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## Oxidation of Mono- and Dinitro-Substituted Phenols by Hydrogen Peroxide in the Presence of Iron (II) and (III)

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### Abstract

A systematic study was performed concerning decomposition kinetics for 3-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol effected by hydrogen peroxide in the presence of iron (II) and (III). Relative reactivity was established for the mentioned dinitrophenols during oxidative degradation.

**Key words:** oxidative degradation, nitrophenols, hydrogen peroxide

### INTRODUCTION

The implementation of novel technologies for the treatment of wastewater, groundwater and drinking water contaminated with organic substances, is essential in the cases when the matter concerns detoxify pollutants resistant with respect to biodegradation. The oxidative degradation of organic pollutants is nowadays considered an alternative with respect to biodegradation. At the same time, oxidants are charged with very severe requirements: an oxidant, oxidative degradation products and possible intermediates of the oxidation processes are important to be less toxic and resistant with respect to degradation than initial compounds. In this respect, hydrogen peroxide is one of the most promising oxidants. However, its own redox potential is low. More efficient are oxidation system, wherein radical species are generated from hydrogen peroxide. The best known system among such ones is presented by the Fenton's reagent, representing hydrogen peroxide in combination with iron (II) ions. The formation of hydroxyl radicals occurs as it follows [1]



Large-scale production and use of substituted phenols and their derivatives in the chemical industry (the synthesis of dyes, pesticides, explosives, etc.) resulted in a significant contamination of soil and groundwater by these compounds. Biodegradation of phenol nitro derivatives is extremely difficult due to their toxicity with respect to microorganisms, especially at high concentration values.

The analysis of published data [2–4] demonstrates that the oxidation of nitroaromatic compounds by hydrogen peroxide is one of the most promising directions for the development of technologies for water and soil treatment. The most detailed degradation of nitro-substituted phenols under the action of Fenton's reagent and photo-Fenton process was investigated in [5], but no data concerning the degradation of 3-nitrophenol are presented therein.

The present study demonstrates results obtained for the oxidative degradation of mono- and dinitro-substituted phenols such as 3- and 4-nitrophenol (3-NP, 4-NP, respectively), 2,4- and 2,6-dinitrophenol (2,4-DNP, 2, 6-DNP, respectively). As the method of decomposition, we chose oxidation of nitrophenol by hydrogen peroxide in the presence of iron (II) or (III).

## EXPERIMENTAL

In all the experiments, we studied the oxidation of nitro-substituted phenols at 23 °C in aqueous solution, 25 mL in volume. The initial substrate concentration was similar for all the experiments and amounted to 0.25 mmol/L. To the solution under analysis, we added a calculated amount of hydrogen peroxide solution and iron (II) or (III) sulphate solution.

Changing the concentration of nitrophenols in a solution was determined using by spectrophotometry. The absorption maximum was determined for each nitrophenol. Spectra were registered on a Specord 50 UV/Vis spectrophotometer.

The value of pH was measured using a Mettler Toledo pH meter.

The study of nitrophenol oxidative degradation products was performed by means of PMR spectroscopy. In order to eliminate the influence of solvent protons upon the spectrum of the solutions were prepared using heavy water. The NMR spectra were registered on a Tesla BS-567A spectrometer at 20 °C. DSSA (4,4-dimethyl-4-silapentane-1-sulphinic acid) was used as a calibration standard.

## RESULTS AND DISCUSSION

In order to establish the laws of the oxidation process, first of all, information is important concerning final products and stable intermediates. The reaction mixture consisting of an organic substrate (3-NP), hydrogen peroxide and iron (II) ions after completing of the oxidation process was studied using PMR spectroscopy. The spectrum of the reaction mixture did not demonstrate the signals of aromatic protons, any new signals corresponding to organic protons were not detected; only signals from water protons were observed, which is consistent with the concept that water in this case represents one of the main oxidation products. Thus, there is the reason to consider the process under study as an irreversible reaction of complete substrate mineralization.

The kinetics of mono- and dinitrophenol oxidation by hydrogen peroxide in the presence of iron (II) sulphate was studied at different concentrations of the oxidant, since the ratio

of  $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{substrate}$  depends on oxidation mechanism [6–8]. The concentration of hydrogen peroxide was varied from 2 to 16 mmol/L whereas the concentration of iron (II) ranged from 0.03 to 0.50 mmol/L.

Figures 1 and 2 demonstrate the kinetic curves for the oxidation of 2,4-DNP at various concentrations of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ . The curves for the 3-, 4-NP and 2,6-DNP are similar. It is seen that for 2,4-DNP the optimum concentration of hydrogen peroxide is equal to 8 mmol/L.

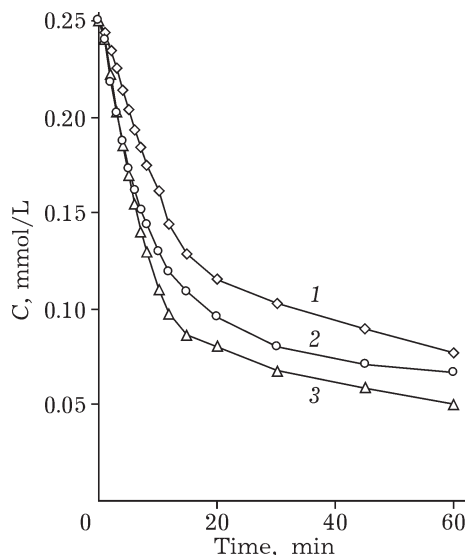


Fig. 1. Kinetic curves for the decomposition of 2,4-DNP in the solutions containing different amounts of  $\text{H}_2\text{O}_2$ .  $[\text{Fe}^{2+}] = 0.25 \text{ mmol/L}$ ;  $[\text{H}_2\text{O}_2]$ , mmol/L: 4 (1), 8 (3), 16 (2).

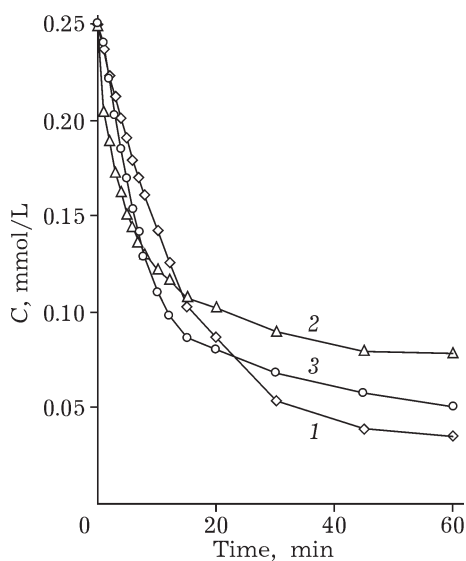
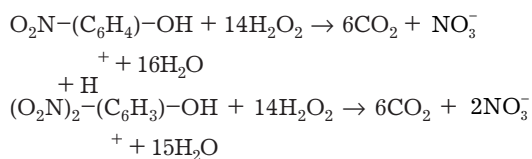


Fig. 2. Kinetic curves for the decomposition of 2,4-DNP in the solutions containing different amounts of  $\text{Fe}^{2+}$ .  $[\text{H}_2\text{O}_2] = 8 \text{ mmol/L}$ ;  $[\text{Fe}^{2+}]$ , mmol/L: 0.125 (1), 0.25 (3), 0.5 (2).

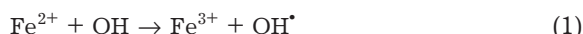
Both reducing and increasing the content of hydrogen peroxide causes the efficiency of the process to decrease. The oxidation of 2,6-DNP and mononitrophenols exhibits a similar trend.

According to the conditional scheme of complete oxidation, the demand level for hydrogen peroxide should be the same for mono- and dinitrophenol:

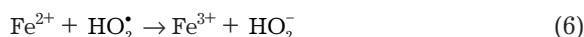
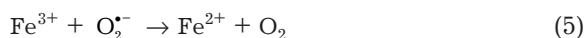
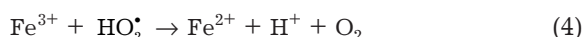


However, a real flow rate value for hydrogen peroxide in the experiment for both substrates is approximately 2.3 times higher than the estimated amount of hydrogen peroxide. To all appearance, there is a side-reaction consumption of hydrogen peroxide occurring, for example, due to decomposition with the liberation of oxygen. For other organic compounds, such a situation is described in [9, 10], it is inherent in the case when the initial reagent ratio value  $[\text{Fe}^{2+/3+}] \ll [\text{H}_2\text{O}_2]$ .

Reducing the efficiency of oxidation at high concentration of hydrogen peroxide (see Fig. 1) could be connected with the properties of the oxidant rather than the substrate under oxidation. According to [10], with increasing the  $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$  ratio, one can observe decreasing the contribution of reaction



The decomposition of hydrogen peroxide occurs mainly according to the equations



with the liberation of molecular oxygen and the simultaneous rapid accumulation of  $\text{Fe}^{3+}$  in the solution, since the regeneration of the catalyst occurs *via* the reactions (4) and (5) those are characterized by rate constant values being an order of magnitude lower than that for reaction (1).

The efficiency of oxidation processes for nitrophenols depends also on the content of iron (II) in the solution (see Fig. 2). The analysis of kinetic curve shape allows one to note that in the presence of a large amount of iron ions there is an inhibition occurring with respect to

nitrophenol oxidation. To all appearance, the generation of a required amount of oxidants (hydroxyl radicals) occurs when a high concentration of iron ions is observed at the initial stage. This explains a favourable effect of high iron concentration in the beginning of the experiment. To all appearance, as the reaction proceeds, the iron begins to play another role as a participant in the chain termination stage:  $\text{Fe}^{2+} + \cdot\text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^-$

The most efficient oxidation of nitrophenol compounds in the presence of hydrogen peroxide and  $\text{Fe}^{2+}$  ions occurs at a ratio of reagents  $[\text{NP}] : [\text{H}_2\text{O}_2] : [\text{Fe}^{2+}] = 1 : 32 : (0.5-1)$ .

In order to evaluate the oxidation efficiency for various substrates and to compare them between each other, we used an initial consumption rate of nitrophenols (Table 1).

According to the magnitude of the initial consumption rate, the substrates form the following series: 3-NP > 4-NP > 2,4-DNP  $\approx$  2,6-DNP.

In order to correctly compare our results with those from [5], Table 1 also demonstrates the parameters such as half-time and 90 % conversion time for the substrates. The most reactive nitrophenol (3-NP) among those under investigation was described in [5]. When comparing mono and dinitrophenols, our findings are consistent with the results of [5], the decomposition rate for mononitrophenols by the Fenton reagent is higher than that for dinitrophenols. The sequence established could be caused not only by difference in the structure of the substrate molecules, but also by different pH of the solutions (see Table 1).

The system containing hydrogen peroxide and  $\text{Fe}^{3+}$ , is also characterized by destructive oxidative destruction of the organic substrates.

Unlike systems with ferrous iron, the effect of hydrogen peroxide concentration therein

TABLE 1

Initial oxidative destruction rate values for different nitrophenols at a ratio of reagents  $[\text{NP}] : [\text{H}_2\text{O}_2] : [\text{Fe}^{2+}] = 1 : 32 : 1$

Parameters	3-NP	4-NP	2,4-DNP	2,6-DNP
$W_0$ , mol/(L · min)	0.06	0.06	0.02	0.02
pH of reaction	2.65	2.80	3.00	3.00
$t_{1/2}$ , s	210	210	540	540
$t_{90\%}$ , s	2400	6600	6000	6600

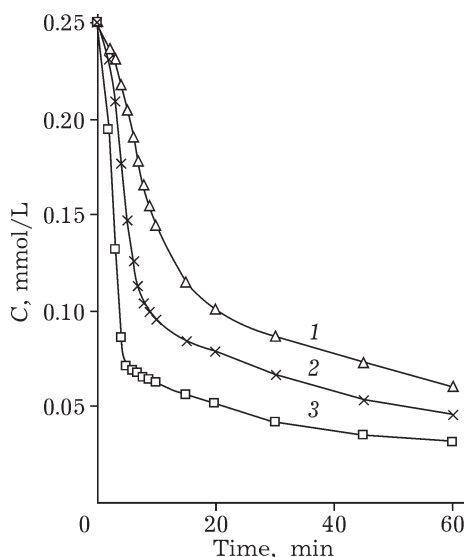


Fig. 3. Kinetic curves for the decomposition of 3-NP in the solutions containing different amounts of  $\text{Fe}^{3+}$ .  $[\text{H}_2\text{O}_2] = 8 \text{ mmol/L}$ ;  $[\text{Fe}^{3+}]$ , mmol/L: 0.0625 (1), 0.125 (2), 0.25 (3).

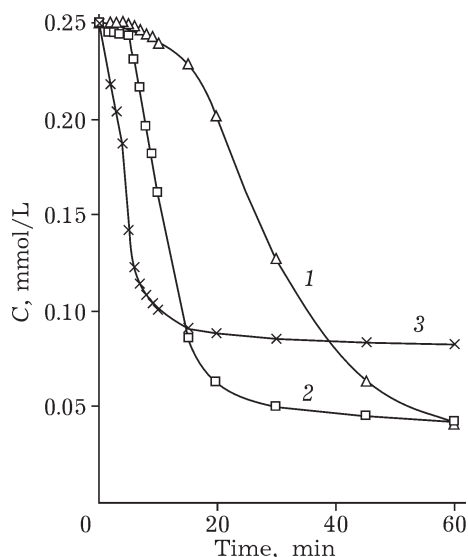
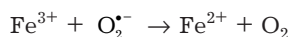
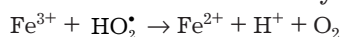


Fig. 4. Kinetic curves for the decomposition of 4-NP in the solutions containing different amounts of  $\text{Fe}^{3+}$ .  $[\text{H}_2\text{O}_2] = 8 \text{ mmol/L}$ ;  $[\text{Fe}^{3+}] = 0.125$  (1), 0.25 (2), 0.5 (3).

is not so significant. However, there is a much more significant, comparing to the classical Fenton system, influence of iron ion concentration in the course of the process (Figs. 3, 4). There is an extreme character of the oxidation initial rate depending on the concentration of iron ions distinctly pronounced (seen from the slope of the initial part of the curves in Figs. 3, 4).

It should be noted that there is the presence of induction period on the kinetic curves is observed (see Fig. 4). This fact is consistent with the concept available from the literature that the catalytic decomposition mechanisms for hydrogen peroxide in the systems and  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2/\text{Fe}^{3+}$  are similar to a considerable extent [11, 12]. The difference consists in the mechanism of the initiation process: the initial rate of  $\text{H}_2\text{O}_2$  decay in the presence of  $\text{Fe}^{2+}$  is significantly higher than in the case of  $\text{Fe}^{3+}$ , which is usually explained by a low concentration of  $\text{HO}_2^\bullet$  radicals, involved in the initiation stage. It takes some time for the formation of  $\text{Fe}^{2+}$  ions in the system [12]:



After the accumulation of such ions, the process propagates according to the Fenton type.

Below, calculated values are presented concerning the initial rate values for nitrophenol oxidative conversion in the presence of  $\text{Fe}^{2+}$  or

$\text{Fe}^{3+}$ , respectively, at the concentration values of 0.25 mmol/L ( $[\text{NP}] = 0.25 \text{ mmol/L}$ ,  $[\text{H}_2\text{O}_2] = 8 \text{ mmol/L}$ ):

2,4-DNP	2,6-DNP	3-NP	4-NP
0.02/0.01	0.02/0.02	0.06/0.07	0.06/0.01

A high reactivity of 3-NP is conserved even when replacing  $\text{Fe}^{2+}$  by  $\text{Fe}^{3+}$ . The situation with 4-NP is not so obvious: the initial part of its in the presence of iron (III) is very low, but after an induction period, the degradation rate increases rapidly to become comparable with respect to the rate of 3-NP decomposition. This fact is indicated an almost same slope of the kinetic curves presented in Figs. 3 and 4.

The reaction series of nitrophenols under investigation with replacing  $\text{Fe}^{2+}$  by  $\text{Fe}^{3+}$  and with the induction period taken into account could be presented as it follows: 3-NP  $\gg$  2,6-DNP  $>$  2,4-DNP  $\approx$  4-NP.

The optimum ratio between the reactants for the oxidation of nitrophenol compounds in the presence of hydrogen peroxide and iron (III) ions is the same as that for the system with iron (II) ions.

## CONCLUSION

Oxidation kinetics was studied for 3-nitrophenol, 4-nitrophenol, 2,4- and 2,6-dinitrophenol.

nols with the use of radical species formed from hydrogen peroxide in aqueous solution in the presence of iron (II) at a room temperature and atmospheric pressure. It was found that the greatest initial rate of oxidative degradation for the substrates under investigation form the following series: 3-NP > 4-NP > 2,4-DNP  $\approx$  2,6-DNP.

The sequence revealed is caused not only by the difference in the structure of substrate molecules, but also by different pH values of the solutions.

It was found that when iron (III) ions being used instead of iron (II) for the generation of radical species, the initial rate of oxidative degradation of nitro-substituted phenols is 2 to 6 times reduced. The value of the initial velocity is changed as it follows: 3-NP  $\gg$  2,6-DNP > 2,4-DNP  $\approx$  4-NP.

Reducing the rate is connected with the induction period to appear due to the accumulation of Fe(II) ions in the system.

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