Reaction of *tert*-butyl hypochlorite with carbonium ion from styrene epoxide in an acidic alcoholic solution*

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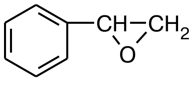
The kinetic regularities of the change in the concentration of *tert*-butyl hypochlorite in the presence of the binary system (BS) styrene epoxide—*p*-toluenesulfonic acid in a *tert*-butanol solution were studied using iodometry and HPLC and compared with the data obtained earlier for hydroperoxide decomposition. The expressions for the rates of transformation of Bu^{t}OCl, epoxide, and ROOH in the BS through the reactant concentrations are of the same type (the first order for the acid and the zero order for epoxide, Bu^{t}OCl, and ROOH) and indicate that the reactions are related to epoxide heterolysis. Dioxygen ceases ROOH decomposition in the BS but exerts no effect on the decrease in the concentration of Bu^{t}OCl, which efficiently inhibits the O_2 uptake in the BS and almost an order of magnitude retards the accumulation of benzaldehyde (the product of styrene epoxide oxidation) with a low (up to 15%) decrease in the heterolysis rate. The inhibition effect is due to the heterolytic interaction of Bu^{t}OCl with the carbocation formed by the cleavage of the three-membered ring of protonated styrene epoxide. The introduction of Bu^{t}OCl in the BS decreases the stationary concentration of the carbocation and, as a consequence, the stationary concentration of phenylcarbene responsible for O_2 uptake.

Key words: styrene epoxide, *p*-toluenesulfonic acid, oxidation with molecular oxygen, *tert*-butyl hypochlorite, inhibition, carbocation, phenylmethylene.

The overall consumption of styrene epoxide (**1**) catalyzed by *p*-toluenesulfonic acid (**2**) proceeds by ~95% *via* the heterolytic mechanism.[1] The route representing ~5% of the total decrease in epoxide **1** concentration occurs in parallel to the heterolysis. This route is manifested by the ability of active intermediates to react with dioxygen, whereas in the absence of dioxygen they decompose hydroperoxides (ROOH).[2,3] The mechanism with the intermediate formation of phenylmethylene carbene (**3**) was proposed and explains the oxidation of reactant **1** with dioxygen to benzaldehyde (**4**), the decomposition of hydroperoxides in an oxygen-free atmosphere, and its suppression by dioxygen.[2] The present study of the regularities of transformation of *tert*-butyl hypochlorite (**5**) in the presence of binary system (BS) **1**—**2** unambiguously indicates the relationship between the consumption of compound **5** and heterolysis of **1**, which is manifested in the identical expressions for the consumption rates of epoxide **1**, ROOH, and compound **5** through the reactant concentrations: $V_1 = k_1[\mathbf{2}]^1[\mathbf{1}]^0$, $V_{\mathrm{ROOH}} = k_{\mathrm{ROOH}}[\mathbf{2}]^1[\mathbf{1}]^0[\mathrm{ROOH}]^0$, and $V_5 = k_5[\mathbf{2}]^1[\mathbf{1}]^0[\mathrm{Bu^tOCl}]^0$. A substantial distinction between the transformations of Bu^{t}OCl and ROOH is that bubbling of dioxygen prevents the consumption of ROOH in the presence of BS **1**—**2** but does not retard the consumption of compound **5** under similar conditions, which indicates the different nature of the decomposition of ROOH and Bu^{t}OCl in the presence of epoxide **1** and acid **2**.



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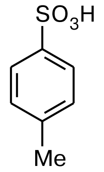

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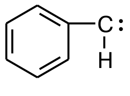

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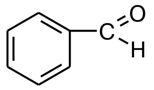

4

Bu^t–O–Cl

5

Experimental

Hypochlorite **5** was synthesized and purified as described earlier.[4] Experiments on its decomposition in an alcoholic medium BUC (Bu^{t}OH (90 vol.%)—chlorobenzene (10 vol.%)) were carried out in a glass molybdenum bubbling reactor. Taken sam-

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* Dedicated to Academician of the Russian Academy of Sciences O. M. Nefedov on his 80th birthday.

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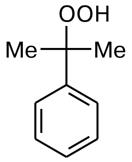
ples of the reaction mixture (0.3—0.6 mL) with the content of ~0.1 mmole of Bu^{t}OCl were placed in 100-mL flasks, then glacial AcOH (10 mL) was poured to each flask, and the flasks were purged with argon with the addition of a saturated solution of KI in MeOH (2 mL to each flask). In 3 min, iodine was titrated off with 0.05 *N* solution of $Na_2S_2O_3$. All other experimental details (purification of the reagents, apparatus, analysis) were described previously.[1—3]

Results and Discussion

Reactant **5** is a labile substance and a strong oxidant with the pronounced properties of radical reaction initiator, including catalysis with acids.[5,6] Therefore, at first we tested the thermal stability of individual compound **5** in a BUC solution and its stability in the presence of particular components of BS **1**—**2**. A comparison of the results presented in Fig. 1 (curves *1* and *2*) shows that the presence of epoxide **1** exerts almost no effect on the slow consumption of hypochlorite **5**. In an acidic medium in the absence of epoxide **1**, reactant **5** is consumed with a noticeable rate, which is the same under argon and oxygen (see Fig. 1, curve *3*). The consumption corresponds to the first order with respect to [Bu^{t}OCl] (see Fig. 1, curve *3*) and is linearized in the semilogarithmic coordinates. The first-order rate constant calculated from the slope ratio of straight line *4* ($\tan_4 = 0.434k$) is $k = 1.15 \cdot 10^{-4}$ s^{-1}, and the initial consumption rate of reactant **5** (see Fig. 1, curve *3*) is $V \approx 4.6 \cdot 10^{-5}$ mol L^{-1} s^{-1}. The shape of the kinetic curves of reactant **5** consumption changes and the rate increases with the simultaneous introduction of the both components of BS (**1** and **2**) into the solution (Fig. 2, curves *1*—*4*). The initial consumption rates in oxygen and argon are the same (see Fig. 2, curve *1*). The reaction under argon is accelerated with time (see Fig. 2, crosses), the consumption kinetics becomes more complicated, and an additional experiment is required for the elucidation of the reason for this complication. It is important in experiments (see Fig. 2) that the consumption of Bu^{t}OCl in ternary system **1**—**2**—**5** does not ceases under oxygen as it takes place in the case of ternary systems **1**—**2**—ROOH. This result is unexpected in the light of the previous data[2,3] on the decomposition of H_2O_2 and cumene (**6**) and phenylethene (**7**) hydroperoxides: ROOH are not consumed under O_2 in system **1**—**2**—ROOH.



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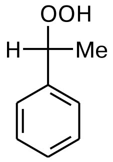

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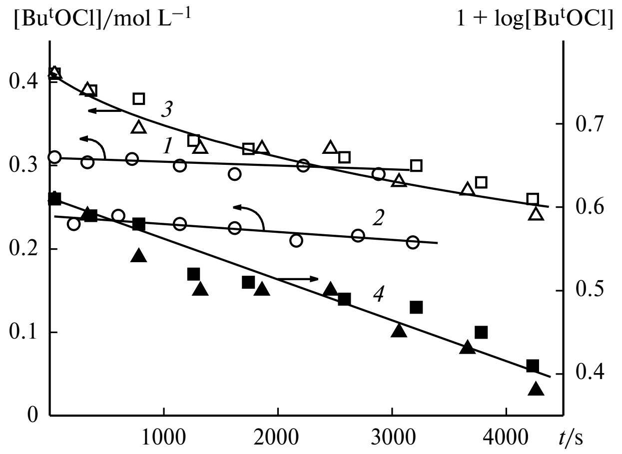


Fig. 1. Kinetic curves of thermal decomposition of Bu^{t}OCl in a neutral solution of BUC (*1*) and upon the addition of 0.81 *M* epoxide **1** (*2*), the kinetic curves of Bu^{t}OCl consumption in the presence of 0.013 *M* acid **2** under oxygen (squares) and argon (triangles) (*3*), and the semilogarithmic anamorphosis of the data of curve *3* (*4*); 343 K.

The replacement of O_2 by argon induces decomposition corresponding to the zero order of the reaction with respect to ROOH and the first order with respect to the acid. The character of the kinetic curves of hypochlorite **5** consumption under oxygen also indicates the zero order: the rate of Bu^{t}OCl decay is constant in time. The deviation from the zero order is observed at low $[\mathbf{1}]_0$; the consumption of epoxide **1** decreases the concentration of intermediate active species reacting with hypochlorite **5** (see Fig. 2, curve *1* (circles)), in this entry $[\mathbf{1}]_0 = 0.29$ mol L^{-1}, which is a minimum value for $[\mathbf{1}]_0$. Curve *5* (see Fig. 2) for the lowest value of $n = [\mathbf{1}]_0/[\text{Bu}^t\text{OCl}]_0 = 0.64 < 1$ should be commented: it was empirically found that in entries at $n < 1$ the decrease in [Bu^{t}OCl] is accelerated in the pro-

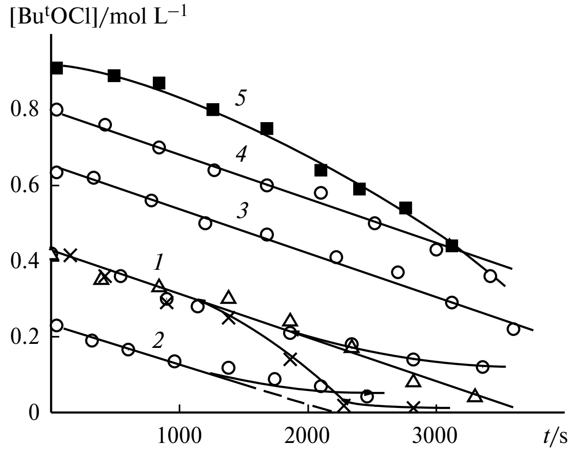


Fig. 2. Kinetic curves of consumption of Bu^{t}OCl (reactant **5**) in a solution of BUC in ternary system **1**—**2**—**5** at 343 K; [**2**] = 0.013 mol L^{-1}, $[\text{Bu}^t\text{OCl}]_0$ = 0.41 mol L^{-1}: triangles at $[\mathbf{1}]_0$ = 0.87 mol L^{-1}, oxygen (*1*); circles: $[\mathbf{1}]_0$ = 0.29 mol L^{-1}, oxygen; crosses: $[\mathbf{1}]_0$ = 0.59 mol L^{-1}, argon; $[\mathbf{1}]_0$ = 0.58 mol L^{-1}, [**2**] = 0.013 mol L^{-1}, oxygen (*2*, *3*, and *5*; for clarification, see text); $[\mathbf{1}]_0$ = 0.87 mol L^{-1}, [**2**] = 0.013 mol L^{-1}, oxygen (*4*).

cess. The latter indicates that the studied system **1**—**2**—**5** is complicated. A special experiment is needed to confirm the assumption about the importance of acid-base equilibria in the polar solvent

$$\mathrm{SH^+} + \mathbf{1} \rightleftharpoons (\mathbf{1})\mathrm{H^+} + \mathrm{S},$$

$$\mathrm{SH^+} + \mathrm{Bu^tOCl} \rightleftharpoons (\mathrm{Bu^tOCl})\mathrm{H^+} + \mathrm{S}$$

(S is the solvent, SH^+ is the dissociated acid). In this case, experiments were carried out under the conditions where $n \geq 1$ (see Fig. 2, curves *1—4*). The data on studying the particular orders of hypochlorite **5** consumption in system **1**—**2**—**5** are shown in Fig. 3. The transformation rates (*i.e.*, the slope angles of curves of the type *1—4* in Fig. 2) are given as functions of the concentration of acid **2** and the initial concentrations of compounds **1** and **5**. The distinct first order of the reaction with respect to acid **2** was determined (see Fig. 3, curve *1*) at the ~15% increase in V and the fourfold increase in $[\mathrm{Bu^tOCl}]_0$ (see Fig. 3, curve *3*), as well as a weak decrease in the rate (see Fig. 3, curve *2*) with an increase in $[\mathbf{1}]_0$. Small effects of the rate decrease with an increase in $[\mathbf{1}]_0$ were observed when studying the decomposition of H_2O_2 and compound **6** (see Fig. 3 of this work and Fig. 5 in Ref. 2).

For compound **5** we have $V_5 = k[\mathbf{2}]^1[\mathbf{1}]^0[\mathrm{Bu^tOCl}]^0$, which is identical to the equations of the decomposition rate of hydroperoxide **7** in solutions of BUC and MeCN.[2,3] As in the case of this hydroperoxide,[3] the reaction order of $\mathrm{Bu^tOCl}$ consumption depends on the presence of epoxide **1** in the system: without reactant **1** the reaction order is first (see Fig. 1), in the presence of **1** the reaction order is zero (see Fig. 2); *i.e.*, the presence of epoxide **1** changes the mechanism of the decomposition reaction. A substantial point should be mentioned: the decomposition of $\mathrm{Bu^tOCl}$ was studied under oxygen, and the decomposition of hydroperoxides could be observed only in the absence of O_2. The oxygen supply to the reactor ceased the consumption of ROOH. This observation and the equality of the initial rate of consumption of **5** under argon and oxygen assume the ionic (heterolytic) character of transformation of $\mathrm{Bu^tOCl}$ in ternary system **1**—**2**—**5**.

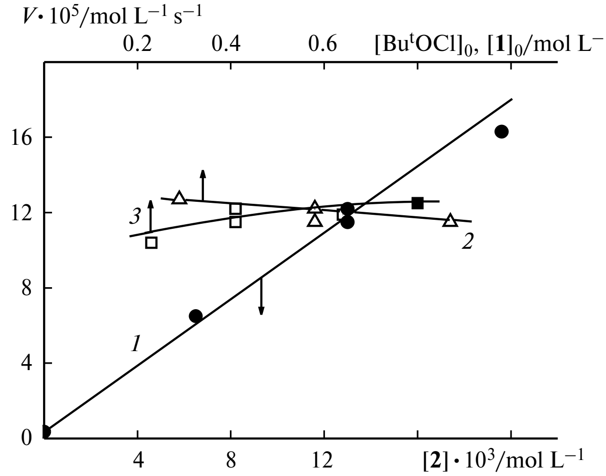


Fig. 3. Consumption rate of $\mathrm{Bu^tOCl}$ in BUC at 343 K *vs* concentration of acid **2** at $[\mathrm{Bu^tOCl}]_0 = 0.41$ mol L^{-1}, $[\mathbf{1}]_0 = 0.58$ mol L^{-1} (*1*); *vs* initial concentration of styrene epoxide ($[\mathbf{1}]_0$) at $[\mathbf{2}] = 0.013$ mol L^{-1} and $[\mathrm{Bu^tOCl}]_0 = 0.41$ mol L^{-1} (*2*); *vs* $[\mathrm{Bu^tOCl}]_0$ at $[\mathbf{2}] = 0.013$ mol L^{-1} and $[\mathbf{1}]_0 = 0.58$ mol L^{-1} (3); dark square is the entry at $[\mathbf{1}]_0 = 0.87$ mol L^{-1}.

An additional information is provided by the comparative study of the oxygen uptake by systems **1**—**2** and **1**—**2**—**5** in the reactor of the manometric setup (Fig. 4). Curve *1* (see Fig. 4) characterizes the fast oxygen uptake in the reactor of the manometric setup by system **1**—**2**. The solution containing **2** + $\mathrm{Bu^tOCl}$ (in the absence of **1**) does not absorb O_2 at all, whereas the absorption of **1** + $\mathrm{Bu^tOCl}$ (in the absence of **2**) is negligible (see Fig. 4, *cf.* curves *3* and *4*). Both the absence of absorption and the increasing in time gas evolution were observed in ternary system **1**—**2**—$\mathrm{Bu^tOCl}$ (see Fig 4, curve *2*). Since it is impossible to measure the oxygen uptake rate at the unknown gas evolution rate in the system, we carried out additional experiments in the bubbling reactor with the binary and ternary systems with the measurement of the consumption of **1** and **5** at the accumulation of the product of oxidation of epoxide **1**, *viz.*, benzaldehyde **4** (Fig. 5). The data in Fig. 5 show that the introduction of hypochlorite **5** in BS **1**—**2** decreases the rate of consumption of **1** by ~15%: $V_1 = 2.12 \cdot 10^{-4}$, $V_3 = 1.83 \cdot 10^{-4}$ mol L^{-1} s^{-1}, where V_1 and V_3 are the rates calculated from the slopes of curves *1* and *3*, respectively (see Fig. 5). Two explanations for the small decrease in V_1 in the presence of hypochlorite **5** are possible. One of them is related to the decrease in the concentration of protonated epoxide in the

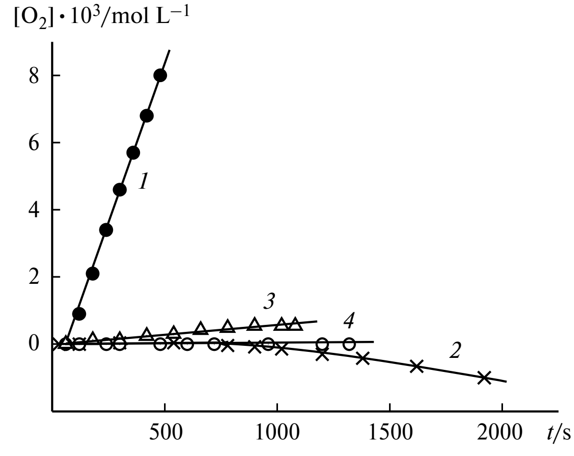


Fig. 4. Kinetic curves of oxygen uptake by binary system **1**—**2** (*1*), ternary system **1**—**2**—**5** (*2*), a solution of epoxide **1** + $\mathrm{Bu^tOCl}$ (*3*), and a solution of acid **2** + $\mathrm{Bu^tOCl}$ (*4*); $[\mathbf{1}]_0 = 0.58$ mol L^{-1}, $[\mathbf{2}] = 0.013$ mol L^{-1}, $[\mathrm{Bu^tOCl}]_0 = 0.41$ mol L^{-1}; BUC, 343 K.

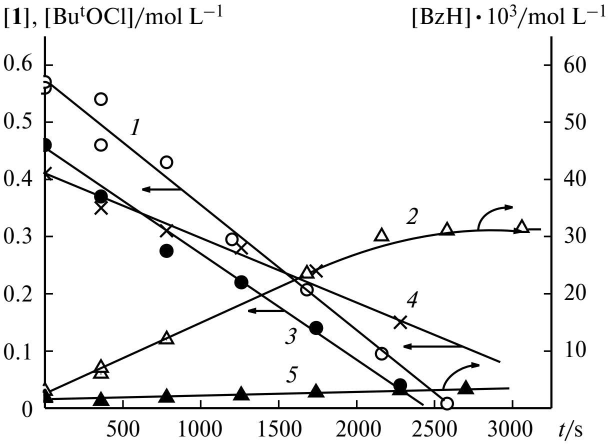


Fig. 5. Consumption curves of epoxide **1** (*1*) and accumulation curves of **4** (BzH) (*2*) in BS **1—2** (light points); consumption of epoxide **1** (*3*) and Bu^{t}OCl (*4*), as well as the accumulation of BzH (*5*) in ternary system **1—2—5** (dark points); [**2**] = = 0.013 mol L^{-1}, BUC, 343 K.

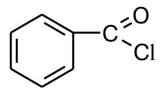
ternary system compared to the binary system because of the equilibrium

$$(\mathbf{1})\mathrm{H}^+ + \mathrm{Bu^tOCl} \rightleftharpoons \mathbf{1} + (\mathrm{Bu^tOCl})\mathrm{H}^+$$

(as mentioned above), and the second explanation is related to the inhibition effect of the Cl$^-$ ions formed, possibly, from hypochloride **5** in the ternary system, to the heterolysis of epoxide **1**, and to its oxidation (the report on the topic will be published in the Neftekhimiya Journal). These results concern the inhibition of heterolysis of epoxide **1** in BS **1—2** by tetraalkylammonium halide salts and the simultaneous oxygen uptake with BzH accumulation and indicate a rigid quantitative relationship of these processes: the *m*-fold retardation of the heterolysis rate of epoxide **1** by the chloride anion induces the *m*-fold decrease in the rate of O_2 uptake and accumulation of benzaldehyde **4**.

The data in Fig. 5 indicate that the introduction of Bu^{t}OCl into BS **1—2** decreases V_1 by ~15%, and V_4 decreases more than an order of magnitude. It resumes that the inhibition processes of heterolysis and oxidation of epoxide **1** in the presence of hypochlorite **5** differ in nature and cannot be explained by the formation of Cl$^-$ in ternary system **1—2—5**. An unusual situation, where the introduction into the oxidized system of Bu^{t}OCl with pronounced properties of the oxidant and radical initiator retards the oxygen uptake (see Fig. 4) and, hence, the accumulation of oxidation product **4** (see Fig. 5) needed an additional checking.

It is known[5] that Bu^{t}OCl can rapidly oxidize aldehydes, particularly, BzH. Therefore, it cannot be excluded that under the experimental conditions (see Fig. 5) the concentration of accumulated product **4** decreases, to some extent, because of its consumption in the reaction with hypochlorite. In the experiment similar to that presented in Fig. 5, BzH ($2.4 \cdot 10^{-2}$ mol L^{-1}) was introduced into the initial solution with an increase in the concentration of compound **4** by almost an order of magnitude (*cf.* Figs 5 and 6). It was established that at first, on mixing of the initial solution containing BzH with Bu^{t}OCl, a portion of the starting aldehyde is rapidly oxidized to benzoyl chloride (**8**). Further, during the experiment, both [BzH] and [BzCl] change slightly (see Fig. 6) and the sum [BzH] + [BzCl] increases slowly in time (see Fig. 6, curve *5*). The introduction of a high concentration of BzH at the very beginning of the experiment exerts almost no effect on the consumption rates of epoxide **1** and Bu^{t}OCl and on the consumption rate of the sum [BzH] + [BzCl]. This experiment confirmed the ability of hypochlorite **5** to inhibit the oxidative transformation of epoxide **1** to aldehyde **4**. This inhibition is caused, most likely, the complicated and many-stage character of the oxidation of epoxide **1** in the presence of acid **2**. Based on the above presented experimental data, we assume that the inhibition of oxidation of BS **1—2** is a consequence of the fast decay of the carbocation (**9**), formed upon the decomposition of the protonated epoxide cycle (**10**), in the reaction with Bu^{t}OCl, which reacts as a nucleophile in this case.



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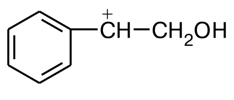

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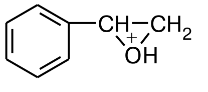

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This conclusion is consistent with the experimental data obtained earlier and in the present work: dioxygen

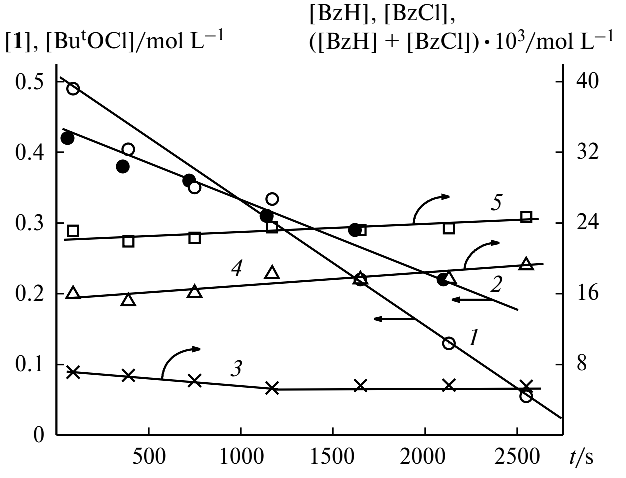
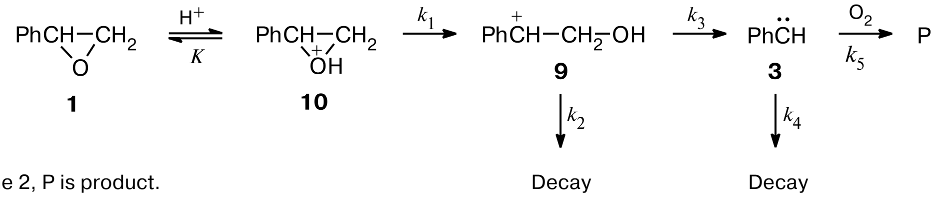


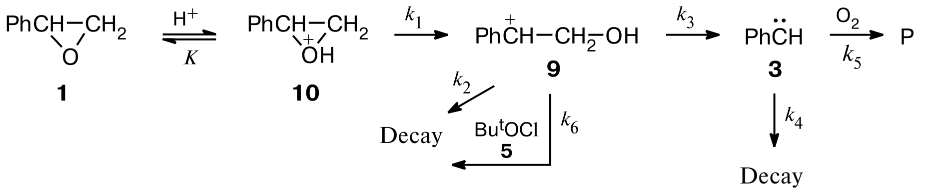
Fig. 6. Consumption curves of epoxide **1** (*1*), Bu^{t}OCl (*2*), and BzCl (*3*) and the accumulation curves of BzH (*4*) in the entry with $[\mathrm{BzH}]_0 = 2.4 \cdot 10^{-2}$ mol L^{-1}, as well as the change in the sum [BzH] + [BzCl] in time (*5*); BUC, 343 K.

Scheme 1



Here and in Scheme 2, P is product.

Scheme 2



does not inhibit the consumption of $\mathrm{Bu^tOCl}$ in the ternary system. This is the main argument in favor of the heterolytic mechanism of hypochlorite consumption. Remind that the heterolysis rates of styrene epoxide under argon and oxygen[1] are equal. However, oxygen suppressed the decomposition of hydroperoxides by system **1**—**2**.[2,3] An argument in favor of the heterolysis of compound **5** is the relative similarity of the consumption rates of reactants **1** and **5** and the apparent rate constants of this consumption. According to the data of Fig. 5, they differ by 1.5—2 times ($k_1 = 1.46 \cdot 10^{-2}$ s^{-1}, $k_5 = 0.87 \cdot 10^{-2}$ s^{-1}). It is not excluded that this divergence is related to the stoichiometry of the reaction in which two epoxide molecules are consumed and induce the disappearance of one $\mathrm{Bu^tOCl}$ molecule. At the same time, the specific consumption rates of ROOH are much lower and close by an order of magnitude to the specific rate of oxygen uptake by system **1**—**2**. In the case of hydroperoxide **6**, this characteristic is nearly equal to the rate constant of oxidation of BS **1**—**2**: $k_6 = 7.5 \cdot 10^{-4}$ s^{-1} and $k_{O2} = 6.0 \cdot 10^{-4}$ s^{-1}.[2] A comparison of the values of k_5 and k_6 shows that the specific rate of $\mathrm{Bu^tOCl}$ consumption is an order of magnitude higher than the characteristic of decomposition of hydroperoxide **6**, which is an argument in favor of the distinction of the nature of decomposition processes of reactants **5** and **6** in the presence of compounds **1** and **2**.

The mechanism explaining the oxidation of epoxide **1** with dioxygen in the presence of the acid and the decomposition of hydroperoxide in an oxygen-free atmosphere in the presence of the epoxide and acid was proposed[2] (Scheme 1).

When the process is quasi-stationary, the concentration of carbene **3** (PhHC:) is presented, according to Scheme 1, by the equation [PhHC:] = $(k_1k_3[\mathbf{1}\mathrm{H}^+])/(k_2 + k_3) \cdot (k_4 + k_5[\mathrm{O_2}])$. Taking into account the above experimental data, we may conclude that the inhibition of the oxidation with hypochlorite can be presented by Scheme 2 (*i.e.*, Scheme 1 supplemented by the channel of carbocation decay in the reaction with $\mathrm{Bu^tOCl}$ with the rate constant k_6).

In this case, the equation of the stationary concentration of phenylmethylene **3** changes: [PhHC:] = $= (k_1k_3[\mathbf{1}\mathrm{H}^+])/(k_2 + k_3 + k_6[\mathrm{Bu^tOCl}])(k_4 + k_5[\mathrm{O_2}])$; the ratio of stationary concentrations of carbene **3** in the reaction in the absence of hypochlorite **5** ($[\mathrm{PhHC:}]_0$) and in its presence ([PhHC:]) is $[\mathrm{PhHC:}]_0/[\mathrm{PhHC:}] = (k_2 + k_3 + k_6[\mathrm{Bu^tOCl}])/(k_2 + k_3) = 1 + k_6[\mathrm{Bu^tOCl}]/(k_2 + k_3)$. At $[\mathrm{Bu^tOCl}] \approx 0.4$ mol L^{-1}, the oxidation rate V measured by the accumulation rate of BzH is by ~10 times lower than V_0 in the entry without $\mathrm{Bu^tOCl}$ (see Fig. 5, curves *2* and *5*), $V_0/V = [\mathrm{PhHC:}]_0/[\mathrm{PhHC:}] \approx 10 = 1 + k_6[\mathrm{Bu^tOCl}]/(k_2 + k_3)$. For the oxidation of BS **1**—**2** without $\mathrm{Bu^tOCl}$, only ~5% of consumed epoxide **1** are transformed into benzaldehyde **4** (oxidation product).[1] Whence it can be concluded that $k_2 >> k_3$ (see Scheme 1), whereas $k_6[\mathrm{Bu^tOCl}]/k_2 = 9$ and $k_6/k_2 \approx 22$ L mol^{-1}. The introduction of $\mathrm{Bu^tOCl}$ into BS **1**—**2** decreases the stationary concentration of carbocation **5** and, as a consequence, the stationary concentration [PhHC:] responsible for the $\mathrm{O_2}$ uptake.

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