Russian Journal of General Chemistry, Vol. 74, No. 3, 2004, pp. 376–378. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 3, 2004, pp. 415–418.
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Formal Bleaching Kinetics of Acid Blue 80 in Weakly Acidic, Neutral, and Basic Aqueous Media

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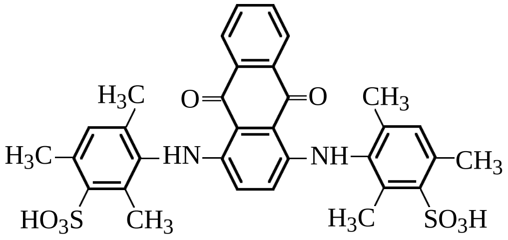
Received July 16, 2001

Abstract—General kinetic relations were established for the first step of oxidation of Acid Blue 80 in weakly acidic, neutral and basic media in the following systems: Fe^{2+}–H_2O_2, Mn^{2+}–HCO_3^-–H_2O_2, and Cu^{2+}–phenanthroline–H_2O_2. The rate constant for the reaction of hydroxyl radical with the dye and the dependence of the degree of bleaching upon oxidant and catalyst concentrations were determined.

The system Fe^{2+}–H_2O_2 (Fenton's reagent) [1] is widely used for oxidation of various organic and inorganic substrates, including indicators [1, 2], in acidic medium (pH 1–3). Addition of some ligands to that system makes it possible to avoid precipitation of iron(II) and iron(III) hydroxides and to effect oxidation in weakly acidic and neutral media [3]. The system Mn^{2+}–HCO_3^-–H_2O_2 is known [4] to be highly effective in the oxidation of a number of organic substrates in neutral medium; its efficiency is only slightly lower than that of iron(III) complexes with triethylenetetramine ("inorganic catalase," the most effective catalyst for decomposition of hydrogen peroxide among low-molecular-weight compounds). Also, the high peroxidase and catalase activity of various copper(II) complexes in alkaline medium has been reported [5]. In particular, we selected the Cu^{2+}–Phen–H_2O_2 system as the most efficient to examine the oxidation process. The above systems can be used to oxidize Acid Blue 80 (C.I. 61 585; D), which is a large-scale product, over a wide range of pH (from 2 to 12). This process attracts considerable interest from the viewpoint of solving various applied problems in analytical chemistry (e.g., elaboration of new catalymetric methods for determination of iron, copper, and manganese on a micro level) and ecological chemistry (analysis of natural waters [6]). Oxidation of the dye in the above systems destroys its chromophoric and auxochromic groups. Insofar as the final oxidation products (which may be toxic) were not identified in this work, the use of the results in technological processes requires additional purification procedures (adsorption, photocatalysis, ozonation, etc.).

Bleaching of Acid Blue 80 was examined under aerobic conditions. Experiments were performed in a cell which was maintained at a constant temperature (298 K) and ensured control over pH variation during the reaction (with the aid of a 673M pH-meter). The dye gives rise to two absorption maxima in the electronic spectrum at λ 581 and 625 nm. The substrate consumption was followed by measuring the optical density A at λ 625 nm ($\varepsilon = 13.8 \times 10^3$ l mol^{-1} cm^{-1}). The other components of the reaction mixture, i.e., hydrogen peroxide and metal complex catalyst, do not contribute appreciably to the optical density at the selected wavelength. All solutions were prepared using doubly distilled water. The optical densities were measured on SF-46 and Specord M-40 spectrophotometers. The structure of the molecule of Acid Blue 80 is shown below (M 634).



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We examined the kinetics of bleaching of Acid Blue 80 with Fenton's reagent in acidic medium. The initial concentrations were as follows: $[Fe^{2+}]_0 = 1 \times 10^{-5}$, $[H_2O_2]_0 = 0.1$, $[D]_0 = 4 \times 10^{-5}$ M; pH 2. Below are given the dependences of the bleaching rate W^D upon $[Fe^{2+}]_0$, $[H_2O_2]_0$, $[D]_0$, and pH:

$[Fe^{2+}]_0 \times 10^5$, M	1.0	1.7	2.3	6.5
$W^D \times 10^7$, l mol^{-1} s^{-1}	3.1	4.4	5.0	10.9
$[H_2O_2]_0 \times 10^2$, M	5.0	7.5	10.0	15.0
$W^D \times 10^7$, l mol^{-1} s^{-1}	3.2	4.1	4.7	5.9
$[D]_0 \times 10^5$, M	2.0	4.0	6.0	8.0
$W^D \times 10^7$, l mol^{-1} s^{-1}	2.5	5.3	8.3	10.4
pH	2.0	2.5	3.0	
$W^D \times 10^7$, l mol^{-1} s^{-1}	5.5	2.8	1.4	

[†] Deceased.

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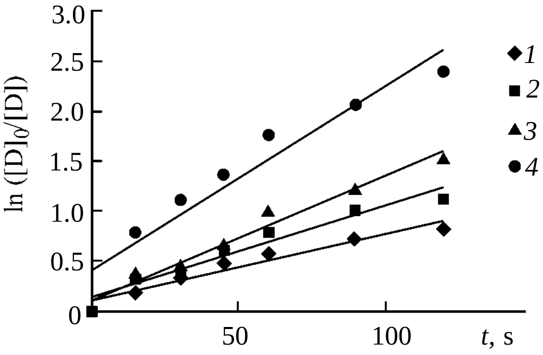

Fig. 1. Semilog plots for bleaching of Acid Blue 80 at different concentrations of iron(II) ions. $[Fe^{2+}]_0 \times 10^5$, M: (*1*) 1, (*2*) 1.7, (*3*) 2.3, and (*4*) 6.5. pH 2; $[H_2O_2]_0 = 1 \times 10^{-1}$, $[D]_0 = 4 \times 10^{-5}$ M.

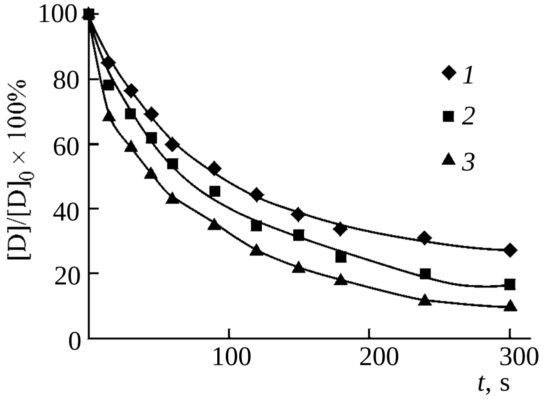

Fig. 2. Kinetic curves for bleaching of Acid Blue 80 ($[D]/[D]_0 \times 100\%$) in the system Fe^{2+}–H_2O_2–Dye at different hydrogen peroxide concentrations. $[H_2O_2]_0 \times 10^2$, M: (*1*) 5, (*2*) 10, and (*3*) 15. pH 2; $[D]_0 = 4 \times 10^{-5}$, $[Fe^{2+}]_0 = 1 \times 10^{-5}$ M.

It is seen that the rate of bleaching strongly depends on pH. No oxidation occurs at pH > 3. Reduction of the oxidizing power of Fe^{2+}–H_2O_2 with increasing pH is likely to result from formation of inactive complexes like $Fe(OH)^+$. An almost complete bleaching of the dye is attained within 4–5 min, and the residual chromaticity decreases from 21.8 to 11% (Fig. 1) as the catalyst concentration increases from 1×10^{-5} to 6.5×10^{-5} M. The degree of substrate bleaching rises from 69.1 to 83.6%, depending on the oxidant concentration (Fig. 2). Using these data, by the van't Hoff method we calculated the partial orders of the reaction with respect to all the components. The overall kinetic equation for the reaction rate as a function of reactant concentrations in Fenton's system looks as follows:

$$W_1^D = k_1[Fe^{2+}]^{0.8}[H_2O_2]^{0.5}[D]^1[H^+]^{0.6}.$$

Here, k_1 is the apparent rate constant.

We also examined the formal kinetics of bleaching in neutral medium in the presence of hydrogen carbonate manganese(II) complexes as catalysts. The rate of decomposition of the dye increases with rise in the concentration of Mn^{2+} and HCO_3^- ions and H_2O_2. While finding optimal conditions and determining the partial orders of the reaction, the initial concentrations were varied within the following ranges: $[Mn^{2+}]_0$ 1 ? 10^{-6}–3×10^{-6}, $[H_2O_2]_0$ 0.05–0.1, $[HCO_3^-]_0$ 0.2–0.5, $[D]_0$ 6×10^{-5}–1×10^{-4} M. The plot of W_2^D versus pH is a parabola with its maximum at pH 8.2–8.4, which corresponds to maximal accumulation of $[Mn(HCO_3)]^+$ and $[Mn(HCO_3)_2]$ complexes in solution [4]. Therefore, the subsequent measurements in these systems were performed at pH 8.3. The results are given below.

$[Mn^{2+}]_0 \times 10^6$, M	1.0	2.0	3.0
$W^D \times 10^7$, l mol^{-1} s^{-1}	1.0	2.2	2.9
$[HCO_3^-]_0$, M	0.3	0.4	0.5
$W^D \times 10^7$, l mol^{-1} s^{-1}	1.0	1.8	2.5
$[H_2O_2]_0 \times 10^2$, M	5.0	8.0	10.0
$W^D \times 10^7$, l mol^{-1} s^{-1}	1.5	1.9	2.1
$[D]_0 \times 10^5$, M	6.0	7.0	8.0
$W^D \times 10^7$, l mol^{-1} s^{-1}	1.5	1.8	2.0
pH	7.9	8.1	8.3
$W^D \times 10^7$, l mol^{-1} s^{-1}	7.9	10.4	12.8

On the basis of these data (by the van't Hoff method) we obtained the following overall kinetic equation:

$$W_2^D = \frac{k_2[Mn^{2+}]^1[HCO_3^-]^{1.7}[H_2O_2]^{0.5}[D]^1}{[H^+]^{0.4}}.$$

Here, k_2 is the apparent rate constant.

The concentration of manganese ions in the system Mn^{2+}–HCO_3^-–H_2O_2–D considerably affects the dgree of dye bleaching.

$[Mn^{2+}]_0 \times 10^7$, M	1	2	4	6	8	10
$[D][D]_0 \times 100\%$	80.0	76.4	44.9	25.5	4.9	2.4

pH 8.3; $[H_2O_2]_0$ 0.05, $[HCO_3^-]_0$ 0.35, $[D]_0$ 6×10^{-5} M.

In this system, at a hydrogen peroxide concentration $[H_2O_2]_0$ of 0.1 M, the residual chromaticity was as low as 3.3%. Simultaneous addition to the reaction mixture of *p*-nitroso-*N*,*N*-dimethylaniline (PNDMA), which is a specific acceptor of $OH^{\cdot}$ radicals, and the dye inhibits oxidation of the latter (Fig. 3). We can conclude that the dye is oxidized with hydroxyl ra-

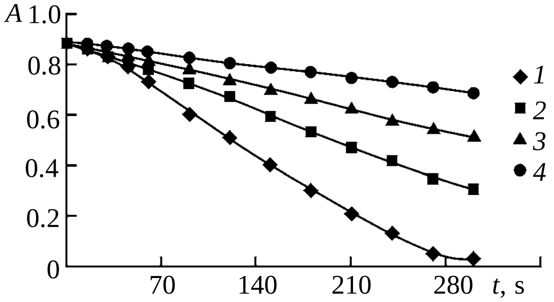

Fig. 3. Effect of *p*-nitrosodimethylaniline (PNDMA) on the oxidation of Acid Blue 80 in the system $Mn^{2+}–HCO_3^-–H_2O_2$. *A* stands for the optical density. [PNDMA] × 10^4, M: (*1*) 0, (*2*) 1, (*3*) 2, and (*4*) 3. $[Mn^{2+}]_0 = 2 \times 10^{-6}$, $[H_2O_2]_0 = 3 \times 10^{-2}$, $[HCO_3^-]_0 = 3 \times 10^{-1}$, $[D]_0 = 8 \times 10^{-5}$, M.

dicals and that inhibition of the process results from competition between *p*-nitrosodimethylaniline and the dye for $OH^·$ radicals generated in the system. Using the competing acceptor technique [7], we determined the elementary rate constant for the reaction of $OH^·$ radicals with Acid Blue 80: $k_{OH+D} = (1.9 \pm 0.2) \times 10^{10}$ l mol^{-1} s^{-1}.

As catalysts for oxidation of Acid Blue 80 in alkaline medium (pH 9–12) we used aqua ions and copper complexes with *o*-phenanthroline (Phen), histidine hydrochloride, 2,2'-bipyridine, tartaric acid, citric acid, ethylenediamine, and tetrasodium ethylenediaminetetraacetate. However, only the system Cu^{2+}–Phen–H_2O_2 turned out to be active in the oxidation. The rates of oxidation of Acid Blue 80 as functions of the initial concentrations of the components are given below.

$[Cu^{2+}]_0 \times 10^6$, M	3.3	5.5	10.0
$W^D \times 10^7$, l mol^{-1} s^{-1}	5.9	7.4	10.0

pH 12; $[Phen]_0$ 1×10^{-4}, $[D]_0$ 4×10^{-5}, $[H_2O_2]_0$ 0.1 M

$[Phen]_0$, M	1.0	2.0	3.0
$W^D \times 10^7$, l mol^{-1} s^{-1}	2.7	6.1	9.8

pH 12; $[Cu^{2+}]_0$ 1×10^{-5}, $[D]_0$ 4×10^{-5}, $[H_2O_2]_0$ 0.1 M

$[H_2O_2]_0 \times 10^2$, M	1.0	5.0	10.0
$W^D \times 10^7$, l mol^{-1} s^{-1}	2.0	3.8	5.1

pH 12; $[Cu^{2+}]_0$ 1×10^{-5}, $[Phen]_0$ 3×10^{-5}, $[D]_0$ 4×10^{-5} M

$[D]_0 \times 10^5$, M	6.0	8.0	10.0
$W^D \times 10^7$, l mol^{-1} s^{-1}	7.9	10.5	12.6

pH 12; $[Cu^{2+}]_0$ 1×10^{-5}, $[Phen]_0$ 3×10^{-5}, $[H_2O_2]_0$ 0.1 M

pH	8.0	9.5	10.5
$W^D \times 10^7$, l mol^{-1} s^{-1}	3.0	8.0	14.9

$[Cu^{2+}]_0$ 1×10^{-5}, $[Phen]_0$ 3×10^{-5}, $[D]_0$ 4×10^{-5},
$[H_2O_2]_0$ 0.1 M

The following overall kinetic equation was derived from these data:

$$W_3^D = \frac{k_3[Cu^{2+}]^{0.5}[Phen]^1[H_2O_2]^{0.5}[D]^1}{[H^+]^{0.3}}.$$

Here, k_3 is the apparent rate constant. As the oxidant concentration increases by an order of magnitude, the degree of bleaching changes within the range from 52.7 to 63.6%.

Analogous kinetic relations were observed for the oxidation with the above three systems of some other acid dyes of the anthraquinone series: Acid Blue 35, Acid Green 27 (C.I. 61 580), and Acid Blue 78. A conclusion can be drawn that the most effective system for the oxidation of Acid Blue 80 is $Mn^{2+}–HCO_3^-–H_2O_2$. It ensures minimal residual chromaticity relative to the other systems even at $[H_2O_2]_0 = 3 \times 10^{-2}$ M, and the required concentration of manganese ions is lower by an order of magnitude than the concentration of copper and iron ions or complexes. The oxidation in acidic or alkaline medium can also be effected with the $Fe^{2+}–H_2O_2$ or Cu^{2+}–Phen–H_2O_2 system, respectively. The use of various transition metals and ligands makes it possible to oxidize large-scale dyes over a wide range of pH with hydrogen peroxide which is one of the least expensive and most ecologically safe oxidants.

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