

STUDIES CONCERNING PHENOLIC COMPOUNDS OXIDATION (2-AMINOPHENOL, 2-CHLOROPHENOL, RESORCINOL) BY CHLORINE DIOXIDE IN WATER SOLUTIONS

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ABSTRACT

This paper objective was searching of oxidation process of some phenolic compounds (2-aminophenol, 2-chlorophenol, resorcinol) with chlorine dioxide, by use of molar ratio method. The analysis of oxidation products in water solutions, allowed identification of benzoquinone formation using ultraviolet and visible spectrophotometry, due to its specific maxima at 247 and 500 nm. Benzoquinone oxidation by chlorine dioxide is a slowly process for about 12- 24 hours, when the solutions become colourless, and pH is reduced with 2-3 units.

The rate constants according to second order reaction, showed the following evolution of oxidation:

- a). a fast step, within a few minutes, $k_2 = 0.145 \cdot 10^3 \text{ mol}^{-1} \text{ s}^{-1}$;*
- b). an intermediate step, in the next 30 minutes, when the reaction rate decreases about 50 times, $k_2 = 0,27 \cdot 10 \text{ mol}^{-1} \text{ s}^{-1}$;*
- c). a third step, a slow one, when benzoquinone is oxidized to organic acids, Phenolic compounds reactivity in the oxidation process with chlorine dioxide, according to the rate constants values was: resorcinol > 2-aminophenol \cong 2-chlorophenol.*

Key words:

phenolic compounds; chlorine dioxide; advanced oxidation

1. INTRODUCTION

Chlorine dioxide, by itself or in combination with other oxidants, is widely used in water and waste water treatment. "WHERE" and "WHEN" can be used this technology, is the way to an efficient and economic, as

well, water treatment.^[1,2,3,4,5] Advantages of chlorine dioxide as oxidant and disinfectant in water technology are due to its properties. The most important properties are:

- chlorine dioxide is efficient in a wide pH interval $\text{pH} = 4 - 10$;
- it does not react with amines, ammonia, or any other inorganic compounds;
- chlorine dioxide can be used at very low concentrations, such as 0.3 – 1.0 ppm, which is enough to control the biological activity;
- a high reaction rate for chlorine dioxide, which is complete in water solutions;
- it is not corrosive, even at a high level of concentration.

From chemical point of view, very important is that the active part of ClO_2 molecule is the O_2 , and not Cl. There are no secondary by-products obtained, using ClO_2 such as using chlorine: trihalomethanes, chlorophenols or other chlorinated aromatic compounds (PCB); most organic compounds reacting with chlorine dioxide leads to simple organic compounds. For water treatment, in order to obtain drinking water, chlorine dioxide replaces chlorine and simultaneously the formation of the organo-halogenated compounds, known as cancerous substances, are not formed ^[6,7,8,9,10,11,12,13].

Phenolic compounds reacts rapidly with chlorine dioxide after a first order reaction. Rate constant for phenol is between $2 - 4 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C at $\text{pH} = 7$. Chlorine dioxide reactivity over phenolic compounds can lead to formation of quinones and chloroquinones, and also, unbinds aromatic compounds forming aliphatic compounds, as well. From this point of view, phenolic compounds can be:

- monophenols, that are not substituted in *para* position and hydroquinone, which are oxidized to quinone and chloroquinones, without unbinding the aromatic cycle;
- phenols substituted in *para* position, di- or triphenols, such as resorcinol, pirogalol or fluoroglucinol, which by oxidation with chlorine dioxide, unbinds the aromatic cycle, obtaining carboxylic acids, such as oxalic acid, maleic, fumaric, and carbon dioxide.

In the paper, the objective was searching the oxidation process for some phenolic compounds (resorcinol, 2-aminophenol and 2-chlorophenol) with chlorine dioxide, using molar ratio method, in water solutions.

2. MATERIALS AND METHODS

Phenolic compound concentration was kept constant, and that of chlorine dioxide has been varied. Chlorine dioxide concentrations dependence versus time, was studied using ferrous ammonia sulphate in presence of N,N-diethyl-p-phenylenediamine (DPD-FAS) method, and phenol concentrations were determined by use of ultraviolet spectrophotometry. Other variable parameters were: pH 6 and 8, and temperatures 20°C and 40°C .

Chlorine dioxide, with a concentration of 2.05 g/l, was generated using solid-solid reaction of potassium chlorate with oxalic acid. For

phenolic compounds were used solutions with a concentration of 0.2 mmol/l. The working solutions were prepared at 100 ml, with molar ratios of chlorine dioxide: phenolic compound in range of 0.02:0.2 – 1.2:0.2 (mmol:mmol).

According to the literature which indicates first order reaction for chlorine dioxide as well for phenolic compounds in water solutions, and a second order for the global reaction ^[14], the relation of rate constant corresponding to second order reaction, with different initial concentrations of reactants was used:

$$K_2 = 1 / t (C_A - C_B) \ln C_B (C_A - X) / C_A (C_B - X) \quad (1)$$

where :

C_A, C_B = the initial reactant concentrations; $X = C_A - C_T$ and $X = C_B - C_T$;
 C_T = each reactant concentration, at time t.

The correlations between ultraviolet absorptions for resorcinol (eq. 2,3), 2-aminophenol (eq.4,5), and 2-clorophenol (eq.6,7) and corresponding concentrations(0.44-22.0 mg/l) were determined, at pH 6 and 8:

$$Y = 0.0165 X + 0.0265 ; r = 0.9905 ; \text{pH} = 6 ; \lambda = 273 \text{ nm} \quad (2)$$

$$Y = 0.0160 X + 0.0116 ; r = 0.9993 ; \text{pH} = 8 ; \lambda = 273 \text{ nm} \quad (3)$$

$$Y = 0.025 X + 0.081 ; r = 0.9980 ; \text{pH} = 6 ; \lambda = 227 \text{ nm} \quad (4)$$

$$Y = 0.0277 X + 0.126 ; r = 0.9971 ; \text{pH} = 8 ; \lambda = 227 \text{ nm} \quad (5)$$

$$Y = 0.0781 X + 0.111 ; r = 0.9994 ; \text{pH} = 6 ; \lambda = 225 \text{ nm} \quad (6)$$

$$Y = 0.0736 X + 0.104 ; r = 0.9780 ; \text{pH} = 8 ; \lambda = 225 \text{ nm} \quad (7)$$

Where, Y =absorptions ; X= concentrations.

3. RESULTS AND DISCUSSION

Preliminary experiments were undertaken, in which phenolic compound concentration was kept constant (0.2 mmol/l) and those of chlorine dioxide were between 0.02 – 1.2 mmol/l, at two pH values, and colour evolution of solutions was followed.

For resorcinol at pH = 6, after chlorine dioxide introduction, the initial colourless of solutions become red and then dark red, in accordance with the concentration increasing, from 0.02 mmol/l to 0.6 mmol/l of oxidant. For higher concentrations of chlorine dioxide the solutions turn to yellow, due to the residual chlorine dioxide. Spectrophotometric analysis of coloured solutions, showed a maximum absorption value at 500 nm that corresponds to benzoquinone, which is formed rapidly in the first contact minutes, and other its specific signal in ultraviolet, at 247 nm.

Hydroquinone formation within the first seconds of reaction between chlorine dioxide and phenolic compounds cannot be spectrophotometric detected; but the quinone formation, in the first 2-3 minutes can be detected, because it is stable for a few hours. The red colour of benzoquinone gets intensive in the first 30-60 minutes in the case of resorcinol, after which its slow oxidation begins, and the process is finished during 12-24 hours, to organic acids: the pH decreases with 2-3 units, the colour intensity decreasing and the disappearing of signal in ultraviolet takes place. For the molar ratio chlorine dioxide:resorcinol of

0.6:0.2 (mmol:mmol), the following successive rapid reactions, characterized by colour changing, were observed: the incolor resorcinol solution is rapidly turning to rose-red-yellow-green within 2-3 minutes, because a chlorine dioxide excess.

Both molar ratio variation and recording of corresponding ultraviolet-visible spectra, allowed identification of oxidation reaction steps. E.g., for the molar ratios chlorine dioxide:resorcinol of 0.2:0.2 and 0.6:0.2 (mmol/mmol), the evolution of absorption spectra versus time, fig. 1 and 2, showed the followings:

- for the first ratio, the disappearance of the 273 nm maximum (samples 2,3,4,5 fig.1) and the moving of maximum from 194 nm to 216 nm; -the presence of absorption in visible region of benzoquinone at 500 nm and that for chlorine dioxide at 360 nm;
- for the second ratio, due to the high chlorine dioxide concentration, resorcinol is oxidized complete, and specific maximum from 194 nm completely disappeared; in the visible spectrum, the signal of benzoquinone is small, $0,011 \text{ cm}^{-1}$, and the dominant color being that of chlorine dioxide excess; after one hour contact chlorine dioxide concentration is 0,15 mmol/l, and after 12 hours 0,02 mmol/l, curve 5 in fig 2, where resorcinol and intermediary benzoquinone are absent, and decreasing pH value from 6 to 3.1 shows organic acids formation. Due to high reactivity of chlorine dioxide with resorcinol, the spectrum at 247 doesn't appear.

Table 1. pH evolution for molar ratios chlorine dioxide : phenolic compounds (mmol/mmol), for solutions with initial pH 6.

0.02 :0.2	0.04 :0.2	0.05: 0.2	0.1 : 0.2	0.2 : 0.2	0.4 :0.2	0.6 : 0.2	1.2 :0.2
5.8 ¹	5.5	5.3	4.1	3.5	3.2	3.1	3.0
5.9 ²	5.6	5.4	4.3	3.6	3.2	3.2	3.1
5.9 ³	5.7	5.5	4.2	3.5	3.1	3.0	2.9

¹ pH variation for molar ratios chlorine dioxide:resorcinol;

² pH variation for molar ratios chlorine dioxide:2-aminophenol;

³ pH variation for molar ratios chlorine dioxide:2-chlorophenol.

Table 2. pH evolution for molar ratios chlorine dioxide : phenolic compounds (mmol/mmol), for solutions with initial pH 8.

0.2 : 0.2	0.4 : 0.2	0.6 : 0.2	1.2 : 0.2
7.30 ¹	7.1	6.7	5.8
7.40 ²	7.3	6.5	5.5
7.42 ³	7.2	6.8	5.6

^{1,2,3} idem, table 1

For 2-aminophenol and 2-chlorophenol similar evolutions were recorded by chlorine dioxide oxidation. Quinone formation is slower than in case of resorcinol, in 2-3 hours for aminophenol and 3-4 hours for chlorophenol.

In order to compute kinetics parameters for phenolic compounds oxidation with chlorine dioxide, chlorine dioxide and phenolic compounds concentrations against time were analysed, in solutions in which the molar ratios for chlorine dioxide:phenolic compound were 6:1 and 3:1, at pH =

6 and 8 and two temperatures of 20° and 4°C. The results are presented in tables 3,4,5,6. The reaction rate is high within the first contact minutes of reactants.

For molar ratio of 3:1, half time of reaction $t_{1/2}$, is 5 minutes for resorcinol and 20 minutes for chlorine dioxide; and for molar ratio of 6:1, $t_{1/2}$ is about 2 minutes at pH=6. At pH=8, the reaction rate increases: 50% of initial concentration of resorcinol is consumed within the first 2 minutes. Temperature decreasing from 20° to 4°C, decreases the reaction rate: $t_{1/2}$ for resorcinol is about 60 minutes, at 4°C. Determination of rate constants corresponding to second order reaction, showed that the process complexity:

- a very fast step, within first minutes of introducing chlorine dioxide in resorcinol solution; the constant rates for this step, at pH = 6 and 8, are $k_2 = 0,145 \cdot 10^3 \text{ mol}^{-1}\text{s}^{-1}$ and $0,186 \cdot 10^3 \text{ mol}^{-1}\text{s}^{-1}$, at 20°C; decreasing the temperature to 4°C, decreases their values to $0,077 \cdot 10^3 \text{ mol}^{-1}\text{s}^{-1}$;
- an intermediary step in the next 30 minutes, when the reaction rate decrease, and the corresponding constant values are $0.27 \cdot 10 \text{ mol}^{-1}\text{s}^{-1}$ for pH=6, and $0.34 \cdot 10 \text{ mol}^{-1}\text{s}^{-1}$ at pH=8, they being about 50 times lower than in the fast step; the rapid reactants consumption in the first minutes, is due to phenolic compound oxidation to hidroquinone, followed by immediate transformation into benzoquinone, praised by the red colour of solutions, that intensifies during 0.5 – 1.0 hours;
- in the last step, a slow one, takes place the p-benzoquinone oxidation to organic acids, accompanying by a slow pH decreasing with 2-3 units in 12-20 hours, and disappearance of corresponding absorption maximum in ultraviolet, as well in visible spectra.

For 2-aminophenol and 2-chlorophenol, similar evolutions were detected. The first step, is not as quickly as for resorcinol, k_2 values are two times lower at pH=6 and 1.6 time lower at pH=8; for the second step, k_2 for 2-aminophenol are closed to the resorcinol, and those for 2-chlorophenol are lower with 21,2-36,3%. Phenolic compounds reactivity in the oxidation reaction with chlorine dioxide, according to reaction rates values, is: resorcinol > 2-aminophenol \cong 2 chlorophenol.

Table 3. Chlorine dioxide and resorcinol concentration dependence against contact time, pH and temperature (res* - resorcinol; ** - initial concentrations).

Timp (min)	Working conditions (pH, temperature)							
	pH = 6; t = 20°C				pH = 8; t = 20°C		pH = 6; t = 4°C	
	ClO ₂ mMol/l	res.* mMol/l	ClO ₂ mMol/l	res.* mMol/l	ClO ₂ mMol/l	res.* mMol/l	ClO ₂ mMol/l	res.* mMol/l
0	0.6**	0.2**	1.2**	0.2**	1.2**	0.2**	1.2**	0.2**
2	0.450	0.130	0.474	0.110	0.330	0.100	0.920	0.160
5	0.326	0.100	0.467	0.080	0.310	0.070	0.860	0.140
10	0.313	0.087	0.447	0.076	0.300	0.060	0.810	0.136
15	0.306	0.082	0.405	0.073	0.280	0.055	0.796	0.134
20	0.300	0.078	0.389	0.070	0.270	0.051	0.750	0.128
30	0.282	0.073	0.360	0.067	0.250	0.048	0.720	0.122
40	0.273	0.070	0.355	0.060	0.240	0.045	0.680	0.118
50	0.239	0.065	0.345	0.057	0.230	0.043	0.620	0.115

60	0.204	0.061	0.335	0.053	0.210	0.041	0.580	0.100
120	0.160	0.053	0.256	0.047	0.180	0.034	0.550	0.080
180	0.143	0.046	0.178	0.034	0.150	0.027	0.490	0.070
210	0.099	0.040	0.151	0.027	0.130	0.021	0.470	0.065
240	0.082	0.032	0.142	0.021	0.120	0.016	0.460	0.062
320	0.060	0.020	0.120	0.010	0.100	0.010	0.450	0.060

Table 4. Chlorine dioxide and 2-aminophenol concentration dependence on contact time, pH and temperature (2-AF* = 2- aminofenol ; ** - initial concentrations).

Timp (min)	pH = 6; t = 20 °C		pH = 8; t = 20 °C		pH = 6; t = 4 °C	
	ClO ₂ mMol/l	2-AF* mMol/l	ClO ₂ mMol/l	2-AF* mMol/l	ClO ₂ mMol/l	2- AF* mMol/l
0	1.2**	0.2**	1.2**	0.2**	1.2**	0.2**
2	0.850	0.150	0.600	0.120	1.070	0.180
5	0.830	0.140	0.590	0.110	1.010	0.170
10	0.765	0.130	0.580	0.102	0.988	0.165
15	0.730	0.125	0.560	0.098	0.955	0.160
20	0.695	0.120	0.540	0.096	0.936	0.157
30	0.652	0.115	0.490	0.090	0.925	0.155
40	0.610	0.110	0.420	0.087	0.910	0.152
50	0.550	0.100	0.370	0.083	0.895	0.150
60	0.480	0.095	0.280	0.075	0.835	0.140
120	0.260	0.075	0.190	0.060	0.775	0.130
180	0.220	0.060	0.120	0.040	0.710	0.125
210	0.210	0.050	0.110	0.035	0.650	0.120
240	0.170	0.040	0.100	0.030	0.640	0.120
320	0.150	0.040	0.100	0.020	0.640	0.110

Table 5. Chlorine dioxide and 2-chlorophenol concentration dependence on contact time, pH and temperature (2-CF* = 2- clorophenol ; ** - initial concentrations).

Timp (min)	pH = 6; t = 20 °C		pH = 8; t = 20 °C		pH = 6; t = 4 °C	
	ClO ₂ mMol/l	2-CF* mMol/l	ClO ₂ mMol/l	2-CF* mMol/l	ClO ₂ mMol/l	2-CF* mMol/l
0	1.2**	0.2**	1.2**	0.2**	1.2**	0.2**
2	0.945	0.67	0.805	0.148	1.142	0.191
5	0.935	0.160	0.790	0.135	1.090	0.185
10	0.928	0.155	0.780	0.132	1.078	0.180
15	0.910	0.152	0.748	0.128	1.016	0.170
20	0.898	0.150	0.725	0.125	0.995	0.166
30	0.885	0.148	0.680	0.120	0.974	0.163
40	0.810	0.145	0.540	0.116	0.880	0.160
50	0.740	0.142	0.420	0.114	0.820	0.157
60	0.650	0.139	0.360	0.110	0.780	0.155
120	0.520	0.136	0.230	0.108	0.710	0.153
180	0.380	0.132	0.190	0.104	0.700	0.150
210	0.330	0.110	0.180	0.080	0.680	0.145
240	0.300	0.090	0.170	0.065	0.650	0.130
320	0.250	0.080	0.150	0.050	0.600	0.120

Table 6. Constant rates values (k₂) for resorcinol, 2-aminophenol, 2-chlorophenol oxidation with chlorine dioxide, the fast step (1^a, 2^a, 3^a) and the intermediary step (1^b, 2^b, 3^b).

	PH = 6		PH = 8
	20 ° C	4 ° C	20 ° C
^{1A}	0.145 · 10 ³ MOL ⁻¹ S ⁻¹	0.077 · 10 ³ MOL ⁻¹ S ⁻¹	0.186 · 10 ³ MOL ⁻¹ S ⁻¹
^{1B}	0.27 · 10 ³ MOL ⁻¹ S ⁻¹	0.126 · 10 ³ MOL ⁻¹ S ⁻¹	0.34 · 10 ³ MOL ⁻¹ S ⁻¹
^{2A}	0.077 · 10 ³ MOL ⁻¹ S ⁻¹	0.032 · 10 ³ MOL ⁻¹ S ⁻¹	0.11 · 10 ³ MOL ⁻¹ S ⁻¹
^{2B}	0.28 · 10 ³ MOL ⁻¹ S ⁻¹	0.096 · 10 ³ MOL ⁻¹ S ⁻¹	0.33 · 10 ³ MOL ⁻¹ S ⁻¹
^{3A}	0.07 · 10 ³ MOL ⁻¹ S ⁻¹	0.03 · 10 ³ MOL ⁻¹ S ⁻¹	0.12 · 10 ³ MOL ⁻¹ S ⁻¹
^{3B}	0.049 · 10 ³ MOL ⁻¹ S ⁻¹	0.11 · 10 ³ MOL ⁻¹ S ⁻¹	0.26 · 10 ³ MOL ⁻¹ S ⁻¹

¹ constant rates for resorcinol oxidation with chlorine dioxide;² constant rates for 2-aminophenol oxidation with chlorine dioxide;

³ constant rates for 2-chlorophenol oxidation with chlorine dioxide.

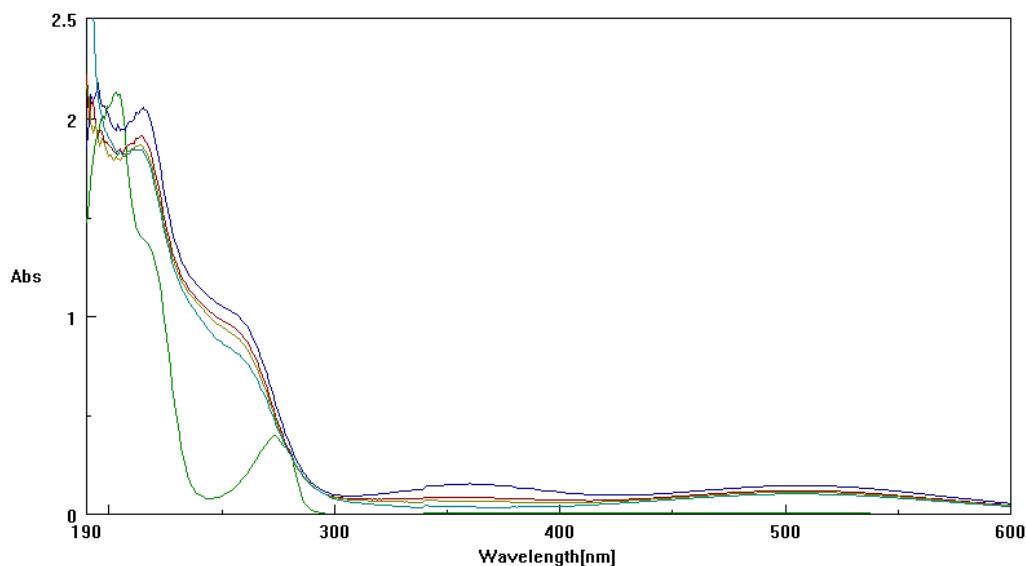


Fig. 1 Absorption spectra evolution in ultraviolet and visible, for molar ratio chlorine dioxide:resorcinol of 0.2 : 0.2 (mmol:mmol), depending on time (1-resorcinol; 2,3,4,5-resorcinol and chlorine dioxide, after 2, 5, 10, 60 minutes contact), at pH=6.

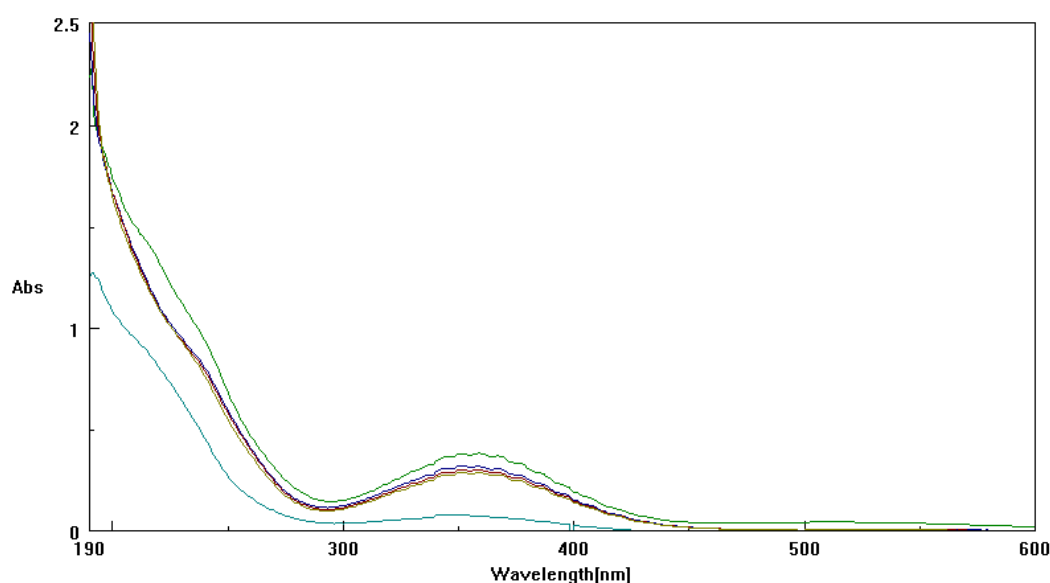


Fig. 2 Absorption spectra's evolution, in ultraviolet and visible, for molar ratio chlorine dioxide:resorcinol of 0.6 : 0,2 (mmol:mmol), depending on time (1-2 minutes; 2-5 minutes; 3-10 minutes; 4-60 minutes; 5-12 hours), at pH=6.

CONCLUSIONS

Analyzing phenolic compounds (resorcinol, 2-aminophenol and 2-chlorophenol) reactivity versus chlorine dioxide in water solutions through molar ratios method, allowed benzoquinone identification by ultraviolet and visible spectrophotometry, with absorption maximum at 247 nm and 500 nm.

For molar ratio of 3:1, half time of reaction $t_{1/2}$, is 5 minutes for resorcinol and 20 minutes for chlorine dioxide; and for molar ratio of 6:1, $t_{1/2}$ is about 2 minutes at pH=6. At pH=8, the reaction rate increases:

50% of initial concentration of resorcinol is consumed within the first 2 minutes. Temperature decreasing from 20°C to 4°C, decreases the reaction rate: $t_{1/2}$ for resorcinol is about 60 minutes, at 4°C. Determination of rate constants corresponding to second order reaction, showed that the process complexity:

- a very fast step, within first minutes of introducing chlorine dioxide in resorcinol solution; the constant rates for this step, at pH = 6 and 8, are $k_2 = 0,145 \cdot 10^3 \text{ mol}^{-1}\text{s}^{-1}$ and $0,186 \cdot 10^3 \text{ mol}^{-1}\text{s}^{-1}$, at 20°C; decreasing the temperature to 4°C, decreases their values to $0,077 \cdot 10^3 \text{ mol}^{-1}\text{s}^{-1}$;
- an intermediary step in the next 30 minutes, when the reaction rate decrease, and the corresponding constant values are $0.27 \cdot 10 \text{ mol}^{-1}\text{s}^{-1}$ for pH=6, and $0.34 \cdot 10 \text{ mol}^{-1}\text{s}^{-1}$ at pH=8, they being about 50 times lower than in the fast step; the rapid reactants consumption in the first minutes, is due to phenolic compound oxidation to hidroquinone, followed by immediate transformation into benzoquinone, praised by the red colour of solutions, that intensifies during 0.5 – 1.0 hours;
- in the last step, a slow one, takes place the p-benzoquinone oxidation to organic acids, together with pH decreasing with 2-3 units, in 12-20 hours, and disappearance of corresponding absorption maximum in ultraviolet, as well in visible spectra. For 2-aminophenol and 2-chlorophenol, similar evolutions were detected. According to rate constant values in the oxidation process with chlorine dioxide, reactivity of phenolic compounds was: resorcinol > 2-aminophenol \cong 2-chlorophenol.

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