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Oxidative Destruction of Anthraquinone and Indigoid Compounds in Aqueous Solutions of Sodium Hydroxymethylsulfinate

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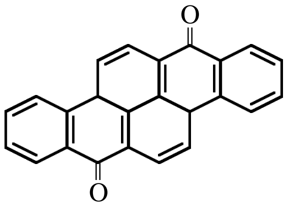
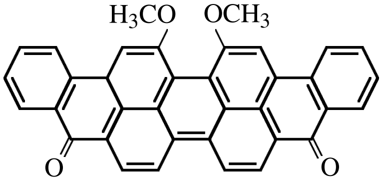
Abstract—Kinetics of quinone–hydroquinone equilibria of tetrabromoindigo, benzopyrene quinone, and dimethoxybenzanthrone in the presence of a reducer and atmospheric oxygen were studied by spectrophotometry. The reason for the destruction of the dyes both in acidic and alkaline media is the molecular oxygen primarily present in the system. The destruction mechanism is considered on an example of disodium 5,5-indigosulfonate.

Water-insoluble pigments of the anthraquinone and indigoid series are widely applied in textile industry as dyes. The water-soluble leuco form of the compounds is obtained by their treatment with sulfoxylate reducers, such as sodium hydroxymethylsulfinate (HMS), in alkaline medium. Once the dye has redistributed into fibers, the leuco compound is oxidized into the initial pigment. However, coloration results may strongly vary, which is a technological defect. One of the reasons for less intense and variable shades of the resulting colors are considered to lie in "overreduction" of polycycloquinone dyes, i.e. disturbance of the system of conjugated double bonds. In practice, sodium hydroxymethylsulfinate is used in a 10–25-fold molar excess with respect to dye [1], which is required for preventing oxidation with atmospheric oxygen. Most commonly the destruction of cycloquinones is associated with insufficiently careful meeting reduction parameters. Thus, Peters [2] explains changes in cyclic anthraquinones by the deficit of alkali. At the same time, sodium hydroxymethylsulfinate with its redox potential attaining –1000 mV at pH 12.5 and 100°C [3] cannot cause dye destruction. According to [4, 5], aromatic quinones are capable of undergoing photooxidative and photoreductive destruction. Taking this into account, we can expect that the oxygen primarily present in the system would exert a negative effect on the dye during reduction. Processes that occur in the dye–sodium hydroxymethylsulfinate–oxygen system, as well as reasons for dye destruction during reduction have never been considered in literature. In this connection it is important to examine the mechanism of destruction of polycycloquinones in the course of their reduction with sodium hydroxymethylsulfinate in aqueous solutions and to reveal the role of molecular oxygen in this process.

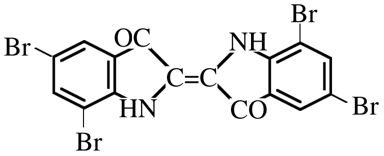
We explored changes in the state of compounds **I**–**III** in many times repeated cycles involving reduction with sodium hydroxymethylsulfinate followed by oxidation with atmospheric oxygen in a hermetic cell.



Dibenzopyrene quinone (**I**)
(vat golden yellow)



Dimethoxybenzanthrone (**II**)
(vat bright green C)



Tetrabromoindigo (**III**)

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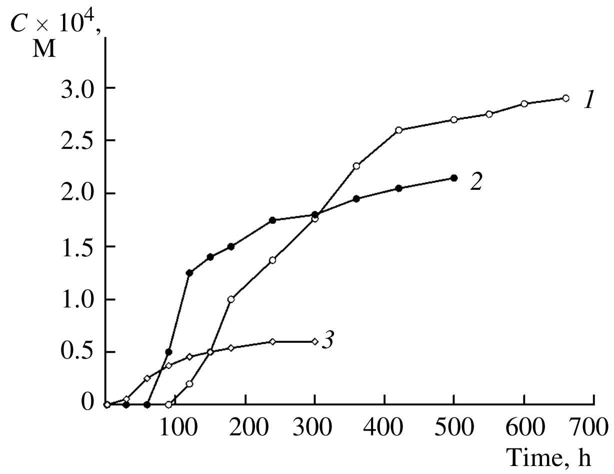


Fig. 1. Kinetic curves of reduction of tetrabromoindigo with sodium hydroxymethylsulfinate in consecutive redox cycles in the presence of dissolved oxygen. (*1*) 1st cycle, (*2*) 3rd cycle, and (*3*) 6th cycle.

The degree of conversion of the compounds in the oxidation–reduction cycles was estimated by the results of five runs. As an example we give on Fig. 1 the kinetic curves of reduction of tetrabromoindigo (**III**) in six consecutive redox cycles. The reduction rate constants calculated for each of the cycles are close to each other (~10^{-3} s^{-1}). The attenuation of the absorption maximum of the reduced form is indicative of side reactions that affect the state of the dye or cause its destruction. The greatest deviation of the equilibrium concentration of the leuco form from the initial value was detected for compound **III** (35 ± 5%). The losses for compound **I** were found to be 15 ± 5%, and for compound **II** they did not exceed the measurement error.

In the initial stage, the dissolved oxygen present in the system produces oxidative destruction of sodium hydroxymethylsulfinate (C–S bond cleavage) to form the sulfoxylate ion $H\dot{S}O_2^-$, the dithionite ion $S_2O_4^{2-}$, and the radical ion $^{\cdot}SO_2^-$ [3].

$$HOCH_2SO_2H \rightleftarrows H\dot{S}O_2^- + {}^{\cdot}CH_2(OH), \quad (1)$$

$$H\dot{S}O_2^- \rightleftarrows H^+ + \dot{S}O_2^{2-}. \quad (2)$$

The radical ion reacts with oxygen, yielding the superoxide ion $^{\cdot}O_2^-$ which disporoportionates into peroxides [6, 7].

$$^{\cdot}SO_2^- + O_2 = SO_2 + {}^{\cdot}O_2^-, \quad (3)$$

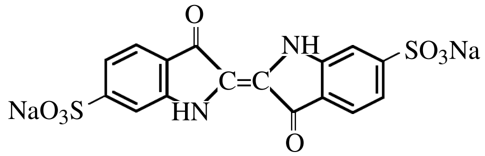
$$H^+ + {}^{\cdot}O_2^- = {}^{\cdot}HO_2, \quad (4)$$

$$^{\cdot}O_2^- + H\dot{O}_2 + H^+ = O_2 + H_2O_2, \quad (5)$$

$$^{\cdot}HO_2 + {}^{\cdot}HO_2 = O_2 + H_2O_2. \quad (6)$$

The presence in the system of peroxides was established by qualitative reactions with titanium sulfate and phenolphthalein [8]. The hydrogen peroxide evolved can accumulate in the system, since, as found in [9], sodium hydroxymethylsulfinate very slowly reacts with H_2O_2. At pH 4.0, *T* 293K, and [HMS] = [H_2O_2] = 7.6 M, the reaction time is 3 h. With increasing pH, the reaction is even stronger decelerated [10], and in alkaline media it scarcely occurs.

Dye reactions with hydrogen peroxide in neutral and alkaline solutions of sodium hydroxymethylsulfinate was studied on an example of a water-soluble model of polycycloquinone dyes, specifically, disodium 5,5-indigosulfonate [indigocarmine (**IV**)].



Indigocarmine (**IV**)

It was found that the time of this reaction is several hours. In experiments with additions of hydrogen peroxide into the HMS–indigocarmine system we observed no negative effect of H_2O_2 on the dye during reduction.

Oxidation of the leuco form of a dye to the initial quinone with H_2O_2 solutions is a known, widely used method of textile dyeing, and further oxidation of the quinone under these conditions is practically impossible. Apparently, the losses of the dye in repeated redox cycles are explained by other reasons, and not by the appearance of hydrogen peroxide in the system.

Taking into account that reduction of the carbonyl groups of polycycloquinones occurs stepwise, via semiquinone radical formation, we can suggest that the most probable reason for the destruction of dyes is reaction of their half-reduced form with the superoxide ion $^{\cdot}O_2^-$ which is a precursor of H_2O_2. Evidence for this suggestion comes from the results of model experiments, when Mn^{2+} ions were added into the system to catalyze superoxide destruction. In these conditions, no indigocarmine destruction was observed.

To obtain evidence for the proposed destruction mechanism, we studied the kinetics of reaction of sodium hydroxymethylsulfinate with indigocarmine at room temperature. The quinone–hydroquinone transitions were studied in the range 280–700 nm at pH 4.95, 7.0, 8.1, and 9.35 in the presence of dissolved oxygen. Indigocarmine absorbs at λ 610 nm and its leuco form, at 360 nm. Figure 2 shows the absorption curves of the initial quinone form of compound **IV** and products obtained by oxidation of the leuco form with atmospheric oxygen. The attenuation of the absorption maximum (curves *2–4*) compared with initial (curve *1*) indicates that indigocarmine undergoes destruction both in acidic and in alkaline media.

Figure 3 depicts the absorption spectra of indigoarmine (**IV**) during reduction at various instants of time and at fixed pH values. Analysis of the experimental data showed that increasing alkalinity of the medium shifts the absorption maximum of the reduced form from 360 (Fig. 3a) to 410 nm (Fig. 3d), which is associated with deprotonation of the corresponding groups.

$$>C{-}OH \underset{H^+}{\overset{OH^-}{\rightleftarrows}} >C{-}O^-$$

Initially, the absorption band of the leuco form is lacking (Fig. 3a), and it appears only after 360 s.

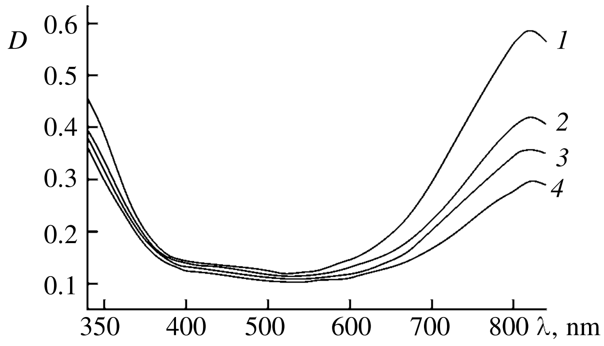


Fig. 2. Spectra of indogocarmine (**IV**) after reduction with sodium hydroxymethylsulfinate and subsequent air feeding (*T* 323 K; [**IV**]$_0$ 3.33×10^{-5}, [HMS]$_0$ 6.96×10^{-3} M. (*1*) Initial quinone form of compound **IV** and (*2–4*) regenerated forms at pH 9.35, 7.00, and 4.10, respectively.

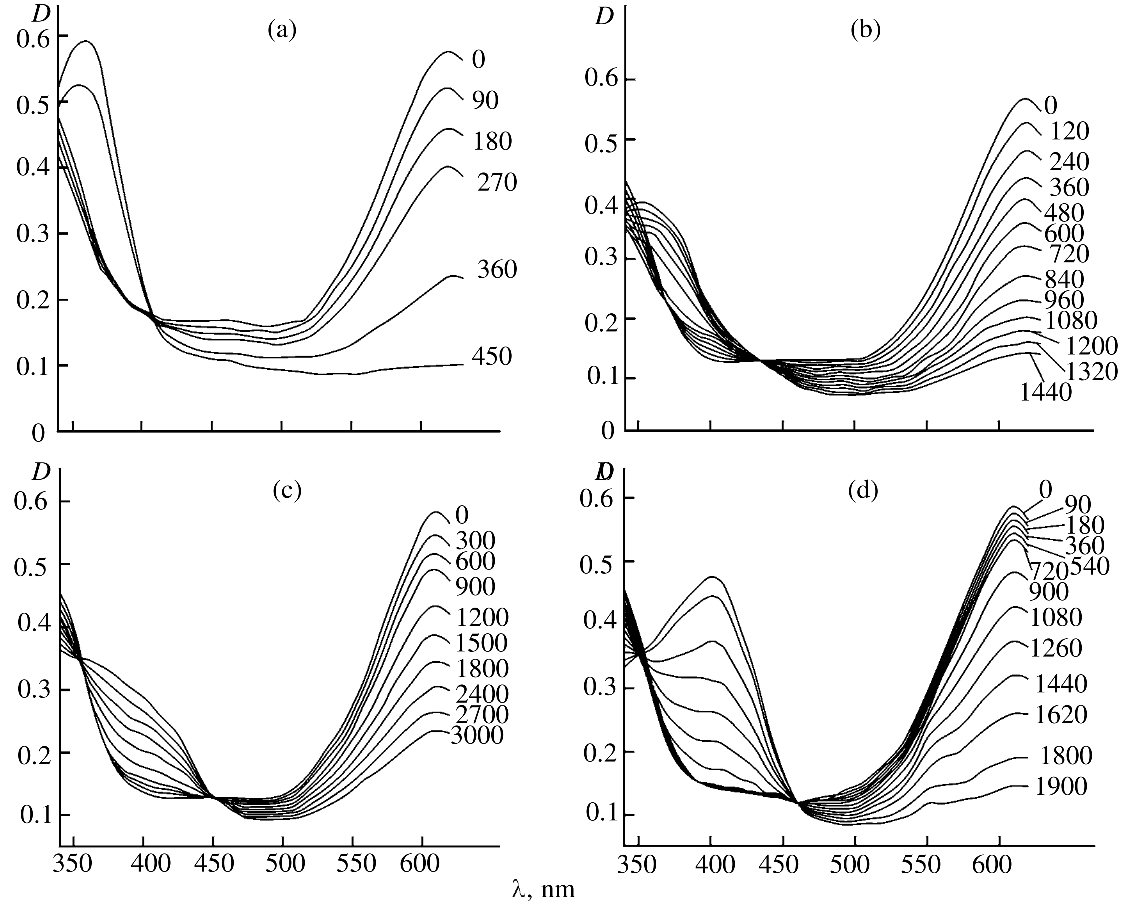
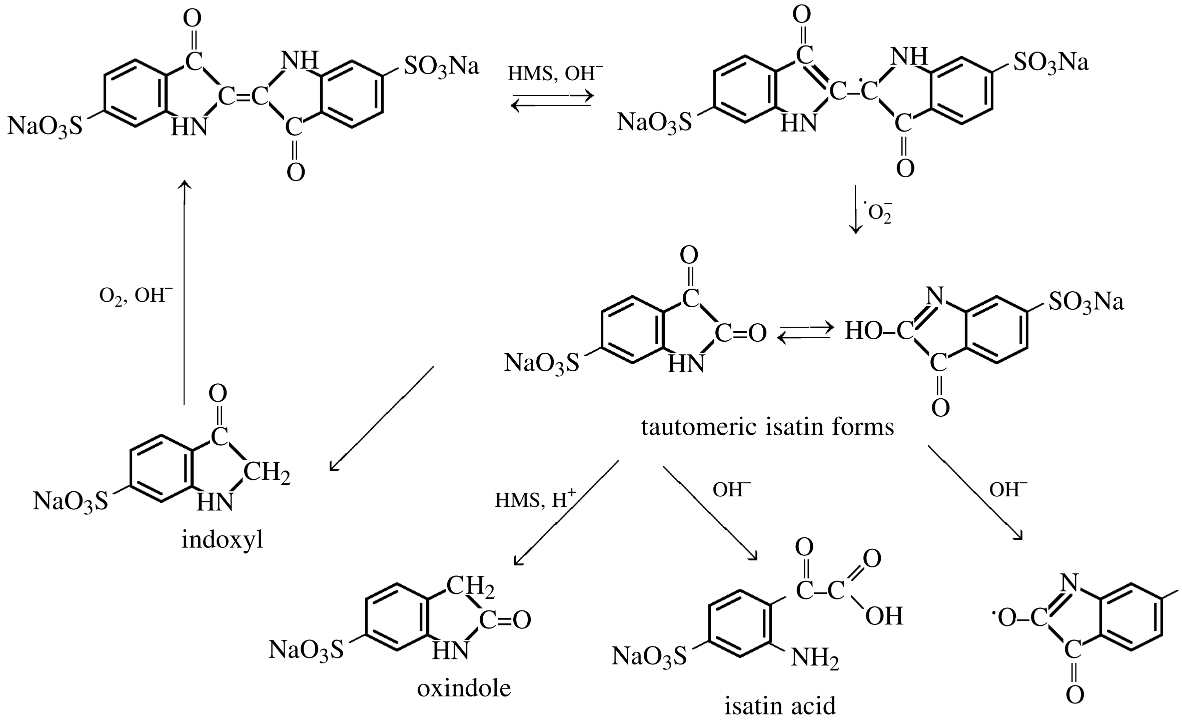


Fig. 3. Transformation of the spectrum of indigocarmine (**IV**) at fixed instants of reduction in a solution of sodium hydroxymethylsulfinate, containing oxygen (*T* 323 K; [**IV**]$_0$ 3.33×10^{-5}, [HMS]$_0$ 6.96×10^{-3} M. pH: (a) 4.95, (b) 7.0, (c) 8.10, and (d) 9.35.

In passing from acidic to neutral media, the optical density at λ_{max} 400 nm (Fig. 3b) begins to grow. The appearance of the latter band might be explained by deprotonation of the leuco form, but, if this were so, the absorbance in this region would enhance with increasing alkalinity of the medium. However, we observe the spectra of the leuco form (λ 360 nm) and intermediate compound whose absorption maximum begins to attenuate beginning with pH 8.10 (Fig. 3c) and almost disappears at pH 9.35 (Fig. 3d). The observation of two isosbestic points in Figs. 3b–3d provides evidence showing that a third compound, along with the reduced and oxidized forms, is present in the solution. The band at λ 400 nm is likely to belong to isatin derivatives formed by C–C bond cleavage in the dye [11, 12]. The semiquinone radical formed by reduction of the cycloquinone [13] (as judged from the presence of an absorption maximum at λ 553 nm in Fig. 3d) will react with the superoxide ion by the following scheme. In the course of reduction, depending on the acidity of the medium, the isatin forms can convert into oxindole and indoxyl, with regeneration of the indigoid form by oxidation of the latter.



Isatin is stable in neutral and weakly alkaline media [14]. In alkaline media, isatin can react with hardness salts to form sparingly soluble colored compounds which affect color shade and deteriorate mechanical stability parameters. Moreover, the cycle may be interrupted with formation of isatin acid and color loss.

The induction period observed in the kinetic curves (Fig. 3) at almost any pH values is a time required for accumulation of oxidative destruction products of sodium hydroxymethylsulfinate, their attack on the semiquinone form of the dye, and destruction of the latter.

Consequently, the reduction–oxidation of polycycloquinone dyes with sodium hydroxymethylsulfinate in the presence of oxygen is a fully reversible process. The presence of atmospheric oxygen in the course of reduction causes destruction of the dyes both in acidic and alkaline media. The dye loss per one redox cycle is 15–40% (depending on the dye structure). The oxidative destruction of the dyes is initiated by the radicals formed reaction by sodium hydroxymethylsulfinate with molecular oxygen.

EXPERIMENTAL

The kinetics of reduction of benzopyrene quinone and tetrabromoindigo were studied by spectrophotometry in a hermetic cell in the presence of atmospheric oxygen. Quinoid forms **I**–**III** were studied as finely dispersed hydrosols prepared as described in [15]. The hydrosols were resistant to sedimentation for 72 h, and their absorbance obeyed the Bouguer–Lambert– Beer law up to a concentration of 10^{-4} M. The concentration of dissolved oxygen in the hydrosols corresponded to its equilibrium concentration in water at 95°C and at a pressure equal to atmospheric. Reducer solutions were prepared by solution of crystalline sodium hydroxymethylsulfinate in deaerated distilled water.

Reduction of cycloquinones was performed in oxygen-proof cells to constant optical density. Oxygen was then fed, and the reduced (hydroquinone) form was oxidized to constant quinone concentration. With a large excess of reducer, the oxidation and reduction processes were repeated several times. Measurements were performed on a Specol-211 spectrophotometer at 300–700 nm, pH 12.5, and a dye–sodium hydroxymethylsulfinate molar ratio of 1 : 100. The reduction temperature (95°C) was maintained with a thermostat with an accuracy of 0.1°C.

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