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# Reaction of chlorine dioxide with phenol

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The kinetics of phenol oxidation with chlorine dioxide in different solvents (2-methylpropan-1-ol, ethanol, 1,4-dioxane, acetone, acetonitrile, ethyl acetate, dichloromethane, heptane, tetrachloromethane, water) was studied by spectrophotometry. In all solvents indicated, the reaction rate is described by an equation of the second order $w = k[\mathrm{PhOH}]\cdot[\mathrm{ClO_2}]$. The rate constants were measured (at 10—60 °C), and the activation parameters of oxidation were determined. The reaction rate constant depends on the solvent nature. The oxidation products are a mixture of *p*-benzoquinone, 2-chloro-*p*-benzoquinone, and diphenoquinone.

**Key words:** oxidation, chlorine dioxide, phenol, rate constants.

The action of oxidants is one of the most popular methods for the functionalization of compounds belonging to different classes. From this point of view, chlorine dioxide is of great interest. The most part of works on the chemistry of chlorine dioxide were carried out in aqueous solutions at low concentrations of reactants. Data on the reactions of chlorine dioxide in organic solvents are lacking. At the same time, its use as an oxidant in the synthetic organic chemistry is of considerable interest.

The oxidation of phenols with chlorine dioxide was intensely studied[1—4] because the latter is used in some countries for purification of drinking water (first of all, from phenols). The products and main kinetic regularities of oxidation were studied. However, the oxidation of phenols in nonaqueous solvents was not virtually studied.

In this work, we established the kinetic regularities of phenol oxidation with chlorine dioxide in different solvents (2-methylpropan-1-ol (**1**), ethanol (**2**), 1,4-dioxane (**3**), acetone (**4**), acetonitrile (**5**), ethyl acetate (**6**), dichloromethane (**7**), heptane (**8**), tetrachloromethane (**9**), and water (**10**)) at 10—60 °C.

## Experimental

Chlorine dioxide was synthesized by the reaction of potassium perchlorate with oxalic acid in the presence of sulfuric acid.[5] The $\mathrm{ClO_2}$ flow was passed through a trap with $\mathrm{P_4O_{10}}$ for dehydration and then through a column packed with silica gel and cooled to 0 °C, where $\mathrm{ClO_2}$ was adsorbed. To obtain solutions of $\mathrm{ClO_2}$, the column was heated in a thermostat to 30—35 °C, and $\mathrm{ClO_2}$ was blown out by gaseous argon into a trap filled with a solvent. The concentration of $\mathrm{ClO_2}$ in a solution was determined iodometrically using the Bray method[5] and spectrophotometrically.[1] Potassium perchlorate and oxalic acid (both reagent grade) were purified by recrystallization from water. Phenol (reagent grade) was purified by double distillation in argon. All solvents were purified using known procedures.[6,7]

The reaction kinetics was studied spectrophotometrically by monitoring the chlorine dioxide consumption (using the change in the absorption at $\lambda$ = 400 nm) with a Specord M40 instrument (Carl Zeiss, Jena, Germany). The contribution of the absorption of phenol and resulting products at this wavelength to the absorbance can be neglected.[8,9] The temperature of cells with a solution of phenol and a solvent was maintained at 10—60 °C in the chamber of the spectrophotometer. Then a necessary amount of a solution of $\mathrm{ClO_2}$ was added to the working cell, and the change in its absorbance was monitored. The initial concentrations of phenol and $\mathrm{ClO_2}$ were varied within $(0.1—10.0)\cdot 10^{-2}$ and $(0.5—1.2)\cdot 10^{-3}$ mol $\mathrm{L^{-1}}$, respectively.

In order to study the oxygen effect on the kinetic regularities of the process, oxygen or an inert gas (argon) was bubbled through the cell containing a solution of phenol, a necessary amount of a solution of $\mathrm{ClO_2}$ was added, and the consumption kinetics was detected.

Reaction products were analyzed by GLC using a Chrom-5 instrument (column 3.5 m × 3 mm, 5% SE-30 on Chromaton) and $^1$H NMR spectroscopy using a Bruker AM-300 instrument (300 MHz) with $\mathrm{CDCl_3}$ as a solvent and $\mathrm{Me_4Si}$ as a reference. Benzene was used as a label for the quantitative determination of products.

## Results and Discussion

**Reaction products.** It is established that at equimolar amounts of $\mathrm{ClO_2}$ and phenol the reaction products are *p*-benzoquinone (50%), 2-chloro-*p*-benzoquinone (20%), and diphenoquinone (10%). A similar composition of the products was found for the oxidation of phenol with chlorine dioxide in water.[2,10]

**Reaction kinetics.** The reaction kinetics was studied at $[\mathrm{ClO_2}]_0 \ll [\mathrm{PhOH}]_0$ ($[\mathrm{ClO_2}]_0$ and $[\mathrm{PhOH}]_0$ are the initial

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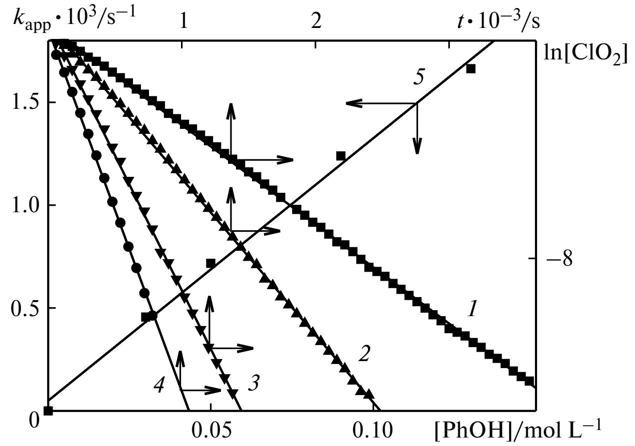


**Fig. 1.** Semilogarithmic anamorphoses of chlorine dioxide consumption in the reaction with phenol (solvent — acetone, $T = 30$ °C): $[PhOH]_0 = 3\cdot10^{-2}$ (*1*), $5\cdot10^{-2}$ (*2*), $9\cdot10^{-2}$ (*3*), and $13\cdot10^{-2}$ mol L$^{-1}$ (*4*) and the apparent rate constant of the reaction ($k_{app}$) as a function of the phenol concentration (*5*).

concentrations of chlorine dioxide and phenol, respectively). In all solvents indicated, the kinetic curves with the high correlation coefficient (0.980—0.999) are described by an equation of the first order (Fig. 1). The apparent rate constants of the first order $k_{app} = k\cdot[PhOH]^n$ ($k$ is the second-order rate constant) were calculated from the semilogarithmic anamorphoses of the kinetic curves. The plot of $k_{app}$ *vs.* $[PhOH]_0$ is linear (see Fig. 1), which indicates the first order with respect to phenol. In this case, the kinetic equation of the reaction has the form

$$-d[ClO_2]/dt = k[ClO_2]\cdot[PhOH].$$

Similar results were obtained by the oxidation of phenol in water.[11] The temperature plot of the rate constant was measured, and the activation parameters were determined in several solvents (Table 1). It is seen from the data in Table 1 that the increase in the activation energy $E_a$ is accompanied by the increase in the pre-exponential factor $A$ (compensation effect)

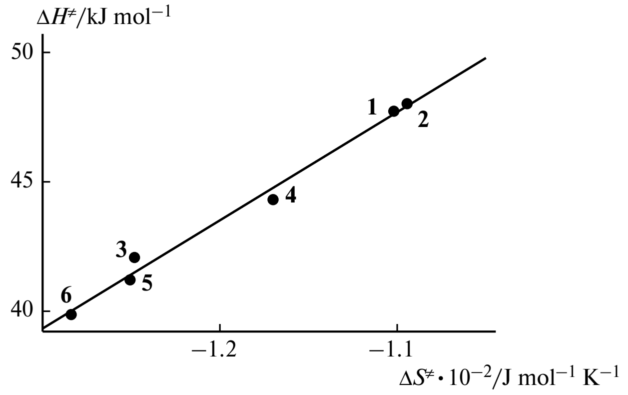


**Fig. 2.** Activation enthalpy ($\Delta H^{\neq}$) as a function of the activation entropy ($\Delta S^{\neq}$) for the oxidation of phenol with chlorine dioxide in different solvents ($T = 25$ °C; number of the point corresponds to the number of the solvent).

$$E_a = -(2.7\pm0.5) + (3.4\pm0.4)\cdot\ln A \qquad (r = 0.99).$$

The linear plot of the activation enthalpy ($\Delta H^{\neq}$) *vs.* entropy ($\Delta S^{\neq}$) (Fig. 2) is expressed by the equation

$$\Delta H^{\neq} = (93.7\pm2.6) + (0.42\pm0.02)\cdot\Delta S^{\neq} \qquad (r = 0.99).$$

The presence of the compensation effect indicates, most likely, that the reaction mechanism in this series of solvents remains unchanged.

**Effect of the solvent nature on the reaction rate constant.** The isokinetic temperature calculated from the slope of the plot of $\Delta H^{\neq}$ *vs.* $\Delta S^{\neq}$ is 150±20 °C, which is much higher than the reaction temperature (10—60 °C). Therefore, the solvent effect on the kinetic regularities of oxidation can be analyzed in the studied temperature interval. Analysis of the data presented in Table 1 shows that the reaction rate increases in the following series of solvents:

**Table 1.** Activation parameters of the oxidation of phenol with chlorine dioxide in several solvents ($T = 25$ °C)

| Solvent | $k\cdot10^2$ /L mol$^{-1}$ s$^{-1}$ | ln$A$ | $E_a$ | $\Delta H^{\neq}$ | $\Delta G^{\neq}$ | $\Delta S^{\neq}$ /J mol$^{-1}$ K$^{-1}$ | $B$* |
|---|---|---|---|---|---|---|---|
| | | | kJ mol$^{-1}$ | | | | |
| **1** | 0.61±0.03 | 15±1 | 50±4 | 48±3 | 81±5 | −110±8 | 236 |
| **2** | 0.60±0.03 | 15±1 | 51±4 | 48±3 | 81±6 | −109±7 | 235 |
| **3** | 1.12±0.06 | 13±1 | 45±3 | 42±2 | 79±5 | −124±8 | 237 |
| **4** | 1.12±0.06 | 14±1 | 47±3 | 44±3 | 79±5 | −117±6 | 224 |
| **5** | 1.51±0.07 | 13±1 | 44±3 | 41±2 | 78±5 | −125±8 | 181 |
| **6** | 1.72±0.08 | 13±1 | 42±2 | 40±3 | 78±6 | −128±8 | 160 |
| **7** | 28.0±1.4 | — | — | — | — | — | 23 |
| **8** | 37.0±1.9 | — | — | — | — | — | 0 |
| **9** | 49.0±3.4 | — | — | — | — | — | 0 |
| **10** | 24.0±1.6 | — | — | — | — | — | 156 |

* According to the data in Ref. 12.

**1** < **2** < **3** < **4** < **5** < **6** < **7** < **8** < **9**. This implies a tendency for decreasing the rate constant of phenol oxidation with an increase in the polarity of the medium.

We failed to describe the influence of the solvent nature on the reaction rate constant taking into account only the polarity of the solvent. This can be explained, most likely, by the contribution of specific solvation. It is known[13] that the affinity of phenol to form hydrogen bonds with the solvent plays a substantial role in its reactivity. For example, when tetrachloromethane, which does not form hydrogen bonds, is substituted by 1,4-dioxane, the rate of the reaction of 2,4,6-tri-*tert*-butylphenoxyl with phenol decreases by ~20 times (from 8 to 0.38 L $\text{mol}^{-1}$ $\text{s}^{-1}$).[14] This is explained by the fact that the solvent forming hydrogen bonds shields the O—H bond of phenol, thus impeding its attack by phenoxyl. In order to take into account this contribution in the total influence of the solvent, we chose as a parameter the donor number $B$, which is determined from the shift of the absorption band of the OH group in the IR spectrum of phenol.[12]

In the framework of the equation $\log k = \log k^0 + \beta B$ ($k^0$ is the reaction rate constant under the conditions accepted to be standard), we obtained the linear correlation (Fig. 3; solvent **10** was excluded from the plot)

$$\log k = -(0.9\pm0.1) - (1.7\pm0.1)\cdot10^{-2}\cdot B \quad (r = 0.98).$$

The negative sign of the β parameter indicates that the transition state is less polar than the initial state.[15]

**Reaction mechanism.** As follows from the analysis of the solvent effect on the rate constant of phenol oxidation with chlorine dioxide, the kinetic data do not obey regularities characteristic of other media when water is used as the solvent. This indicates that the mechanism of the reaction in water differs from that in other solvents.

A series of the data[9,11,16–19] in water suggests the dissociation of phenol to form the phenoxide anion that reacts with $ClO_2$ (Scheme 1).

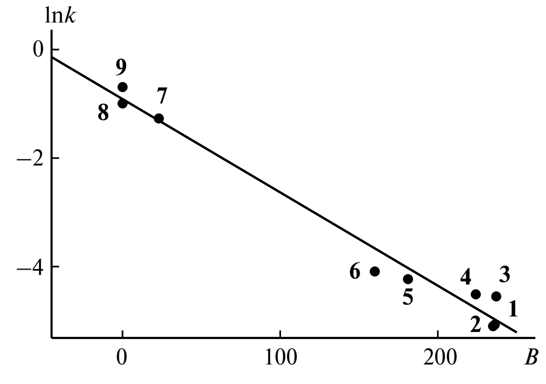
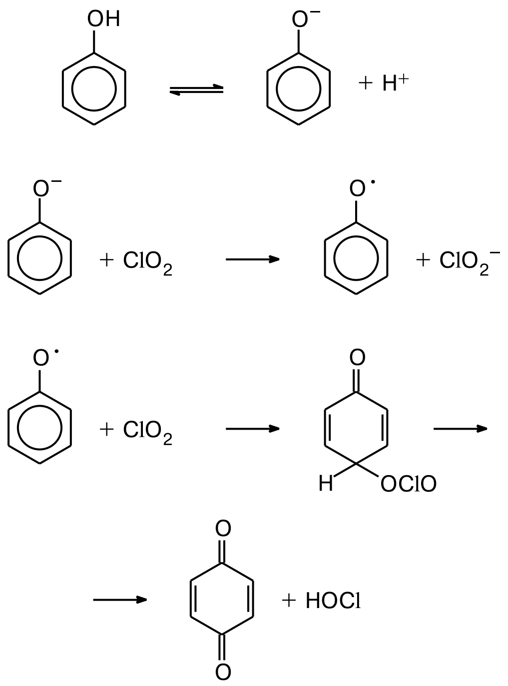


**Fig. 3.** Logarithm of the rate constant of phenol oxidation with chlorine dioxide ($k$) as a function of the donor number of the solvent $B$ ($T$ = 25 °C; solvent **10** is excluded from the correlation).

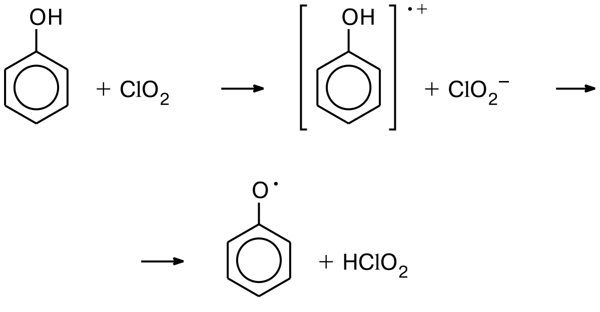
**Scheme 1**



As for the reactions of $ClO_2$ with olefins,[20–22] the formation of an unstable ether intermediate ROClO is postulated, which rapidly decomposes to form hypochlorous acid.

In nonaqueous low-polarity solvents, phenol does not virtually dissociate to the proton and phenoxide anion. Therefore, the transfer of an electron from the phenol molecule to the $ClO_2$ molecule can be considered as the primary act. Then the proton is eliminated to form the phenoxyl radical and chlorous acid (Scheme 2).

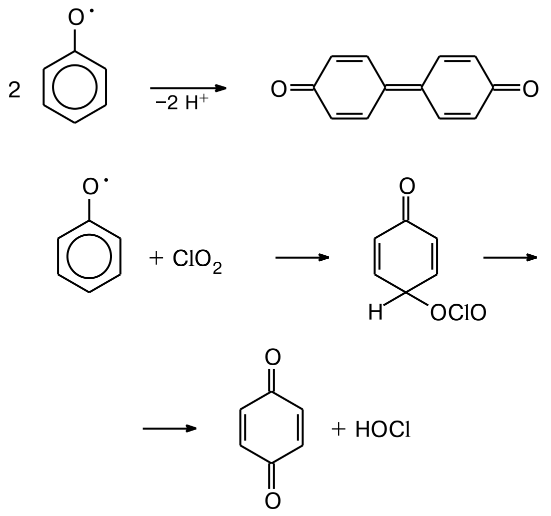
**Scheme 2**



The phenoxyl radical can either react with another phenoxyl radical to form diphenoquinone or undergo further oxidation with chlorine dioxide to form easily decomposing alkyl chlorite (Scheme 3).

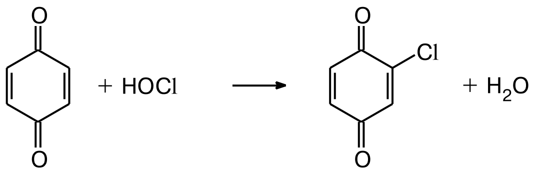
Hypochlorous acid, which appears due to the decomposition of alkyl chlorite, interacts with organic com-

**Scheme 3**



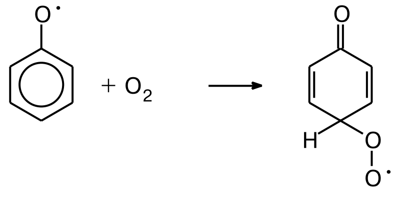
pounds,[5] which explains the formation of the chloro derivatives by the oxidation of phenol with chlorine dioxide (Scheme 4).

**Scheme 4**



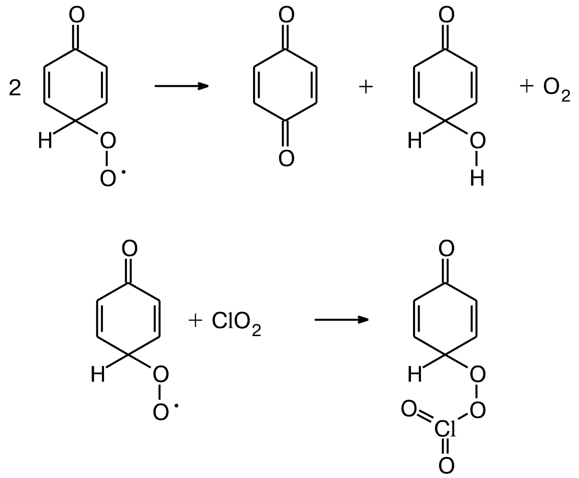
It is known that the phenoxyl radicals readily react with oxygen,[23] whose content during kinetic experiments in solutions is comparable with the concentration of chlorine dioxide ($[ClO_2] = (0.5—1.2) \cdot 10^{-3}$ mol L$^{-1}$, $[O_2] = 1.5 \cdot 10^{-3}$ mol L$^{-1}$).[24] For example, the rate constant of the reaction of the 2,4,6-tri-*tert*-butylphenoxyl radical with oxygen is reported to be temperature-independent and equal to 2400 L mol$^{-1}$ s$^{-1}$.[13] Therefore, the reaction of the phenoxyl radical with oxygen should be taken into account (Scheme 5).

**Scheme 5**



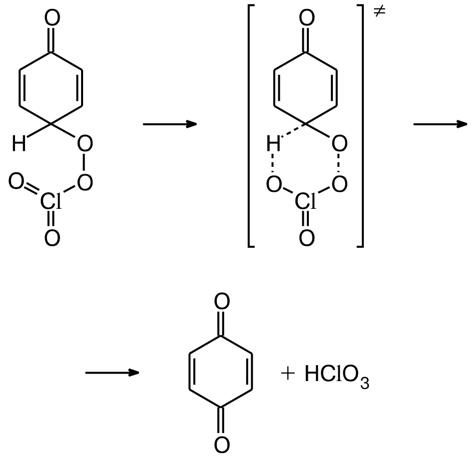
The peroxy radicals formed can either disproportionate or decay in linear termination with chlorine dioxide. In the latter case, the O-centered radical adds to the Cl atom[25] to form peroxy ether of chloric acid (Scheme 6).

**Scheme 6**



By analogy to alkyl chlorites, peroxychlorate decomposes to quinone and chloric acid (Scheme 7).

**Scheme 7**



Let us consider how the involvement of molecular oxygen in the reaction influences the kinetics using the simplified scheme

$$\mathrm{PhOH} + \mathrm{ClO_2} \xrightarrow{k_1} \mathrm{PhO^{\bullet}} + \mathrm{HClO_2},$$

$$\mathrm{PhO^{\bullet}} + \mathrm{ClO_2} \xrightarrow{k_2} \mathrm{OClOPhO},$$

$$\mathrm{PhO^{\bullet}} + \mathrm{O_2} \xrightarrow{k_3} \mathrm{OOPhO^{\bullet}},$$

$$\mathrm{OOPhO^{\bullet}} + \mathrm{OOPhO^{\bullet}} \xrightarrow{k_4} \text{Termination},$$

$$\mathrm{OOPhO^{\bullet}} + \mathrm{ClO_2} \xrightarrow{k_5} \mathrm{ClO_2OOPhO^{\bullet}}.$$

In this case, the expression for the consumption rate of chlorine dioxide takes the form

$$-\mathrm{d}[\mathrm{ClO_2}]/\mathrm{d}t = k_1[\mathrm{PhOH}][\mathrm{ClO_2}] + k_2[\mathrm{PhO}^{\bullet}][\mathrm{ClO_2}] + k_3[\mathrm{OOPhO}^{\bullet}][\mathrm{ClO_2}].$$

When the quasistationarity condition is applied with respect to the $\mathrm{PhO}^{\bullet}$ radical, we obtain

$$\mathrm{d}[\mathrm{PhO}^{\bullet}]/\mathrm{d}t = k_1[\mathrm{PhOH}][\mathrm{ClO_2}] - k_2[\mathrm{PhO}^{\bullet}][\mathrm{ClO_2}] - k_3[\mathrm{PhO}^{\bullet}][\mathrm{O_2}] = 0,$$

$$[\mathrm{PhO}^{\bullet}] = (k_1[\mathrm{PhOH}][\mathrm{ClO_2}])/(k_2[\mathrm{ClO_2}] + k_3[\mathrm{O_2}]).$$

A similar approach to the determination of the quasistationary concentration of $\mathrm{OOPhO}^{\bullet}$ leads to the trinomial equation and a complicated expression for the reaction rate. Therefore, let us consider two ultimate cases: $\mathrm{OOPhO}^{\bullet}$ reacts only with $\mathrm{OOPhO}^{\bullet}$ (square termination) and $\mathrm{OOPhO}^{\bullet}$ reacts only with $\mathrm{ClO_2}$ (linear termination). In the first case, where $w_5 = 0$, from the quasistationarity condition we have

$$\mathrm{d}[\mathrm{OOPhO}^{\bullet}]/\mathrm{d}t = k_3[\mathrm{PhO}^{\bullet}][\mathrm{O_2}] + k_4[\mathrm{OOPhO}^{\bullet}]^2 = 0,$$

$$[\mathrm{OOPhO}^{\bullet}] = [(k_3[\mathrm{PhO}^{\bullet}][\mathrm{O_2}])/k_4]^{0.5}.$$

In this case, the reaction rate is

$$-\frac{\mathrm{d}[\mathrm{ClO_2}]}{\mathrm{d}t} = k_1[\mathrm{PhOH}][\mathrm{ClO_2}] + \frac{k_1k_2[\mathrm{PhOH}][\mathrm{ClO_2}]^2}{k_2[\mathrm{ClO_2}] + k_3[\mathrm{O_2}]}.$$

In another case, where $w_4 = 0$, we have

$$\mathrm{d}[\mathrm{OOPhO}^{\bullet}]/\mathrm{d}t = k_3[\mathrm{PhO}^{\bullet}][\mathrm{O_2}] - k_5[\mathrm{OOPhO}^{\bullet}][\mathrm{ClO_2}] = 0,$$

$$[\mathrm{OOPhO}^{\bullet}] = (k_3[\mathrm{PhO}^{\bullet}][\mathrm{O_2}])/(k_4[\mathrm{ClO_2}]),$$

$$[\mathrm{OOPhO}^{\bullet}] = \frac{k_3[\mathrm{O_2}]}{k_5[\mathrm{ClO_2}]}\cdot\frac{k_1[\mathrm{PhOH}][\mathrm{ClO_2}]}{k_2[\mathrm{ClO_2}] + k_3[\mathrm{O_2}]},$$

$$-\mathrm{d}[\mathrm{ClO_2}]/\mathrm{d}t = k_1[\mathrm{PhOH}][\mathrm{ClO_2}] + \frac{k_2[\mathrm{ClO_2}]}{k_2[\mathrm{ClO_2}] + k_3[\mathrm{O_2}]}k_1[\mathrm{PhOH}][\mathrm{ClO_2}] + \frac{k_3[\mathrm{O_2}]k_5[\mathrm{ClO_2}]}{(k_2[\mathrm{ClO_2}] + k_3[\mathrm{O_2}])k_5[\mathrm{ClO_2}]}k_1[\mathrm{PhOH}][\mathrm{ClO_2}] = 2k_1[\mathrm{PhOH}][\mathrm{ClO_2}].$$

The kinetics of chlorine dioxide consumption fits the first-order law, and this favors the latter assumption: the rate of the reaction of the peroxy radicals with $\mathrm{ClO_2}$ is much higher than that of the reaction with oxygen.

Additional data on the role of oxygen in the reaction were obtained by measuring the rate in the reaction mixtures pre-saturated with oxygen or purged with an inert gas. It turned out that the additional bubbling of the reaction mixture with oxygen or an inert gas does not affect the kinetic regularities of the consumption of chlorine dioxide. This can be explained by the fact that the reaction of the phenoxyl radicals with $\mathrm{ClO_2}$ occurs much more rapidly than that with oxygen. Although published data on rate constants of reactions of phenoxyl radicals with chlorine dioxide are lacking, we can assume that these reaction rate constants are close to the rate constants of the diffusion-limited reactions (note that the rate constants of the reaction of $\mathrm{ClO_2}$ with the phenoxide anions range within $10^7$—$10^9$ L mol$^{-1}$ s$^{-1}$).[11]

Thus, the kinetic regularities of phenol oxidation with chlorine dioxide were studied in different solvents, the reaction products were identified, their yields were determined, and the probable mechanism of the reaction was proposed.

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