

# Oxidative Destruction of Dinitrophenols by Fenton's Reagent in the Presence of Inorganic Salts

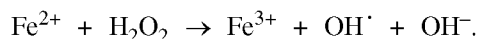
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**Abstract**—The influence of inorganic salts on the kinetics of oxidation of 2,4- and 2,6-dinitrophenols by Fenton's reagent, hydrogen peroxide, in the presence of iron(II) ions was studied.

Nitro derivatives of phenol are basic chemicals in production of some dyes and explosives and are widely used in agriculture as compounds having a multi-purpose pesticide effect. However, by their toxicity for warm-blooded animals, compounds of the nitrophenol series are offensive and highly toxic substances with a cumulative effect. Water treatment to remove nitro derivatives of phenol is an important environmental problem.

Complete oxidation of organic contaminants (so-called mineralization) is considered to be the most reliable procedure of their inactivation. Oxygen, ozone, and hydrogen peroxide can serve as oxidants [1]. Hydrogen peroxide is an environmentally safe oxidant convenient in use. However, its oxidizing potential is insufficient to oxidize many persistent contaminants. More effective are oxidizing systems in which radical species are generated from  $H_2O_2$ . The best known system is Fenton's reagent: hydrogen peroxide in combination with iron(II) ions. Hydroxy radicals are formed by the scheme [2]



Along with organic contaminants, inorganic salts, such as chlorides, sulfates, nitrates, and phosphates, are present in natural and waste water. However, only several studies have been devoted to the influence of these salts on the Fenton process, and only low concentrations of salts have been examined. For example, phenol, 2-chlorophenol, and 2-nitrophenol were oxidized with Fenton's reagent in solutions of sodium chloride and sulfate; the concentrations of salts did not exceed 20 mM [3]. The influence of inorganic ions

on the oxidation of phenol was studied in [4]; the concentration of anions was  $100 \text{ mg l}^{-1}$ .

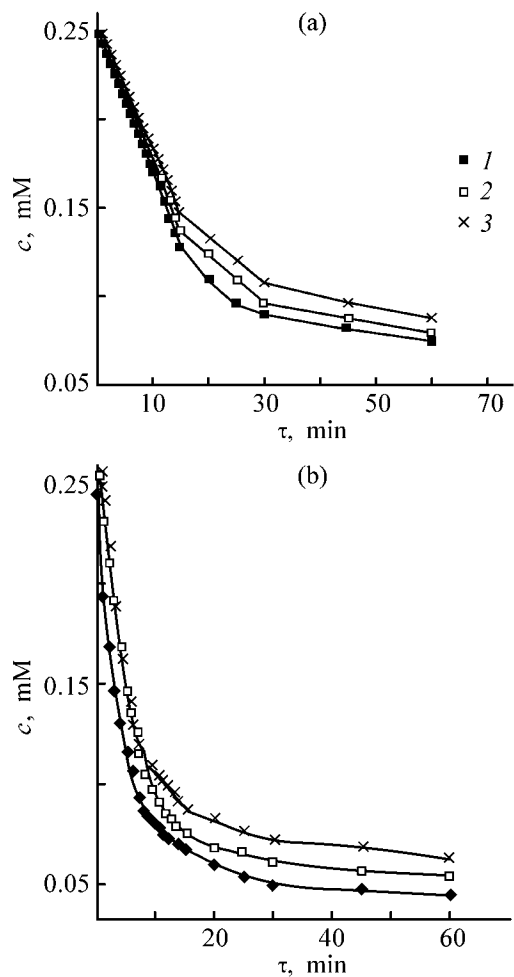
Here we studied mineralization of 2,4- and 2,6-dinitrophenols with Fenton's reagent in the presence of high concentrations of inorganic salts.

## EXPERIMENTAL

We used 2,4- and 2,6-dinitrophenols of analytically pure grade without additional purification.

In all experiments, we studied the oxidation of 2,4- and 2,6-dinitrophenols at  $23^{\circ}\text{C}$  in an aqueous solution with a volume of 25 ml. The substrate concentration was constant and equal to 0.25 mM. Calculated amounts of  $H_2O_2$  and  $FeSO_4$  solutions were added to the test solution. The  $H_2O_2$  concentration was varied from 4 to 16 mM, and the  $FeSO_4$  concentration, from 0.125 to 0.5 mM. The experiment was carried out during for 60 min. The course of the process was monitored by measuring the optical density of the solution on a KFK-3-01 photometer at a wavelength of 345 nm. The pH was measured with a Mettler Toledo pH meter. In all runs, the pH value was kept equal to 3.0.

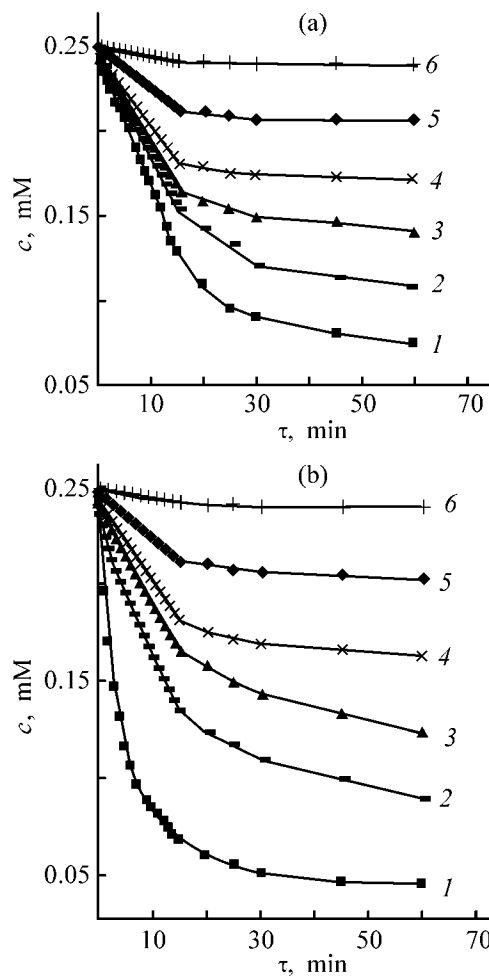
The initial pH value is one of the key parameters in the optimization of processes in the system  $H_2O_2$ - $Fe^{2+}$ -substrate. Oxidation of most of organic compounds, among them such stable as chlorophenols, under the action of Fenton's reagent proceeds more efficiently at the initial pH 2.7–3.5 [5–9]. The dependence observed is caused by the influence of acidity on the rate of  $H_2O_2$  decomposition and on the state of iron(II) ions in the solution and, hence, on their catalytic characteristics.



**Fig. 1.** Variation of the concentration  $c$  of (a) 2,4-dinitrophenol and (b) 2,6-dinitrophenol in the course of oxidation by Fenton's reagent in aqueous solutions of sodium nitrate. ( $\tau$ ) Time; the same for Fig. 2. Concentration of  $\text{NaNO}_3$ , mM: (1) 0, (2) 0.1, and (3) 1.0.

In the first series of experiments, we determined the optimal conditions of decomposition of dinitrophenols and the concentrations of  $\text{H}_2\text{O}_2$  and iron(II) ions, because the oxidation mechanism depends on the  $\text{H}_2\text{O}_2 : \text{Fe}^{2+} : \text{substrate}$  ratio [10]. The experimental results showed that the optimal concentration of  $\text{H}_2\text{O}_2$  for decomposition of dinitrophenols is 8 mM at a  $\text{Fe}^{2+}$  concentration of 0.25 mM. These conditions were maintained in all the subsequent experiments when studying the influence of inorganic salts on the decomposition of dinitrophenols.

It should be noted that the assortment of salts that can be used in the study is rather narrow, since organic anions are excluded due to ease of their oxidation by Fenton's reagent and fluorides, phosphates, and other anions of weak inorganic acids or acids of medium



**Fig. 2.** Variation of the concentration  $c$  of (a) 2,4-dinitrophenol and (b) 2,6-dinitrophenol in the course of oxidation by Fenton's reagent in aqueous solutions of sodium chloride. Concentration of  $\text{NaCl}$ , mM: (1) 0, (2) 0.1, (3) 0.3, (4) 0.5, (5) 0.7, and (6) 1.0.

strength shift the solution pH to the alkaline region, making Fenton's reagent inefficient. In this context we used salts of strong acids.

The kinetic curves of oxidation of dinitrophenols by Fenton's reagent in 0.1 and 1 M  $\text{NaNO}_3$  aqueous solutions are shown in Figs. 1a and 1b. The curves obtained do not significantly depart from the curves of oxidation of the corresponding substrates in distilled water. Ammonium nitrate does not affect the oxidation of dinitrophenols either. The kinetic parameters typical for the process in distilled water are kept in the presence of 0.1–1.0 M  $\text{NH}_4\text{NO}_3$ .

A different situation arises with addition of chloride ions into the solution. As can be seen from Figs. 2a and 2b, the rate of oxidation of dinitrophenols

nols in the presence of NaCl significantly decreases, whereas in an 1 M NaCl solution, the substrates are not oxidized: the concentrations of dinitrophenols do not noticeably vary.

Figures 2a and 2b show that, as the NaCl concentration increases, the kinetics parameters of the process regularly vary. The initial rate of the process and the final degree of conversion depend linearly on the NaCl concentration, with the linear dependence observed for both dinitrophenols (Figs. 3a, 3b).

It can be assumed that chloride ions, rather than sodium ions, are the main inhibiting species, because  $\text{NaNO}_3$  does not exhibit this effect. Substitution of  $\text{Cs}^+$  ions for  $\text{Na}^+$  ions does not essentially alter the influence of the salt on the course of the process. The curves obtained in the presence of CsCl are similar to those obtained with of NaCl. Data for CsCl are described by the same linear dependence as that in the case of NaCl.

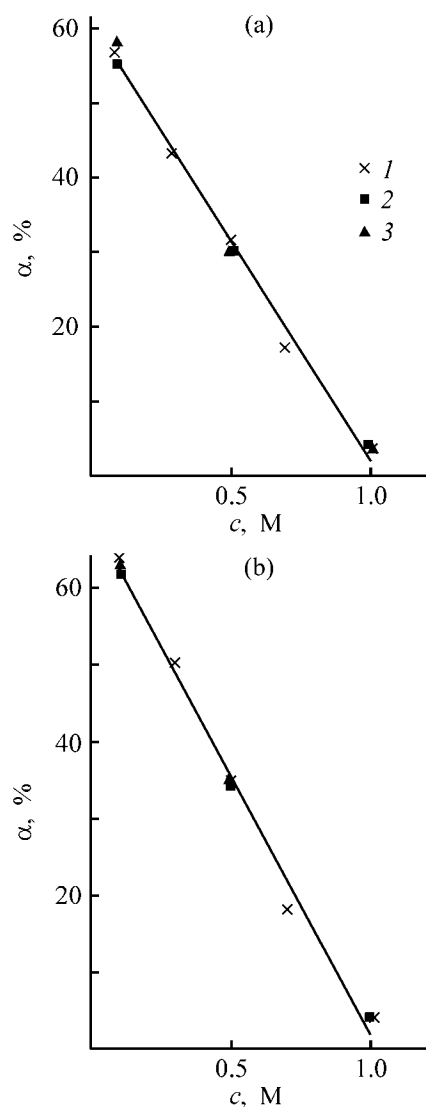
To explain the results obtained, it necessary, first and foremost, to check whether  $\text{H}_2\text{O}_2$  is consumed in side processes, including those involving trace contaminants. The experiment showed that the  $\text{H}_2\text{O}_2$  concentration in NaCl solutions without dinitrophenols and iron(II) ions remains constant for a long time.

According to published data, one of the reasons why anions affect the oxidation by Fenton's reagent is that iron complexes are formed. It was appropriate to study one more anion able to form complexes. The next series of experiments was performed in solutions of sodium sulfate. We revealed no noticeable inhibiting effect of sodium sulfate similar to that of chloride ions. The resulting kinetic curves do not significantly depart from the curve of oxidation of the corresponding substrate by Fenton's reagent in distilled water.

A more probable assumption is that chloride ions are oxidized by Fenton's reagent in the systems studied in parallel with oxidation of dinitrophenol. It has been noted that Fenton's reagent has a high redox potential (2.8 V [11]).

It should be noted that Bali and Catalkaya [4] studied only low concentrations of anions (1–3 mM) and reported only the inhibiting effect of phosphate ions, but no noticeable influence of chloride or sulfate ions on phenol oxidation by Fenton's reagent was not revealed.

The nature of the cation of an inorganic salt does not affect the oxidation of dinitrophenols. It is likely that, in these studies, ammonium cations are not oxi-



**Fig. 3.** Degree of conversion  $\alpha$  of (a) 2,4-dinitrophenol and (b) 2,6-dinitrophenol in oxidation by Fenton's reagent for 60 min vs. salt concentration  $c$ . Salt: (1) NaCl, (2)  $\text{NH}_4\text{Cl}$ , and (3) CsCl.

dized or are extremely weakly oxidized by Fenton's reagent, even though ammonium is a possible reducing agent similarly to chloride ions. In any case, the presence of  $\text{NH}_4\text{NO}_3$  in the system does not affect the course of oxidation of dinitrophenols.

The reducing power of ammonium ions is not manifested when they are added to the system in the form of ammonium chloride. Oxidation of dinitrophenols is inhibited at the same concentrations as in the case of sodium and cesium chlorides, i.e., inhibition is caused by the presence of chloride ions. Data for  $\text{NH}_4\text{Cl}$  are described by the same dependence as data obtained for sodium and cesium chlorides.

## CONCLUSIONS

(1) 2,4- and 2,6-Dinitrophenols are oxidized by Fenton's reagent in the presence of inorganic salts under comparable conditions. Sodium, cesium, and ammonium cations, as well as nitrate and sulfate anions, do not noticeably affect the oxidation of dinitrophenols.

(2) The presence of impurities of fluoride, phosphate, and other anions of weak acids or acids of medium strength in water shifts the solution pH to the range in which Fenton's reagent is ineffective.

(3) The presence of chloride ions in water inhibits the oxidation of dinitrophenol by Fenton's reagent, probably due to a competing oxidation of chloride ions.

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