Oxidation of phenols with chlorine dioxide

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The oxidation of different phenols, *viz.*, phenol, 3-methylphenol, 4-methylphenol, 4-*tert*-butylphenol, 2-cyclohexylphenol, 2,6-di-*tert*-butyl-4-methylphenol, and 2,4-dichlorophenol, with chlorine dioxide in acetonitrile was studied spectrophotometrically. The reaction rate is described by a second-order equation $w = k[PhOH] \cdot [ClO_2]$. The rate constants were measured and activation parameters of oxidation were determined in a temperature interval of 10–60 °C. A dependence of the reaction rate constant on the phenol structure was found. The oxidation products were identified, and their yields were established.

Key words: oxidation, chlorine dioxide, phenols, rate constants.

We have previously¹ studied the kinetics of phenol oxidation with chlorine dioxide in several solvents. However, the influence of the phenol structure on the reaction rate was not considered. In this work, we studied the oxidation of phenols with different structures, viz, phenol (1), 3-methylphenol (2), 4-methylphenol (3), 4-*tert*-butylphenol (4), 2-cyclohexylphenol (5), 2,6-di*tert*-butyl-4-methylphenol (6), and 2,4-dichlorophenol (7), with chlorine dioxide in acetonitrile.

Experimental

Chlorine dioxide was synthesized by the reaction of potassium chlorate with oxalic acid in the presence of sulfuric acid.¹ Phenols 1–3 and 5 (reagent grade) were twice distilled in argon, phenols 4 and 7 (reagent grade) were sublimed *in vacuo*, and phenol 6 (reagent grade) was recrystallized from EtOH followed by sublimation *in vacuo*. Acetonitrile (reagent grade) was purified by distillation and then distilled above P_2O_5 to remove water traces.²

The kinetics of phenol oxidation at 10–60 °C was studied¹ spectrophotometrically by a change in the absorbance of chlorine dioxide at $\lambda = 400$ nm on a Specord M40 instrument (Carl Zeiss, Jena). At this wavelength, the contribution of absorbances from phenols and final products to the total absorbance can be neglected.^{3,4} The initial concentrations of phenols **1–5**, **7** and chlorine dioxide were varied within (0.1–10.0) \cdot 10⁻² and (0.5–1.2) \cdot 10⁻³ mol L⁻¹, respectively. In the case of phenol **6**, the reaction kinetics was studied at equal concentrations of the reactants ([ClO₂]₀ = [**6**]₀ = (0.5–1.2) \cdot 10⁻³ mol L⁻¹).

To study the oxygen influence on the kinetic regularities of the process, dioxygen or an inert gas was passed through the reaction mixture.

Reaction products were analyzed by GLC on a Chrom-5 instrument (column 3.5 m \times 3 mm, 5% SE-30 on Chromatone) and by ¹H NMR spectroscopy on a Bruker AM-300 instrument

(300 MHz) using $CDCl_3$ as a solvent and Me_4Si as a standard. Benzene was used as an internal standard in quantitative determination of the products.

Results and Discussion

Reaction products. The overall conversion of phenols is observed at the molar ratio of phenol to chlorine dioxide equal to 1 : 2. The yields of the identified products are presented in Table 1. Similar products were obtained by the oxidation of 2,6-xylenol and mesitol with chlorine dioxide in water.⁵ Substances formed from phenol 7 were not analyzed. Some other products are present in the reaction mixture along with the indicated products. How-

Table 1. Yields of the products of oxidation of phenols 1-6

Phenol	Product	Yield* (%)	
1	1,4-Benzoquinone		
	2-Chloro-1,4-benzoquinone	20	
	Diphenoquinone	10	
2	2-Methyl-1,4-benzoquinone	40	
	5-Chloro-2-methyl-1,4-benzoquinone	30	
	3,3',5,5'-Tetramethyldiphenoquinone	5	
3	1,4-Benzoquinone	30	
	4-Methyl-p-quinol	30	
4	1,4-Benzoquinone	30	
	4- <i>tert</i> -Butyl- <i>p</i> -quinol	30	
5	2-Cyclohexyl-1,4-benzoquinone	45	
	5-Chloro-2-cyclohexyl-1,4-benzoquinone	20	
	2,2',6,6'-Tetracyclohexyldiphenoquinone	5	
6	2,6-Di- <i>tert</i> -butyl-1,4-benzoguinone	35	
	2,6-Di-tert-butyl-4-methyl-p-quinol	30	

* The yield was recalculated to the consumed oxidant.

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 10, pp. 2184–2187, October, 2004.

1066-5285/04/5310-2281 © 2004 Springer Science+Business Media, Inc.



Fig. 1. Semilogarithmic anamorphoses of the consumption curves of chlorine dioxide in the reaction with phenol (1) (T = 40 °C): $[1]_0 = 0.05$ (I), 0.09 (2), 0.13 (3), and 0.17 mol L⁻¹ (4) and the apparent reaction rate constant (k_{app}) as a function of the phenol concentration (5).

ever, attempts of their identification failed, and their amount was especially large in the case of phenols 3, 4, and 6.

Reaction kinetics. For phenols 1-5 and 7, the reaction kinetics was studied under the condition of $[ClO_2]_0 \ll [PhOH]_0$, where $[ClO_2]_0$ and $[PhOH]_0$ are the initial concentrations of chlorine dioxide and phenol, respectively. For all phenols studied, the kinetic curves with a high correlation coefficient (0.980-0.999) are described by an equation of the pseudo-first order (Fig. 1). The apparent rate constants of the pseudo-first order $k_{app} = k[PhOH]^n$ (k is a rate constant of the second order) were calculated from the semilogarithmic anamorphoses of the kinetic curves. These apparent constants are independent of the ClO₂ concentration. The dependence of k_{app} on $[PhOH]_0$ is linear (see Fig. 1), indicating the first order with respect to phenol. Thus, the kinetic equation of the reaction has the form

$$-d[ClO_2]/dt = k[ClO_2][PhOH].$$
(1)

For phenol **6**, the kinetics was studied at 25 °C under the condition that the initial concentrations of phenol and chlorine dioxide were equal. In this case, the kinetic curves with a high correlation coefficient (0.980-0.999) are described by an equation of the second order, and the form of the kinetic equation is similar to that of Eq. (1). Similar results have been obtained previously⁶ for the oxidation of phenol **1** in water.

The activation parameters of the oxidation process (excluding those for phenol 6) are presented in Table 2.

Influence of the phenol structure on the reaction rate constant. The data presented in Table 2 show that the reactivity of phenols toward chlorine dioxide increases in the series 7 < 1 < 2 < 5 < 4 < 3 < 6.

A commonly accepted approach to establish a relationship between the structure and reactivity of organic compounds is the use of the Hammett equation,⁷ implying a linear dependence of the logarithm of a reaction rate constant on a constant of substituent σ

$$\ln k = \ln k_0 + \rho \sigma,$$

where k_0 and ρ are constants.

An advantage of this approach is that the σ values for di- and trisubstituted organic substances can be calculated as the sum of constants of all substituents ($\Sigma\sigma$). The use of σ constants is somewhat restricted by the absence of data for substituents in the *ortho*-positions of the benzene ring, which is related, first of all, to steric hindrances caused by these substituents.⁸ It has previously⁹ been shown that σ constants of substituents in the *para*-position can be used to describe the influence of substituents in the *ortho*-position. We performed similar data processing and obtained a linear dependence with a low correlation coefficient. When phenols **3** and **6** were excluded from consideration, the dependence gained a pronounced linear character (Fig. 2)

$$\ln k = -(4.02 \pm 0.02) - (3.0 \pm 0.1) \cdot \Sigma \sigma \qquad (r = 0.998).$$

Table 2. Activation parameters of oxidation of phenols 1–7 with chlorine dioxide (T = 25 °C, measurement error $\leq 10\%$)

Phenol	$k \cdot 10^1$	lnA	Ea	ΔH^{\neq}	ΔG^{\neq}	ΔS^{\neq}	$\Sigma \sigma^a$	$E_{1/2}^{b}$
$/L \text{ mol}^{-1} \text{ s}^{-1}$				kJ mol ⁻¹		$/J \text{ mol}^{-1} \text{ K}^{-1}$		/V
1	0.17	13	42	40	83	-145	0.000	0.633
2	0.24	15	46	44	82	-129	-0.069	0.607
3	3.53	11	30	28	76	-160	-0.170	0.543
4	0.33	15	46	43	81	-129	-0.197	0.578
5	0.28	14	44	42	82	-134	-0.150	0.600
6	400	_	_	_	_	_	-0.466	0.381
7	0.05	16	53	51	86	-120	0.600	0.645

^{*a*} According to the published data.¹¹

^b According to the published data.¹⁰



Fig. 2. Logarithm of the rate constant of oxidation of phenols 1, 2, 4, 5, and 7 with chlorine dioxide (*k*) as a function of the substituent constant σ (*T* = 25 °C; phenols 3 and 6 are excluded from correlation).

The negative value of constant ρ indicates that the introduction of electron-releasing substituents into a phenol molecule enhances the electron density on the reaction center and increases the reactivity. It follows from this that chlorine dioxide behaves as an electrophilic agent, and, most likely, the electron transfer from phenol to a chlorine dioxide molecule is the first (limiting) step of the oxidation process. A rather high absolute value of ρ indicates a strong sensitivity of the oxidation rate constant to structural changes in the initial reactants. The calculated ρ value differs slightly from $\rho = -3.2\pm0.4$ obtained for the oxidation of phenols in water.⁶

The use of any measured property of a whole molecule is an alternative for correlations based on substituent constants. For the oxidation of substituted phenols with chlorine dioxide, it seems reasonable to assume a correlation between k and redox potentials of phenols. For example, potentials of the oxidation half-wave $(E_{1/2})$ are known¹⁰ for more than 40 substituted phenols. The obtained potentials of the oxidation half-wave reflect the potential of elimination of the first electron from a phenol molecule to form a phenoxyl radical. The $E_{1/2}$ value depends on the nature of substituents and can be calculated when the structure of substituents in a phenol molecule is known.¹⁰ The $E_{1/2}$ values for all phenols studied are presented in Table 2. The plot of the logarithm of the rate constant vs. $E_{1/2}$ is linear (Fig. 3)

$$\ln k = (16\pm 1) - (33\pm 2) \cdot E_{1/2} \qquad (r = 0.98).$$

It is seen that the reaction rate decreases with an increase in the half-wave potential.

Taking into account the data obtained, the formation of the main reaction products can be presented by Scheme 1, according to which the first (limiting) step is the electron transfer from a phenol molecule to a chlorine dioxide molecule to form a phenoxyl radical.

Then the phenoxyl radical is oxidized by another chlorine dioxide molecule to form quinone (Scheme 2).



Fig. 3. Logarithm of the rate constant of oxidation of phenols 1–7 with chlorine dioxide (*k*) as a function of the half-wave potential of phenol oxidation $(E_{1/2})$ (T = 25 °C).

Scheme 1





For $R^2 = H$, the phenoxyl radicals can dimerize (Scheme 3).

In the case of $R^2 = Alk$, quinols can be formed presumably *via* the following reaction (Scheme 4).

The presence of chlorosubstituted derivatives in the oxidation of phenols with chlorine dioxide can be ex-



Scheme 3





plained by the fact that hypochlorous acid chlorinates organic compounds¹¹ (Scheme 5).

Scheme 5



It is known¹² that phenoxyl radicals react easily with oxygen, whose content in a solution during kinetic experiments is comparable with the chlorine dioxide concentration ([ClO₂] = $(0.5-1.2) \cdot 10^{-3}$ mol L⁻¹, [O₂] = $1.5 \cdot 10^{-3}$ mol L⁻¹).¹³ It turned out that, in the case of

phenols 1-7, bubbling of the reaction mixture with oxygen or an inert gas has no effect on the kinetics of chlorine dioxide consumption.

Thus, in this work, we studied the oxidation of different phenols with chlorine dioxide, established a relationship between the phenol structure and reactivity, identified the main oxidation products, and proposed the reaction scheme consistent with the experimental data.

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Received February 14, 2003; in revised form April 13, 2004