are proportional to [TSA] and do not depend on [SE] at [SE] > [TSA]; i.e., they are first-order in acid and zero-order in SE. The study of SE transformation in the presence of $HClO_4$ has also revealed that, like TSA and sulfuric acid [2, 5], perchloric acid (PCA) mediates both heterolysis and oxygen absorption in a BUCH (90% *tert*-butanol and 10% chlorobenzene by volume) solution; however, the transformation reaction in the presence of $HClO_4$ is kinetically quite different from that in the presence of sulfonic acids.

EXPERIMENTAL

The experimental procedures used were similar to those described in [1–3]. The absorption of oxygen was measured on a manometric unit, and the rates of overall SE consumption and benzaldehyde (BA) buildup in a bubble reactor were measured using liquid chromatography. The solvents were distilled *tert*-butanol and chlorobenzene. The catalyst, aqueous perchloric acid with a concentration of ~13 mol/l, was prepared from commercial technical-grade $HClO_4$ by double distillation in a vacuum. Styrene epoxide purchased from Aldrich had a base substance content of 97% and was used without additional purification.

RESULTS AND DISCUSSION

Figure 1 shows the oxygen uptake rate curves for acidified solutions of SE in the reactor of the manometric unit. There are two distinct differences from the earlier data obtained in experiments with TSA. First, the activity of $HClO_4$ in oxidation is approximately three orders of magnitude higher than that of TSA. Second, there is no induction period in the oxidation reaction with $HClO_4$, which was detectable in the experiments with the SE–TSA binary system at a low TSA concentration, was clearly distinguished in experiments with H_2SO_4, and disappeared when a catalytic amount of a copper salt was introduced into the joint SE and H_2SO_4 solution [5]. Figure 2 depicts the dependence of the initial oxidation rate on [$HClO_4$] and the initial epoxide concentration $[SE]_0$. We again observe a noticeable contrast with the earlier data. Oxygen uptake in the SE + TSA and SE + H_2SO_4 binary systems was described by a simple kinetic equation for the oxidation rate $v = k[SE]^0 [acid]^1$ at [SE] > [acid] [2]. From Fig. 2, it is seen that the reaction order n with respect to $HClO_4$ is greater than unity; calculation by the data points in curve *1* of Fig. 2 gives a value of $n \approx 1.4 \pm 0.15$. We can suggest the cause of the

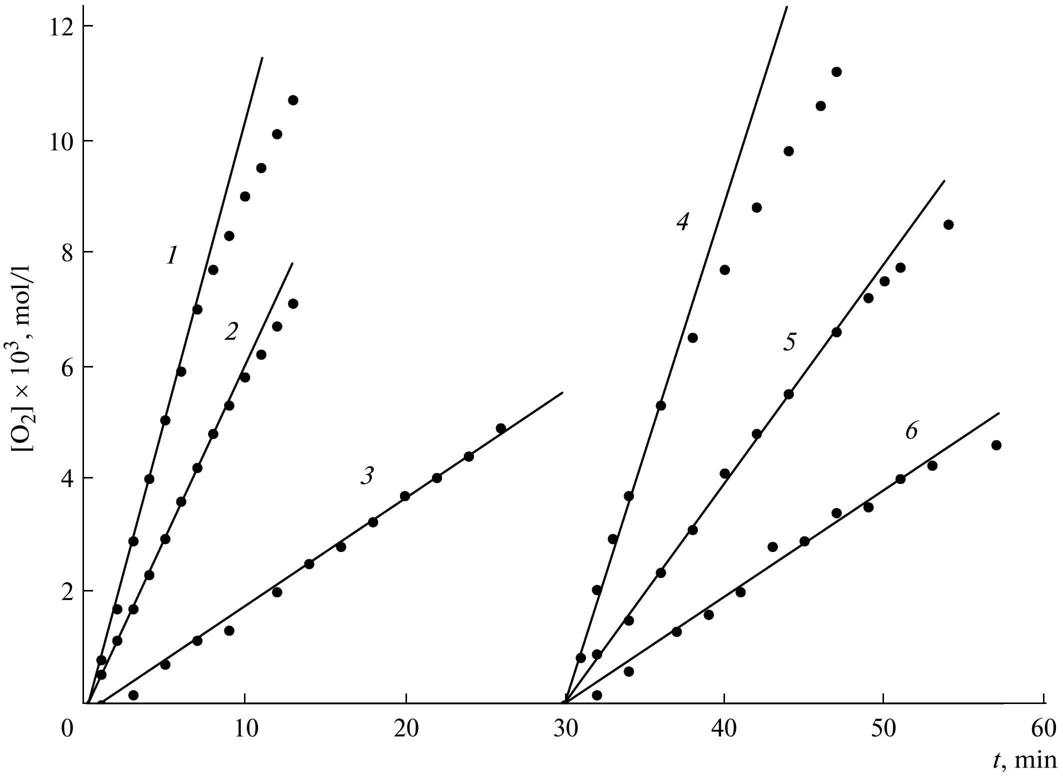

Fig. 1. Rate curves of oxygen uptake in BUCH at 343 K: (*1–3*) $[SE]_0 = 0.87$ mol/l and $[HClO_4] = 2.8 \times 10^{-5}$, 2.1×10^{-5}, and 1.05×10^{-5} mol/l, respectively; (*4–6*) $[HClO_4] = 2.1 \times 10^{-5}$ mol/l and $[SE]_0 = 1.74$, 0.44, and 0.21 mol/l, respectively; the beginning of measurements (0 min) refers to the 30th min.

overestimated order in acid. Comprehensively analyzing our data on the SE + $HClO_4$ system and considering possible causes of the difference of the order in acid from unity, we assume the following. It should not be ruled out that the working epoxide solutions had primordially contained a small amount, on the order of 10^{-5} mol/l, of an organic base that neutralizes part of the acid under the given experimental conditions at $[HClO_4]$ of about 10^{-5} mol/l and decreases the oxidation rate: the lower the $[HClO_4]$, the more pronounced the decrease. In the previous study with TSA, the amount of acid was at least 0.01 mol/l, i.e., two to three orders of magnitude higher, and the effect of trace base impurities could quite definitely be unnoticeable. The amount of a strong base can be estimated as follows. The dashed line in Fig. 2 refers to the first order in acid, it corresponds to the intercept of $\Delta[HClO_4] \approx 5 \times 10^{-6}$ mol/l on the abscissa. Assuming that the amount of the base that in the reactor neutralizes this amount of the acid is even five times greater (i.e., 2.5×10^{-5} mol/l), its concentration in the initial epoxide should be 2.5×10^{-4} mol/l. Under the assumption that the molecular weights of SE and the hypothetical impurity base are equal, this is ~0.003 wt %, an amount that is quite likely to be present in SE. Curve *2* of the dependence of v on $[SE]_0$ plotted in Fig. 2 also differs from the relevant curve for TSA. The oxidation rate at low values of [SE] increases with an increase in $[SE]_0$, then the curve becomes less steep, and the order decreases. A distinct zero order in epoxide was observed at [SE] > [TSA] in the reactions of SE and its two halogenated derivatives. We believe that the partial orders of the oxidation reaction in both components are unity in the SE + $HClO_4$ binary system; that is, $v = k\,[SE]^1\,[HClO_4]^1$. The aforementioned assumption on the presence of a trace base impurity explains the overestimated order in acid, the decrease in the rate order in SE at a high epoxide concentration, and the fact that the v–$[SE]_0$ curve (curve *2* in Fig. 2) passes through the origin. Forcedly looking ahead, we note that the data on the PCA-mediated overall consumption of SE are consistent with the assumption on the presence of an impurity base in SE. The drop in the SE conversion rate constant with an increase in $[SE]_0$ (Fig. 4) is hard to explain another way, if at all. Calculation of the effective bimolecular rate constant of the oxidation of the SE + PCA system from the slope of the dashed line in Fig. 2 ($k_{bO_2} = 0.84$ l/(mol s)) and the slope of the tangent the initial portion of curve *2* in Fig. 2 ($k_{bO_2} = 0.71$ l/(mol s)) gives an average value of $k_{bO_2} = 0.77$ l/(mol s). Since the oxidation rates of the SE +

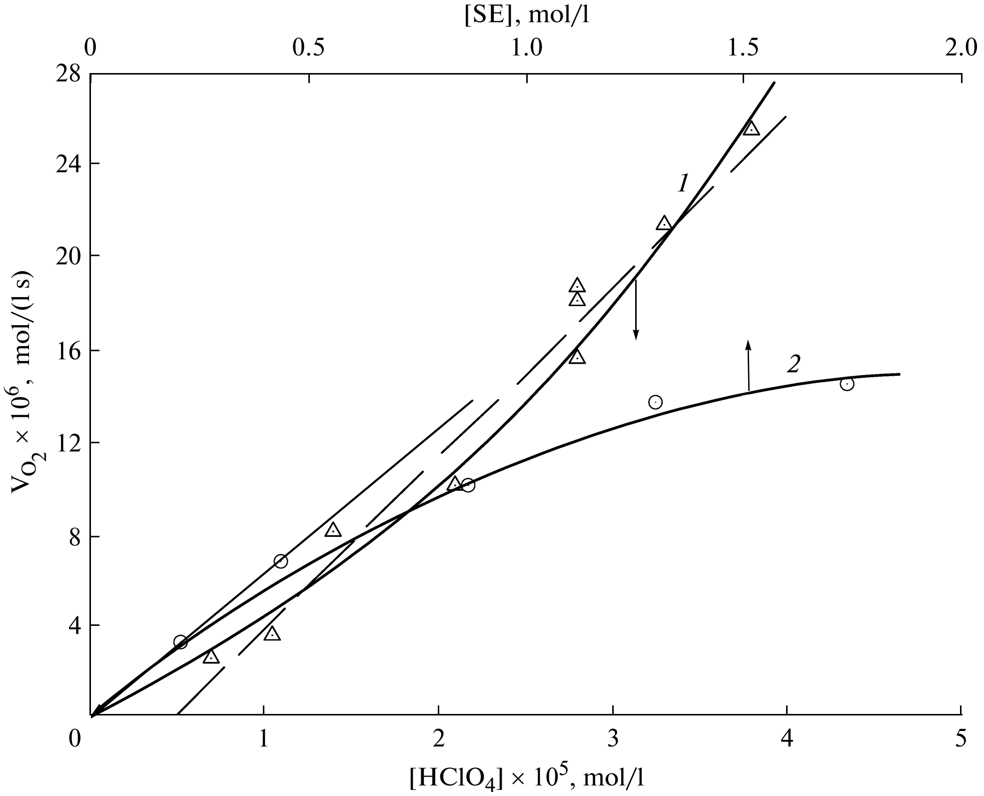

Fig. 2. Dependence of the oxygen uptake rate curves in BUCH at 343 K on (*1*) $[HClO_4]$ at $[SE]_0 = 0.87$ mol/l and (*2*) $[SE]_0$ at $[HClO_4] = 2.1 \times 10^{-5}$ mol/l.

TSA and SE + PCA systems are equal at $[PCA] = 2.65 \times 10^{-5}$ mol/l and $[TSA] = 0.02$ mol/l for $[SE]_0 = 0.5$ mol/l in both cases, $v_{TSA} = k[TSA] = 10.2 \times 10^{-6}$ mol/(l s) ($k = 5.7 \times 10^{-4}$ s^{-1} [2]), $v_{PCA} = k_b[PCA][SE]_0 = 10.2 \times 10^{-6}$ mol/(l s), it follows that the efficiency of perchloric acid as an SE oxidation catalyst is higher than that of TSA by a factor of ~750 (almost three orders of magnitude): at equal rates of oxidation mediated by PCA and PSA, the [PCA]/[TSA] ratio is 1/750.

The results of measuring the overall consumption of SE in the bubble reactor in the presence of PCA are presented in Figs. 3 and 4. Figure 3a shows the typical SE consumption and benzaldehyde buildup rate curves. Benzaldehyde does not seem to form in an argon atmosphere: a barely noticeable rise in the initial BA concentration in argon is most likely due to the carryover of part of the solvent during argon bubbling. As in the case of TSA [1], the oxidation of SE with PCA yields benzaldehyde as a product. However, the SE consumption and BA buildup kinetics are different; both reactions in the presence of PCA follow the first-order law, not zero-order observed in the TSA catalysis [1]. Figure 3b presents semilogarithmic transformations of the rate curves for SE consumption in the presence of PCA. The steady linearization until high degrees of SE conversion suggests the first-order rate. The BA buildup kinetics is also first-order, as we have found from the data of curve *1'* in Fig. 3a. Under the assumption of first-order BA buildup during the conversion of SE at a constant BA yield of $\alpha = \Delta[BA]/\Delta[SE]$ and its independence from the degree of conversion of epoxide, we get $d[BA]/dt = \alpha k[SE]_t = \alpha k[SE]_0 e^{-kt}$ to give by integrating $[BA]_\infty - [BA]_t = [BA]_\infty e^{-kt}$, $\log m = \text{const} - (kt/2.3)$, where $m = [BA]_\infty - [BA]_t$. The BA buildup data for calculating k are given in the table.

From the slope of the straight line in the $\log m - t$ coordinates, a value of $k_{BA} = 2.53 \times 10^{-3}$ s^{-1} was calculated; it is very close to $k_{SE} = 3.15 \times 10^{-3}$ s^{-1} calculated from the slope of curve *1* in Fig. 3b. However, the predicted first order in concentration, i.e., the proportionality of the SE conversion rate to its initial concentration is experimentally not observed, the first-order rate constant calculated from the slopes of straight lines in the $\log[SE] - t$ coordinates (Fig. 3b) drops with an increase in $[SE]_0$ (Fig. 4, curve *1*). Furthermore, the initial rate $v = k[SE]_0$ weakly depends on $[SE]_0$; there is no certain tendency toward a rise or fall in v. For example, five runs at $[SE]_0$ of 0.29, 0.43, 0.61, 0.87, and 1.30 mol/l to yield curve *1* in Fig. 4 corre-

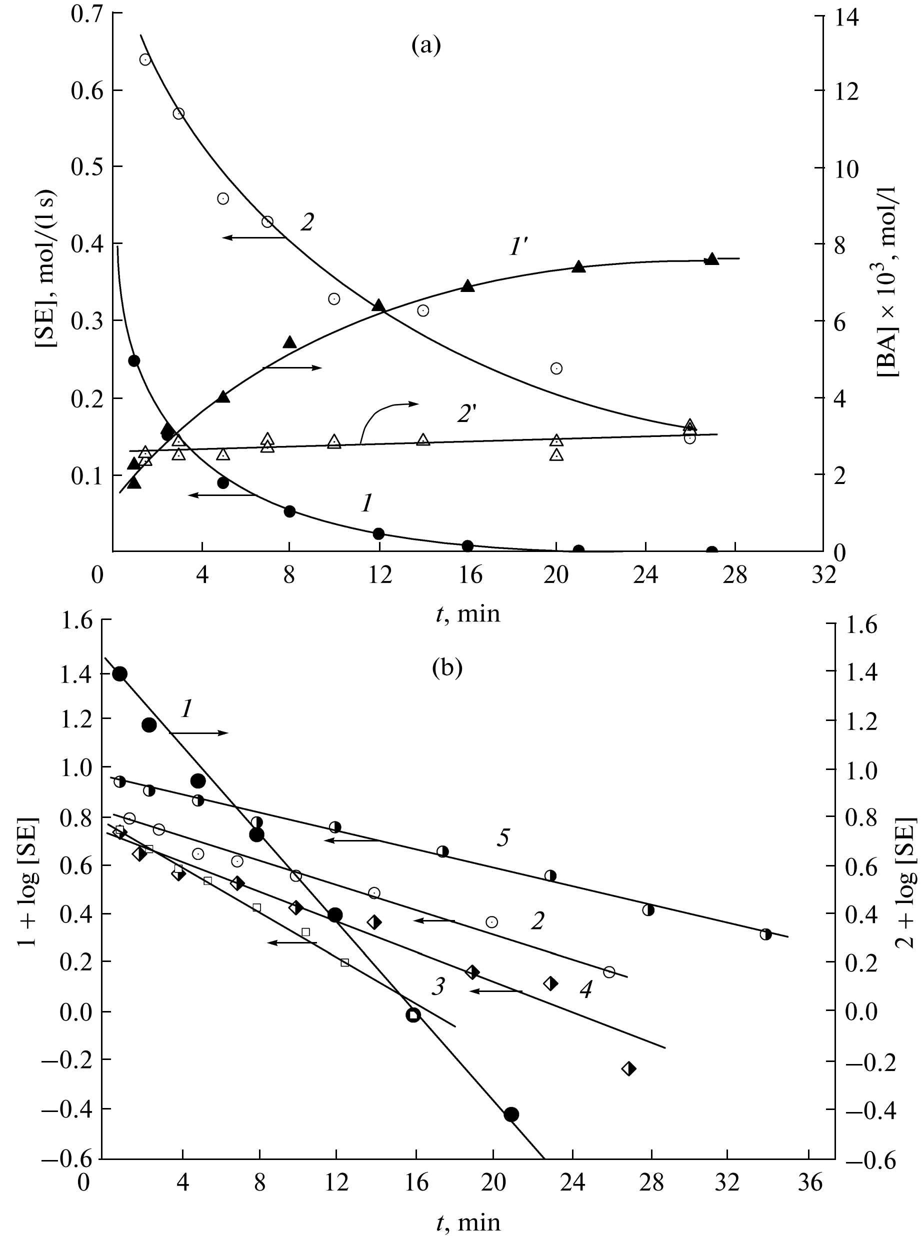

Fig. 3. (a) Rate curves of (*1*, *2*) styrene epoxide consumption and (*1*′,*2*′) benzaldehyde buildup in a BUCH solution in (*1*, *1*′) oxygen and (*2*, *2*′) argon atmospheres at (*1*, *1*′) $[SE]_0 = 0.43$ mol/l and $[HClO_4] = 4.4 \times 10^{-5}$ mol/l and (*2*, *2*′) $[SE]_0 = 0.87$ mol/l and $[HClO_4] = 3.6\ 10^{-5}$ mol/l; (b) semilogarithmic transforms of (*1*, *2*) SE consumption curves *1* and *2* in Fig. 3a, respectively, and those at (*3*) $[SE]_0 = 0.87$ mol/l and $[HClO_4] = 5.3 \times 10^{-5}$ mol/l under argon; (*4*) $[SE]_0 = 0.87$ mol/l and $[HClO_4] = 4.4 \times 10^{-5}$ mol/l, oxygen; and (*5*) $[SE]_0 = 1.3$ mol/l and $[HClO_4] = 4.4 \times 10^{-5}$ mol/l, oxygen; BUCH, 343 K.

spond to $v \times 10^3$ values of 1.26, 1.37, 1.50, 1.15, and 0.95 mol/(l s), respectively. Curve *2* in Fig. 4 illustrates the dependence of the pseudounimolecular rate constant *k* on [PCA]. The data of experiments in oxygen and argon atmospheres are quite close; the bimolecular rate constant calculated from the slope of the dashed line in Fig. 4 is $k_b = 30$ l/(mol s). In the experiments with TSA, a concerted time and concentration order in SE was observed [1]: the invariability of the SE consumption rate with time corresponded to the independence of the rate from $[SE]_0$; this is another difference between the two acid catalysts for the overall conversion of SE. A comparison of the bimolecular rate constants of SE oxidation in the presence of PCA ($k_{bO_2} = 0.77$ l/(mol s) and the overall conversion ($k_b = 30$ l/(mol s) shows that the contribution of oxidation to the overall conversion is approximately 2.5%; i.e., there is one oxidation event per 40 events of disappearance of SE molecules. The proportion of oxidation for the SE + TSA pair was ~4% or one event per 25 events.

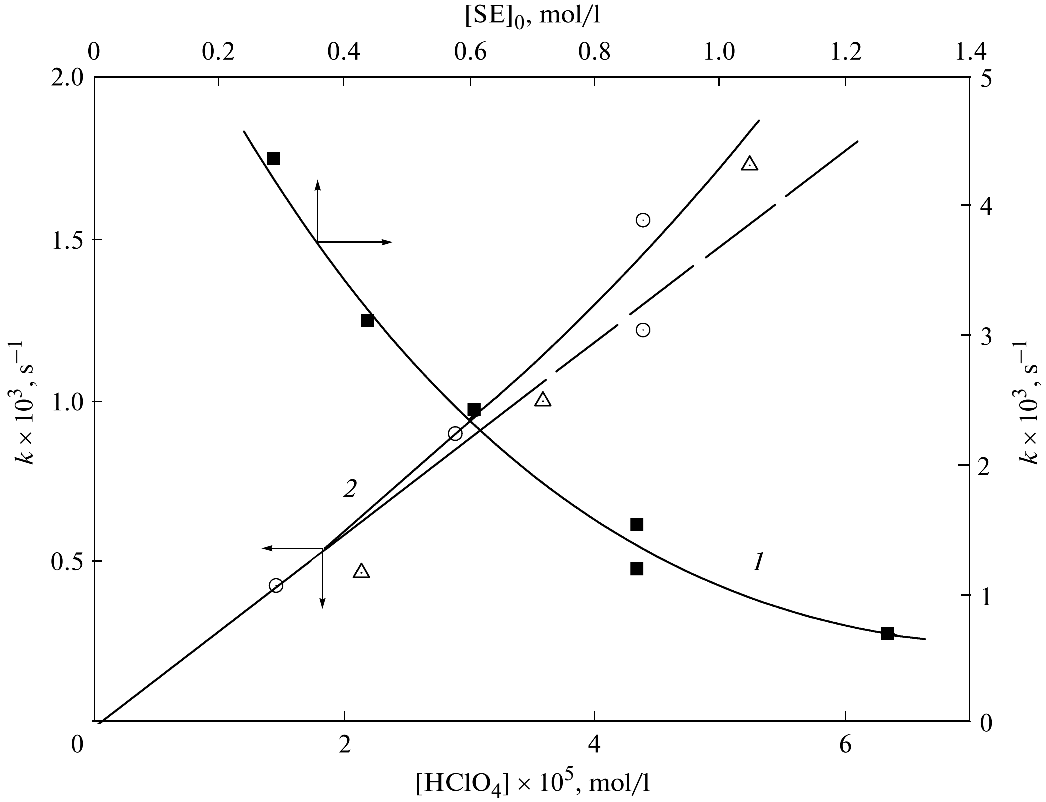

Fig. 4. Dependence of the overall consumption pseudounimolecular rate constant of styrene epoxide in a BUCH solution at 343 K on (*1*) $[SE]_0$ at $[HClO_4] = 4.4 \times 10^{-5}$ mol/l in an oxygen atmosphere and (*2*) $[HClO_4]$ at $[SE]_0 = 0.87$ mol/l in (circles) oxygen and (triangles) argon atmospheres.

The phenomenon of mild oxidation of SE in the presence of TSA was first described in [2]. Comparative experiments on oxidation in alcohol–chlorobenzene (BUCH) and acetonitrile (MeCN) solutions raise the question as to why the oxidation rates are close in solvents that are so different in nature [2]. Why does the reaction in BUCH proceeds faster than in MeCN? The acid type of oxidation catalysis has been clearly demonstrated: the oxidation rate in both solvents is strictly proportional to the acid concentration. Proton transfer from an acid to the substrate, which usually involves the solvent, is the familiar necessary step in an acid-catalyzed reaction. In a protophilic alcohol solution, the concentration of the reactive protonated form should be much lower than in aprotic MeCN because of displacement of the $SE + ROH_2^+ \rightleftharpoons SEH^+ + ROH$ equilibrium to the left. But oxidation in BUCH is faster by a factor of ~2 [2]. Here is a contrasting example from a close field of chemistry, the perchloric acid-catalyzed radical degradation of *tert*-butyl hydroperoxide. The initiation rate at working concentrations of $[HClO_4] = 0.1$ and $[ROOH] = 0.01$ mol/l in an isopropyl alcohol solution is 16 times lower than in a MeCN solution at 343 K [6, 7]. This is the expected, normal ratio. However, a special study of the role of solvent in the TSA-catalyzed oxidation of SE has shown that the higher the polarity of the medium and the greater the concentration of protophilic OH groups in the solution, the faster the oxidation [8]; this is surprising. For comparison, we have shown in [8] that the introduction of alcohol in as low an amount as 10 vol % into MeCN almost stops the classical reaction of acid-catalyzed decomposition of cumyl hydroperoxide. These data illustrate a distinct abnormality of the acid-catalyzed oxidation of SE amongst other acid-catalyzed reactions. This abnormality is manifested to even a greater extant in the case of perchloric acid. It does not catalyze oxidation in MeCN, although its activity in the alcohol medium is almost three orders of magnitude higher than that of TSA. A comparison of the kinetic data for TSA and PCA reveals a noticeable difference between these catalysts in action mechanism. The reactions of overall

Data for calculating k: a run with $[SE]_0 = 0.43$ mol/l and $[HClO_4] = 4.4 \times 10^{-5}$ mol/l under O_2 in BUCH at 343 K

$t_{\min}$	1	2.5	5	8	12	16	21
$1 + \log m$	1.7	1.63	1.54	1.31	1.02	0.78	1.18

consumption of SE with the two acids differ in rate order with respect to epoxide, which are zero for TSA and unity for PCA. The first order is explained by the displacement of the equilibrium to the left:

$$\mathrm{SE} + \mathrm{ROH}_2^+ \underset{k^-}{\overset{k^+}{\rightleftarrows}} \underset{\overset{k'}{\lfloor\!\longrightarrow}}{\mathrm{SEH}^+} + \mathrm{ROH} \qquad (1)$$

(ROH is *tert*-butanol and SEH^+ is protonated epoxide). The SEH^+ formation rate is defined by $d[\mathrm{SEH}^+]/dt = k^+[\mathrm{SE}][\mathrm{ROH_2}^+] - k^-[\mathrm{SEH}^+][\mathrm{ROH}] - k'[\mathrm{SEH}^+]$; in the steady state, $[\mathrm{SEH}^+] = (k^+[\mathrm{SE}][\mathrm{ROH_2}^+])/(k^+ + k^-[\mathrm{ROH}])$ and the overall consumption rate is $v = k'[\mathrm{SEH}^+] = (k'k^+[\mathrm{SE}][\mathrm{ROH_2}^+]/(k^+ + k^-[\mathrm{ROH}]))$. When equilibrium (1) is shifted to the left, $[\mathrm{PCA}] \approx [\mathrm{ROH}_2^+]$ and $v = k_\mathrm{b}[\mathrm{SE}][\mathrm{PCA}]$, $k_\mathrm{b} = (k'k^+)/(k^+ + k^-[\mathrm{ROH}])$, the experimental first-order rate constant is $k = k_\mathrm{b}/[\mathrm{PCA}]$. Considering equilibrium (1) in the presence of an impurity base N, which can be protonated via the reaction with an acid, forming NH^+,

$$\mathrm{N} + \mathrm{ROH}_2^+ \rightleftarrows \mathrm{NH}^+ + \mathrm{ROH}$$

$$\mathrm{SE} + \mathrm{ROH}_2^+ \overset{K_1}{\rightleftarrows} \underset{\overset{k'}{\lfloor\!\longrightarrow}}{\mathrm{SEH}^+} + \mathrm{ROH}$$

where $K_1 = (k^+/k^-)$ is the equilibrium constant, and the mass balance equation $[\mathrm{PCA}] = \mathrm{ROH}_2^+ + \mathrm{SEH}^+ + \mathrm{NH}^+$ gives a simple expression for the overall SE consumption rate that explains the drop in the rate with an increase in $[\mathrm{SE}]_0$ and the conservation of the first order in SE: $v = k'\,[\mathrm{SEH}^+] = k'K_1\,[\mathrm{SE}]_0([\mathrm{PCA}] - [\mathrm{NH}^+])/([\mathrm{ROH}] + K_1[\mathrm{SE}]_0)$ (2).

As $[\mathrm{SE}]_0$ increases, the concentrations of N and its protonated form NH^+ increase and the actual concentration of PCA in the solution decreases. The rate is not proportional to $[\mathrm{SE}]_0$, but the consumption kinetics is first-order in epoxide, since the rate curves are linearized in the semilogarithmic coordinates over the entire range of epoxide concentrations (Fig. 3a); i.e., $K_1[\mathrm{SE}]_0 \ll [\mathrm{ROH}]$ in the denominator of Eq. (2). The zero order in SE in the reaction with TSA suggested the scheme with equilibrium (1) shifted to the right [2]. If equilibrium (1) is shifted to the right in the case of TSA, the same must be true in the solution of PCA, which is a stronger acid. Thus, zero order in SE should be observed then in experiments with PCA, whereas it is first-order in actuality. The contradiction is eliminated if we assume that SE forms a reactive complex with acids containing the $\mathrm{SO_4}$ group, such as TSA and sulfuric acid [5]. In [2] we skated over the feasibility of complexation between TSA and SE. The results of the study of the SE–PCA system force us to recur to this subject. The formal scheme with equilibrium (2) shifted to the right:

$$\mathrm{SE} + \mathrm{HAn} \overset{K}{\rightleftarrows} \mathrm{X} \xrightarrow{k_1} \text{carbene}$$

$$\xrightarrow{\mathrm{O_2}} \text{carbonyl oxide}$$

$$\mathrm{SE} + \mathrm{HAn} \overset{K}{\rightleftarrows} \mathrm{X}$$

$$\xrightarrow{k_2} \text{overall conversion products}$$

suggests that the epoxide and the acid form an intermediate complex X, which is consumed in reactions yielding carbene and heterolysis products. In the quasi-steady-state approximation at $[\mathrm{SE}]_0 > [\mathrm{HAn}]_0$ and $[\mathrm{HAn}]_0 = [\mathrm{HAn}] + [\mathrm{X}]$, we get $K = [\mathrm{X}]/[\mathrm{SE}]_0([\mathrm{HAn}]_0 - [\mathrm{X}])$, $[\mathrm{X}] = K[\mathrm{SE}]_0[\mathrm{HAn}]_0/(1 + K[\mathrm{SE}]_0)$; at $K[\mathrm{SE}]_0 \gg 1$, $[\mathrm{X}] = [\mathrm{HAn}]_0$ and the overall SE consumption rate will be proportional to the acid concentration raised to a power of unity (first order) and independent from [SE] (zero order), $v = (k_1 + k_2)[\mathrm{HAn}]$. A weakness of this scheme as a whole is the lack of any independent piece of evidence for complexation. There are two experimental findings that can be interpreted in favor of complexation. The first is the distinct independence of the SE oxidation rates in the presence of TSA or $\mathrm{H_2SO_4}$ (zero order in SE). The second is the existence of induction periods of oxidation for $\mathrm{SO_4}$-containing acids, especially, sulfuric acid [5]. It is likely that the intermediate reactive epoxide–acid complex is formed during the induction period. Quite an embarrassing feature of the acid catalysis of epoxide oxidation with oxygen that complicates its investigation is a variety of specific actions of the chemicals—solvents, epoxides, acids, etc.—involved in the reactions; here are examples. *para*-Toluenesulfonic acid catalyzes oxidation in both MeCN and BUCH. Perchloric acid catalyzes only in BUCH. Hydrochloric acid does not catalyze the process altogether. The oxidation of the SE + $\mathrm{H_2SO_4}$ pair is characterized by a long induction period, the SE + $\mathrm{HClO_4}$ binary system is oxidized without any induction period, and they are detectable only at very low reactant concentrations in experiments with SE + TSA. However, the para-substituted chloro and fluoro derivatives of styrene epoxide are oxidized with distinct induction periods. All these peculiarities cannot obscure the main point: catalytic amounts of strong protic acids cause fast oxidation of barely oxidizable styrene epoxide and its halogenated derivatives under mild conditions. The main oxidation products are aldehydes and hydrogen peroxide. The formation of aldehydes unequivocally indicates that the conversion of epoxides involves C–C bond cleavage, the mechanism of which is of interest. In an inert gas atmosphere, aldehydes are not produced, but intermediate species decompose hydroperoxides at rates that are quite close to the rate of oxygen absorption in the presence of aldehydes [3].

REFERENCES

1. L. V. Petrov and V. M. Solyanikov, Neftekhimiya **39**, 107 (1999) [Pet. Chem. **39**, 89 (1999)].
2. L. V. Petrov and V. M. Solyanikov, Dokl. Akad. Nauk **350**, 357 (1996).
3. L. V. Petrov and V. M. Solyanikov, Neftekhimiya **45**, 225 (2005) [Pet. Chem. **45**, 202 (2005)].
4. L. V. Petrov, B. L. Psikha, and V. M. Solyanikov, Neftekhimiya **49**, 263 (2009) [Pet. Chem. **49**, 245 (2009)].
5. L. V. Petrov and V. M. Solyanikov, Neftekhimiya **40**, 438 (2000) [Pet. Chem. **40**, 399 (2000)].
6. V. M. Solyanikov and E. T. Denisov, Izv. AN SSSR. Ser. Khim., No. 6, 1391 (1968).
7. L. V. Petrov, V. M. Solyanikov, and E. T. Denisov, Izv. Akad. Nauk SSSR. Ser. Khim., No. 4, 739 (1977).
8. L. V. Petrov, B. L. Psikha, and V. M. Solyanikov, Neftekhimiya **47**, 379 (2007) [Pet. Chem. **47**, 348 (2007)].