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Oxidative Transformations of *p*-Chloro- and *p*-Fluorostyrene Epoxides in the Presence of *p*-Toluenesulfonic Acid

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Abstract—Mild oxidation of two halogenated styrene epoxides, 2-(4-chlorophenyl)oxirane (CSE) and 2-(4-fluorophenyl)oxirane (FSE), was studied in the presence of *p*-toluenesulfonic acid (TSA). Hydrogen peroxide and *p*-chlorobenzaldehyde are the products of CSE oxidation. The kinetics of the overall CSE consumption and oxidation of CSE and FSE are identical to those revealed earlier for the oxidation of styrene epoxide (SE). The consumption and oxidation rates do not depend on the epoxide concentration (zero order) and are proportional to the TSA concentration. At 343 K, the oxidation rate of CSE and FSE are higher than that for SE by factors of 2 and 7, respectively. The introduction of the halogen atoms in the *p*-position on the phenyl ring accelerates the oxidation.

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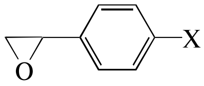
Acid-catalyzed transformation of styrene epoxide (SE) follows two main routes, of which the major route is nonradical polymerization of SE mediated by an acidic agent. Concomitant to this route, there is thea well-documented pathway accompanied by oxygen absorption yielding benzaldehyde and hydrogen peroxide [1–3]. In the absence of oxygen, this route manifests itself in the decomposition of various hydroperoxides added to the binary system (BS) styrene epoxide + *p*-toluenesulfonic acid (SE + TSA) [4].

The objective of this work is to study the oxidative transformation of two halogenated styrene epoxides (SE), 2-(4-chlorophenyl)oxirane (CSE) and 2-(4-fluorophenyl)oxirane (FSE) , where X is halogen, in the presence of TSA. The results of this study show that the unusual oxidation, which has been exemplified by the case of SE alone, also occurs for its derivatives bearing substituents on the phenyl ring. The presence of *p*-substituents, such as chlorine and especially fluorine, significantly accelerates the oxidation almost without a change in the kinetic behavior observed earlier for unsubstituted SE.

EXPERIMENTAL

2-(4-Chlorophenyl)oxirane (CSE) and 2-(4-fluorophenyl)oxirane (FSE) (98%, Aldrich) were used without further purification. Oxidation rates were measured on a volumetric setup. Experiments on the overall consumption of CSE were carried out in a bubble reactor. The CSE consumption and *p*-chlorobenzaldehyde (CBA) formation were analyzed monitored by liquid chromatography. Hydrogen peroxide was analyzed determined by iodometric titration. The details of the kinetic experiment were described elsewhere [1–4]. All experiments were carried out in a binary solvent (BUC) composed of *tert*-butanol and chlorobenzene in a 9 : 1 ratio by volume. Prior to experiments, both components of the solvent were thoroughly purified according to standard procedures.

RESULTS AND DISCUSSION

The kinetics of the CSE consumption in an acidified BUC solution with oxygen bubbling and of the CBA formation is are given in Figs. 1 and 2, respectively. *p*-Chlorobenzaldehyde BA was identified by the equality of matching the retention times of CSE conversion products in a liquid chromatography column (Fig. 1) with that of the authentic compound specially synthesized CBA for the purpose. It is this product of CSE conversion in the presence of oxygen whose formation was predicted, since unsubstituted SE yields benzaldehyde under similar conditions [2]. (Chlorophenyl)oxirane CSE is consumed with at a constant rate practically to the almost complete converssumption in the presence of TSA in BUC (Fig. 1), as it was previously observed for SE in the presence of TSA [2]. This means that the CSE consumption obeys the zero-order rate law in respect to [CSE]. The rate of the CSE consumption and the initial rate of the CBA formation calculated from the slope of the straight lines (Fig. 2) are given in Fig. 3 as a function of [TSA]. One can see that the rates of the CSE conversion and aldehyde formation rates are proportional to the acid concentration, i.e., they are first order in respect to [TSA] is observed. Thus, the expression for the rate of the CSE

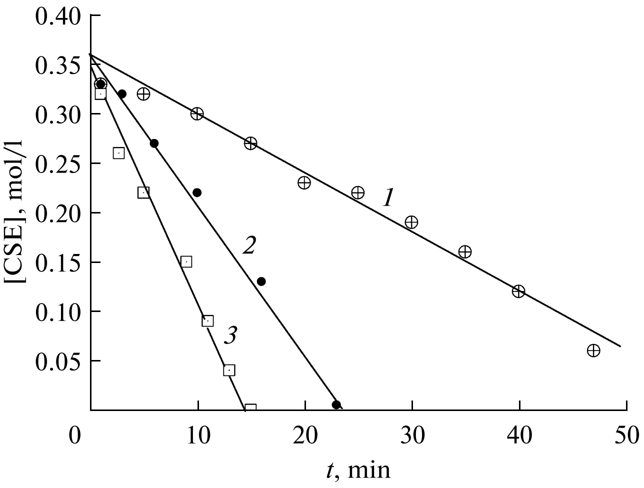


Fig. 1. Kinetics of CSE consumption in the presence of TSA, mol/l: (*1*) 9.5 × 10^{-3}, (*2*) 1.9 × 10^{-2}, and (*3*) 2.7 × 10^{-2}; BUC, oxygen, 343 K.

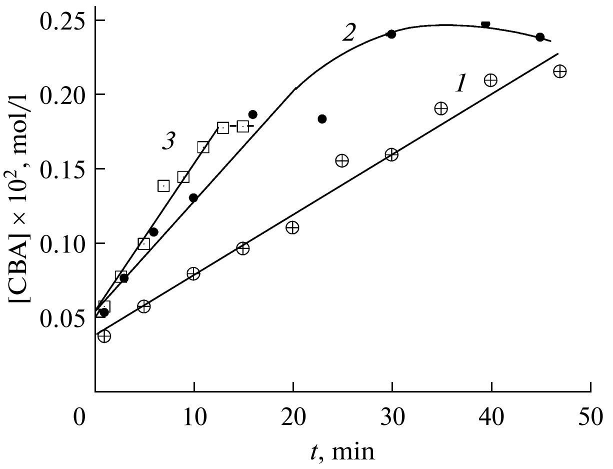


Fig. 2. Kinetics of CBA formation in the presence of TSA, mol/l: (*1*) 9.5 ×10^{-3}, (*2*) 1.9 × 10^{-2}, and (*3*) 2.7 × 10^{-2}; BUC, oxygen, 343 K.

consumption rate has the form: $V_c = k_c[\text{CSE}]^0[\text{TSA}]^1$ and is absolutely identical to the expression for the rate of conversion of unsubstituted SE [2].

As in the case of unsubstituted SE, the binary systems $\text{BS}_{(\text{CSE + TSA})}$ and $\text{BS}_{(\text{FSE + TSA})}$ absorb oxygen [1]. The examples of the oxidation kinetics are given in Fig. 4. After a small short acceleration period, the oxidation occurs with at almost a constant rate up to eitheruntil the end of measurements (Fig. 4, *1*, *3*, *5*), or the complete consumption of the halogenated epoxide (Fig. 4, *2*), or oxygen uptake exhaustion (Fig. 4, *4*). The oxidation rates for the two binary systems as a function of the reactgeant concentrations are given in Fig. 5. In both cases, the first order relative with respect to the TSA concentration and transition to the zero order relative toin CSE and FSE concentrations at their high concentrations are clearly observed, i.e., $V_{\text{O}_2} = k[\text{SE}]^0[\text{TSA}]^1$, and the expression is identical to that obtained in the study of the oxidation of $\text{BS}_{(\text{SE + TSA})}$ [1].

The activation energy of oxidation was determined from the temperature dependence of the oxidation rate V_{O_2} for $\text{BS}_{(\text{CSE + TSA})}$ at $[\text{CSE}]_0$ = 0.5 and [TSA] =0.019 mol/l. Two experiments carried out at T = 333.3 K for reliability gave the same value V_{O_2} = 7 × 10^{-6} mol l^{-1} s^{-1}. At 337.4 and 343 K V_{O_2} = 10.7 × 10^{-6} and 17 × 10^{-6} mol l^{-1} s^{-1}, respectively. The activation energy E_{act} = 20.3 kcal/mole (84.8 kJ/mol) determined from the slope of the straight line in the coordinates $\log V_{\text{O}_2} - (10^3/T)$ is close to the activation energy of the SE oxidation (E_{act} = 83.6 kJ/mol [1]). The pseudo-first-order rate constant of the $\text{BS}_{(\text{CSE + TSA})}$ calculated from the slope of curve *1* (Fig. 5) is equal to $k = 7.9 \times 10^{-4}\ \text{s}^{-1}$ or, in the Arrhenius form, $k = 7.57 \times 10^9 (\exp(-84.8\ \text{kJ mol}^{-1}/RT)\ \text{s}^{-1}$.

The oxidation rate of $\text{BS}_{(\text{FSE + TSA})}$ as a function of the oxygen content in the gas phase of the reactor of the volumetric setup is presented by curve *6* (Fig. 4). The fractional order $n_{\text{FSE}} = 0.33 \pm 0.04$ in the range of O_2 from 21– to 100 vol % O_2 is inconsistent with contradict to the assumption of on radical chain oxidation. The similar value of $n_{\text{SE}} = 0.4$ calculated from the published data [1] for the oxidation of $\text{BS}_{(\text{SE + TSA})}$ in BUC from the data of [1] shows the closeness of the reaction parameters for various epoxides to be evident from this characteristic tooas well. Like the oxidation

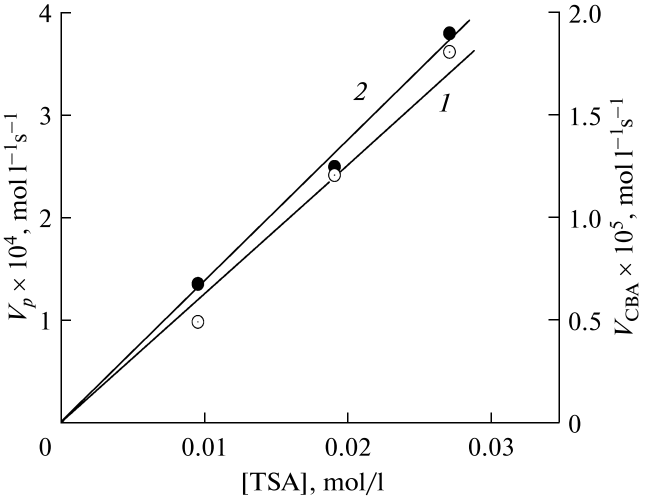


Fig. 3. (*1*) The rate of the CSE consumption (left ordinate axis) and (*2*) the initial rate of *p*-chlorobenzaldehyde formation (right ordinate axis) as a function of [TSA]; $[\text{CSE}]_0$ = 0.33 mol/l, BUC, oxygen, 343 K.

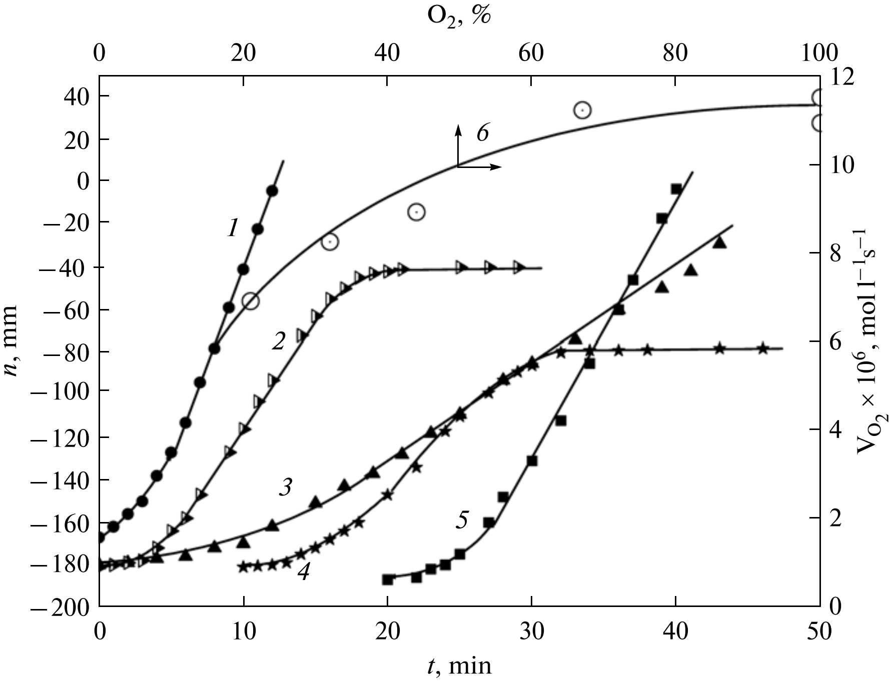


Fig. 4. Kinetics of the oxidation of binary systems (*1, 3*) CSE + TSA (*1, 3*) and FSE + TSA (*2, 4, 5*) FSE + TSA; BUC, 343 K, concentrations in mol/l: (*1*) $[CSE]_0 = 0.5$, [TSA] 0.019, oxygen; (*2*) $[FSE]_0 = 0.135$, [TSA] 0.00312, oxygen; (*3*) $[CSE]_0 = 0.33$, [TSA] 0.0054, oxygen; (*4*) $[FSE]_0 = 0.51$, [TSA] 0.00312, air; and (*5*) $[FSE]_0 = 0.51$, [TSA] 0.00312, oxygen 67% in the mixture; (*6*) the oxidation rate as a function of oxygen content in the gas phase, $[FSE]_0 = 0.51$, [TSA] 0.00312 mol/l.

of SE [3], the oxidation of CSE and FSE yields hydrogen peroxide, as indicated by the fast evolution of iodine from potassium iodide without heating during the course of standard iodometric analysis. In the final oxidation mixtures of the volumetric experiments on CSE and FSE oxidation, the hydrogen peroxide concentration was determined.

Table 1 presents the percentage yield of hydrogen peroxide on an oxygen uptake basis during the oxidation of $BS_{(CSE\,+\,TSA)}$, $P(\%) = ([H_2O_2]/[O_2]) \times 100$, where $[H_2O_2]$ is the concentration of hydrogen peroxide in the oxidation mixture and $[O_2]$ is the total oxygen concentration absorbed in the experiments on oxidation. As follows from the data in Table 1, the yield of hydrogen peroxide changes insignificantly with variation of the oxidation conditions, temperature, and the concentrations of the BS components. If we ignore the data of the first column in Table 1 (26%) corresponding to the smallest concentration of CSE, the average value $P_{av.} = 37\%$ is close to the data on SE oxidation ($P \approx 40\%$ [3]) under similar conditions $(0.3 < [SE]_0 < 1.1$ mol/l, [TSA] = 0.016 mol/l, 343 K). This means that the oxidation of $BS_{(CSE\,+\,TSA)}$ is close also to the oxidation of $BS_{(SE\,+\,TSA)}$ by in this parameter as well. The value of P for $BS_{(SE\,+\,TSA)}$ is significantly higher at 343 K (Table 2).

At first glance, the value of $P = 48\%$ averaged over to the data given in Table 2 insignificantly differs from those given above for SE and CSE. However, the averaging is cannot be used unjustified in this case. It is known that the binary system SE + TSA decomposes the hydroperoxides, including hydrogen peroxide among them, in the absence of oxygen [3]. It is quite likely that, in the oxygen-poor atmosphere, the hydrogen peroxide is partially decomposed in an oxygen-deficient atmosphere. In this case, the data of the first two columns in Table 2 should not be included in averaging for the calculation of the H_2O_2 yield per oxygen absorbed, since the oxidation was carried out at a reduced oxygen concentration. For reliability, the data from the third column in Table 2 should be also neglected. It seems that the yield of H_2O_2 decreases at

Table 1. The yield of H_2O_2 (%) during the oxidation of $BS_{(CSE\,+\,TSA)}$

T, K	343					337.4	333
[TSA], mol/l	0.019	0.0054	0.019	0.019	0.019	0.019	0.019
$[CSE]_0$, mol/l	0.166	0.330	0.330	0.500	0.660	0.500	0.500
P, %	26	38	39	34	34	37	41

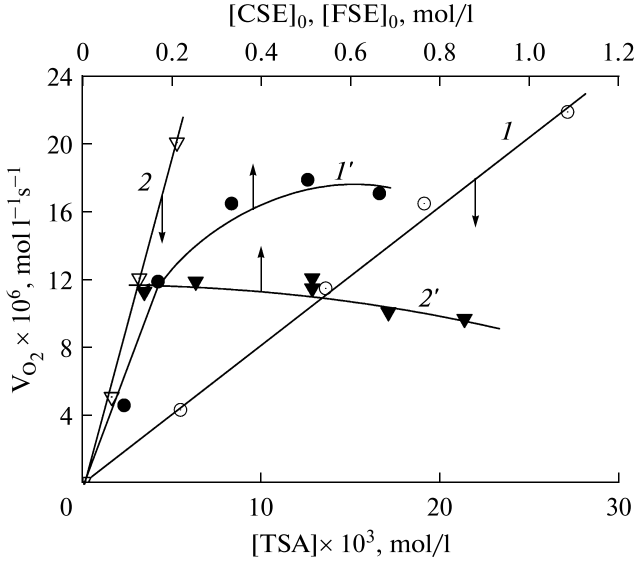


Fig. 5. The rates of oxidation by oxygen for the binary systems (*1, 1′*) CSE + TSA and (*2, 2′*) FSE + TSA as a function of reagent concentrations (mol/l) in BUC solutions at 343 K: (*1*) [TSA], $[CSE]_0 = 0.33$; (*1′*) [CSE], [TSA] = 0.019; (*2*) [TSA], [FSE] = 0.51; and (*2′*) [FSE], [TSA] = 0.0031.

low $[FSE]_0$ and $[CSE]_0$ for unknown reasons (see also the first column in Table 1). Then, the value $P_{av} = 61\%$ for experiments in pure oxygen at $[FSE]_0 > 0.5$ mol/l, which is higher than the peroxide yield for SE and CSE by a factor of 1.5–1.6. It seems is improbable unlikely that this discrepancy implies a serious difference in the oxidation mechanism between the test epoxides. We assume that the FSE oxidation products (for example, the *p*-fluorobenzaldehyde) form the a triple ternary system with the $BS_{(FSE + TSA}$ binary system);, i.e., the radical chain oxidation of the intermediate labile product begins, as it was observed in the experiments with the introduction of styrene and isopropanol into the SE + TSA binary system [5]. In this case, iodometric titration gives the sum $[H_2O_2]$ + [ROOH], where ROOH is the hydroperoxide from the labile intermediate produced during the oxidation of the binary system,. thereby explaining This results in the overestimateding of the value of $P = [H_2O_2]/[O_2] < ([H_2O_2] + [ROOH])/[O_2]$, determined by the titration. This assumption needs additional verification, which is beyond the framework scope of this study.

In summaryconclusion, comparing the oxidation of SE [1–4] and with that of CSE and FSE given here, we can say conclude that the quantitative differences in the parameters of the SE, CSE, and FSE oxidation parameters do not causes qualitative differences. In other words, the oxidation of the three epoxides proceeds follows within the same mechanism, presumobably, with the intermediate formation of carbene, which can absorb oxygen to afford carbonyl oxide [5]. Indeed fact, the expression for of the oxidation rate as through the concentrationsa function of the reactagents has the same form for these epoxides, $V_{O_2} = k'[SE]^0[TSA]^1[O_2]^n = k[SE]^0[TSA]^1$. The oxidation of SE and CSE yields the same main products, the corresponding aldehyde and hydrogen peroxide. As mentioned above, the yields of the latter are very close for these two epoxides. The Arrhenius dependences expressions for the pseudo-first-order rate constants of the SE and CSE oxidation are similar: $k_{SE} = 3.32 \times 10^9\exp(-83.6\ \text{kJ mol}^{-1}/RT)\ \text{s}^{-1}$ and $k_{CSE} = 7.57 \times 10^9\exp(-84.8\ \text{kJ mol}^{-1}/RT)\ \text{s}^{-1}$. The effect of the halogen substituent is clearly observed: $k_{SE} < k_{CSE} < k_{FSE}$ (343 K) : $5.5 \times 10^{-4} < 7.9 \times 10^{-4} < 3.8 \times 10^{-3}\ \text{s}^{-1}$.

Substituted epoxides, especially fluoride, are oxidized more easierly than the styrene epoxide per se. A similar picture is observed when we compare the data on the overall conversion of SE and CSE. As mentioned above, the concentration dependences of the overall SE conversion and oxidation, buildup of the main products, and even the degradation of hydroperoxides added to $BS_{(SE\ +\ TSA)}$ in the an oxygen-free atmosphere are similar. In all these cases, $V_j = k_j[SE]^0[TSA]^1$ [1–4]. Now, this list is complemented by the study of the *p*-chloroine- substituted epoxide, for which the expressions for the rate of oxidation and of the overall- conversion rates have the same form (see Figs. 1 and 3) has the same form: the zero order in with respect to CSE (the constant rate of consumption rate independent of the extent of reaction depth) and the first order in respect to the acid. The pseudo-first-order rate constant of the overall CSE consumption $k_{c,SE} = k_{p.CSE} = (\Delta V_p/[TSA]\ ) = 1.28 \times 10^{-2}\ \text{s}^{-1}$ (343 K) was found from the slope of curve *1* in Fig. 3. The rate constant of the overall consumption of unsubstituted styrene epoxide $k_{c,CSE} = 1.4 \times 10^{-2}\ \text{s}^{-1}$ [2] is close to this value. This means that the *p*-chloroine substituent slightly affects the rate of heterolytic conversion, but significantly increases the oxygen uptake. From the ratio of the slopes of curves *1* and *2* (Fig. 3), we found that only one CSE molecule from out of 18 CSE molecules converted is consumed in the reaction with the participation of oxygen. This ratio for SE is 25 : 1 [2].

Table 2. The yield of H_2O_2 (%) in the oxidation of $BS_{(FSE + TSA)}$

[TSA], mol/l	0.0031	0.0031	0.0031	0.0052	0.0031	0.0031	0.0031
$[FSE]_0$, mol/l	0.51	0.51	0.135	0.507	0.51	0.68	0.85
$[O_2]$, %	21	32	100	100	100	100	100
P, %	33	21	33	69	50	68	59

Finally, the rate constant calculated from the slope of curve *2* for the formation of *p*-chlorobenzaldehyde during the CSE oxidation (Fig. 3), $k_{CBA} = 7.0 \times 10^{-4}$ s^{-1}, is very close to the specific rate of oxygen uptake $k_{CSE} = 7.9 \times 10^{-4}$ s^{-1}. A similar observation was made earlier in the study of SE conversion into benzaldehyde by oxidation [2].

In conclusion, we would like to mention our attempts to study the TSA-catalyzed oxidation of 2,3-diphenyloxirane (stilbene epoxide) and 2-methyl-3-phenyloxirane, i.e., styrene epoxide, in which one methylene H atom of the methylene group is substituted replaced by with the CH_3 group. The acid catalyzes the oxidation of the stilbene epoxide at 343 K. The long induction period can be eliminated by preliminary heating of the epoxide solution in BUC in the an argon atmosphere. The subsequent addition of TSA in the an oxygen atmosphere in to the reactor of the volumetric setup results in immediate oxidation with at a constant rate. Approximately the one -third part of the oxygen absorbed converts into hydroperoxide. Judging from slow iodine evolution during the iodometric titration of the samples, it is not H_2O_2 or is not H_2O_2 alone that is formed; the oxidation is a nonchain radical process, at least in part.

An unexpected result was obtained in the oxidation of the binary system TSA + 2-methyl-3-phenyloxirane. Upon mixing of the reactagents in BUC (343 K), the acid and epoxide are rapidly consumed fast with a stoichiometry of ca. ~1 : 1. When [epoxide] > [TSA], the acid is consumed completely within 1–2 min after mixing; thusat, does not allow uswe failed to reveal whether the oxidation takes place or does not.

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