Physical Chemistry

Kinetic peculiarities of redox reactions sensitized by colloidal CdS under steady-state irradiation. The effect of adsorption-desorption processes on the reaction

*I. N. Mart'yanov, E. N. Savinov, and V. N. Parmon**

G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,
5 ul. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 355 756

Photoreduction of Methyl Orange dye (MOr) by sodium sulfide was studied under steady-state photolysis (λ = 365 nm). The reaction was sensitized by the CdS colloid with the characteristic ~5-nm particle size. The quantum yield of the reaction is independent of the light intensity when the latter is less than 5 mW cm^{-2}. The form of the dependence of the initial quantum yield of the reaction on [MOr] coincides qualitatively with the adsorption isotherm of the dye on the CdS surface. The reaction kinetics under steady-state irradiation were analyzed. The kinetics in solution as a whole are shown to be adequate to those on a single colloidal particle. On the basis of the experimental data, two types of surfaces of the colloidal particles are suggested ("open" and "covered" with macromolecules of a colloid stabilizer), which significantly differ in the rate at which they establish an adsorption-desorption equilibrium with the solution.

Key words: photocatalyst, adsorption, surfactant, kinetics, colloid, cadmium sulfide.

More than a hundred different reactions in which dispersed semiconductors act as photocatalysts are known, and photocatalytic methods are beginning to be used for sewage purification.[1,2] In the majority of cases, the detailed mechanisms of these processes are unknown and they are usually presented as simple chemical schemes, which are, in fact, overall equations of the reactions that occur in the system. Moreover, the mechanism of photocatalytic processes on dispersed semiconductors is usually studied by pulse methods, whereas steady-state irradiation is suggested, as a rule, for their practical use.

Ultradispersed semiconducting particles with $2r \leq 5$ nm are of special interest from the viewpoint of photocatalysis. These particles are intermediate between bulky semiconductors and molecules or clusters of the same chemical composition and are characterized by specific physicochemical and photophysical properties, which have not been adequately studied.

In the present work, the kinetics of the model reduction of Methyl Orange (MOr) dye photosensitized by an ultradispersed CdS colloid under steady-state irradiation at the basic adsorption band of the semiconductor are studied in detail.

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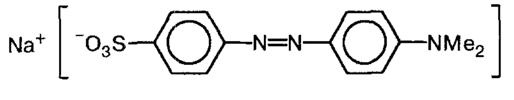
Experimental

Reagents and materials. Distilled water, Na_2SO_3 (analytical grade), $CdCl_2$, $K_2C_2O_4 \cdot H_2O$ (reagent grade), and the MOr anionic organic dye, sodium *para*-(*para*-dimethylaminophenylazo)benzene sulfonate:



were used.

$Na_2S \cdot 9H_2O$ (high-purity grade) and industrial CdS (reagent grade, TU-6-09-3750-74) were used without additional purification. Water-soluble polymers, polyacrylamide (PAA) with the degree of polymerization $n \approx 10^5$, and polyvinyl alcohol (PVA) with $n \approx 10^3$, were used as stabilizers of colloids and suspensions.

Preparation of colloids and suspensions. All colloids and suspensions were prepared by stirring solutions with a magnetic bar at room temperature. To prepare the CdS colloid, two solutions were first prepared. Solution 1 was prepared by adding 15 mL of an aqueous 10^{-2} *M* solution of PAA and then 0.25 mL of an aqueous 10^{-1} *M* solution of $CdCl_2$ to 10 mL of water. Solution 2 was prepared by adding 1 mL of an aqueous 10^{-1} *M* solution of Na_2S to 24 mL of water. Then solution 2 was rapidly added to solution 1. The colloid obtained was kept at least 1 day before use.

Particle size was controlled at the edge of the adsorption spectrum of the CdS colloid (Fig. 1) using the correlation dependence presented in a work previously published (Ref. 3).

Aqueous noncolloidal CdS suspensions were prepared according to the following schemes. The suspension without PAA: {31.5 mL of H_2O + 2.5 mL of $CdCl_2$ (10^{-1} mol L^{-1}) + 10 mL of Na_2S (10^{-1} mol L^{-1})}; the suspension with PAA: {31.5 mL of H_2O + 2.5 mL of $CdCl_2$ (10^{-1} mol L^{-1}) + 10 mL of Na_2S (10^{-1} mol L^{-1}) + 1.5 mL of PAA (10^{-2} mol L^{-1})}.

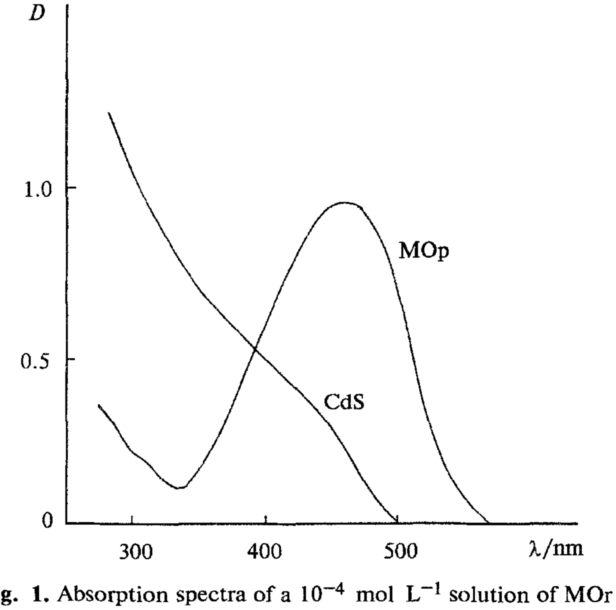


Fig. 1. Absorption spectra of a 10^{-4} mol L^{-1} solution of MOr (in water) and the CdS colloid.

Both of the suspensions were kept at least 1 day before use.

Kinetic experiments. A solution (2 mL) containing all necessary components ([CdS] = $0.4 \cdot 10^{-4}$, [PAA] = $3 \cdot 10^{-3}$, [MOr] = 10^{-4}, [Na_2S] = 10^{-2}, and [Na_2SO_3] = 10^{-2} mol L^{-1}) was placed in a standard quartz cell (optical length 1 cm). Argon was bubbled through the cell for 20 min to remove dissolved oxygen. If necessary, the cells were thermostated at 20 °C.

The sample was irradiated with the filtered light of a DRSh-1000 lamp. Light filters (UFS-2 + SZS-21) were used to pick out the band at λ = 365 nm from the spectrum of the mercury lamp and to suppress the scattered light in the irradiation channel. ZhS-16 + SZS-22 light filters were used in the registration channel.

The light intensity was varied by calibrated metallic grids and neutral glass light filters of the NS series and monitored by a LM-2 intensity gage. The kinetics of the photoreduction of MOr were studied directly in the irradiation process by decolorization at λ = 500 nm, which corresponds to the absorption band of MOr and zero optical density of the colloid, using a Shimadzu UV-300 spectrophotometer.

Since the initial oxidized form of MOr is the single component of the system that absorbs light at the given wavelength, the rate (w) of MOr reduction in the sample studied can be easily calculated from the change in the optical density of the solution:

$$w = \frac{d[\mathrm{MOr}]}{dt} = \frac{1}{\varepsilon \cdot L} \cdot \frac{dD}{dt}, \qquad (1)$$

where D is the optical density of the sample at λ = 500 nm, $\varepsilon \approx 0.6 \cdot 10^4$ L (mol cm)$^{-1}$ is the extinction coefficient of MOr, L = 1 cm is the optical length of the cell with the solution studied.

The experimental quantum yield of the reaction, φ^{exp}, for the sample studied was determined as the ratio of the number of the electrons transferred to MOr due to a photocatalyst to the number of photons absorbed by the CdS colloid. The value of φ^{exp} was calculated by the formula:

$$\varphi^{exp} = \frac{w \cdot V}{\Delta I \cdot S}, \qquad (2)$$

where S = 1 cm^2 is the surface area of the cross section of the irradiating light beam, V = 2 mL is the volume of the sample, and ΔI is the intensity of the light absorbed by the CdS colloid.

Since both the CdS colloid and the MOr dye absorb at 365 nm, we can write the following expression:

$$\Delta I = I_0 \left(1 - 10^{-(D_c + D_{MOr})}\right) \cdot \frac{D_c}{D_c + D_{MOr}}, \qquad (3)$$

where I_0 is the intensity of the light incident on the front wall of the cell, D_c and D_{MOr} are the optical densities of the sample due to the absorption by the colloidal particles and the dye, respectively. Optical densities for a typical sample are the following: D_c = 0.65 for the colloid and D_{MOr} = 0.22 for [MOr] = 10^{-4} mol L^{-1}; therefore, $\Delta I/I_0$ = 64.

Adsorption isotherms. The adsorption isotherm of MOr on the surface of CdS was measured for a suspension of industrial CdS dispersed in water with a UZDN-1 ultrasonic dispergator. The size distribution of the suspension particles (Fig. 2) was determined on a Size-Counter instrument. Two samples were prepared (see Fig. 2): sample *1* contained a sample of indus-

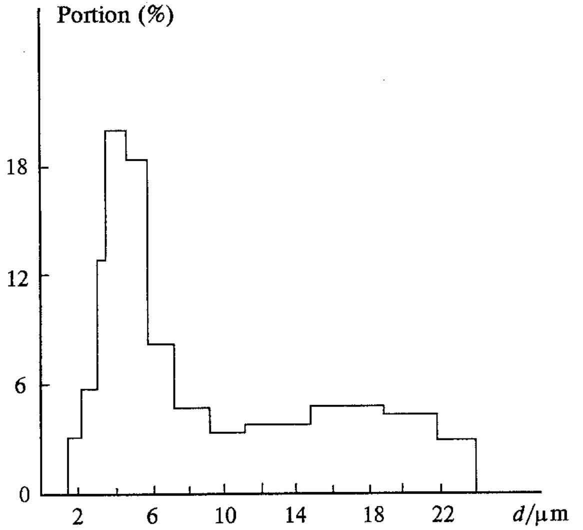


Fig. 2. Size distribution of CdS particles in an aqueous suspension of industrial CdS prepared by ultrasonic dispergation.

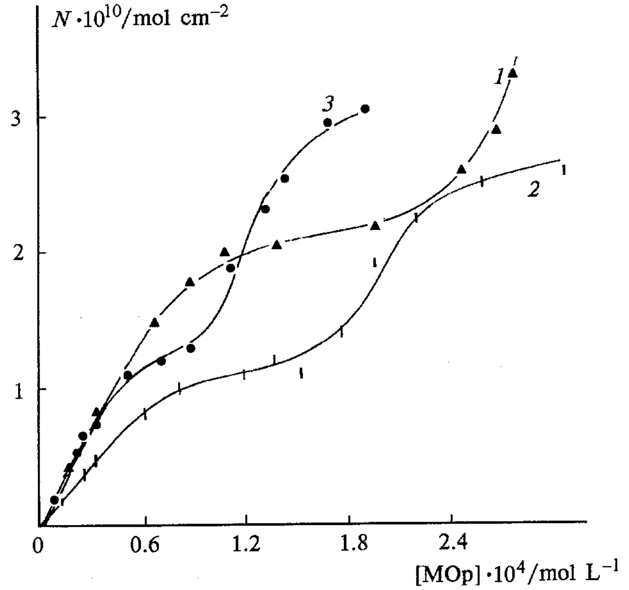


Fig. 3. Adsorption isotherms of MOr on suspended CdS particles at 20 °C in systems containing various additives: 2.00 g of CdS + 15 mL of H_2O (*1*); 2.00 g of CdS + 50 μL of NaCl (0.1 *M*) + 15 mL of H_2O (*2*); 2.87 g of CdS + 3.12 mL of PAA (10^{-2} mol L^{-1}) + 0.33 mL of Na_2S (0.1 *M*) + 11.65 mL of H_2O (*3*).

trial CdS, distilled water, and the corresponding additives (Fig. 3), while sample *2* was of the same composition but without CdS.

The specified amount of MOr was added subsequently to each of the samples, the mixtures were carefully stirred for 5 min, and then the first sample was centrifuged for 3 min on a T-51 centrifuge. The concentrations of MOr in solutions *1* and *2* were compared by spectrophotometry. The *N* value (the number of moles of MOr) adsorbed on 1 cm^2 of the suspension surface was calculated from the difference in optical densities of solutions *1* and *2*. The total surface area of the suspension was calculated on the basis of the size distribution of the particles (see Fig. 2) with the assumption that they were spherical.

Results and Discussion

Reactions in the System

The method of steady-state photolysis was used to study the photosensitized reduction of MOr dye, which is able to act as an electron acceptor.[4] MOr is easily reduced without the formation of dimers. The absorption spectrum of MOr in the pH range from 10 to 12 is nearly unchanged. These facts considerably simplify the interpretation of the experiments on MOr redox transformations.

The CdS colloid with $d \sim 5$ nm served as the photocatalyst. Sodium sulfide was used, as a rule, as an electron donor. In an aqueous solution with pH from 10 to 12, the sulfide ion exists predominantly as the HS^- anion (see Ref. 5).

The photochemical processes in the presence of CdS colloids occur due to the generation of nonequilibrium holes (*h*) and electrons (*e*) in CdS:

$$\mathrm{CdS} \xrightarrow{h\nu} h + e \ .$$

In the photoinduced process, the HS^- ion is oxidized by holes to elemental sulfur:

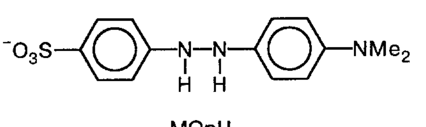
$$\mathrm{HS^-} + 2h \longrightarrow \mathrm{S} + \mathrm{H^+} \ .$$

Then the sulfur formed is removed from the surface of the CdS colloidal particle through a reaction with the sulfite ion:[6]

$$\mathrm{S} + \mathrm{SO_3^{2-}} \longrightarrow \mathrm{S_2O_3^{2-}} \ .$$

In this process, MOr is reduced by nonequilibrium holes of CdS to the $MOrH_2$ leuco-form, which has no absorption band at 500 nm.

$$\mathrm{MOp} + 2e + 2\mathrm{H^+} \longrightarrow \mathrm{MOpH_2}$$



$MOpH_2$

The protonation of the reduced form of MOr is a very fast reaction, which occurs immediately after the electron transfer.[4] No stable one-electron reduced form of MOr is described in the literature. Therefore, we assume that the photocatalyst provides the transfer of a single electron under the action of the photon, while the reduction of MOr and the oxidation of HS^- occur at stages that do not determine the reaction rate.

In terms of these assumptions, the overall scheme of the process studied can be written in the following form:

$$MOr + HS^- + SO_3^{2-} + H^+ \xrightarrow[CdS]{h\nu} MOrH_2 + S_2O_3^{2-}. \quad (4)$$

The estimations of the molar concentration of colloidal particles in the solution and the number of photons absorbed by each colloidal particle in a unit of time are important for the further discussion.

Assuming that the volume of a colloidal particle ($d \approx 5$ nm) is equal to 100 nm^3 and taking into account that the density of CdS is 4.8 g cm^{-3}, the molar mass of CdS is 144.4 g mol^{-1}, and $[CdS] = 0.4 \cdot 10^{-4}$ mol L^{-1}, the concentration of colloidal particles can be estimated as $[C] \approx 2.2 \cdot 10^{-7}$ mol L^{-1}.

It is easy to calculate that the number of photons (ν) absorbed by a colloidal particle in 1 s is equal to

$$\nu \approx \frac{\Delta I \cdot S}{[C] \cdot S \cdot L} \approx \frac{0.64 I_0}{[C] \cdot L} \approx 25 \text{ quantum s}^{-1}$$

when the irradiation intensity $I_0 \approx 3$ mW cm^{-2} $\approx 0.8 \cdot 10^{-8}$ E(Einstein) s^{-1} cm^{-2}. Here ΔI S is the number of photons absorbed by the CdS colloid and $[C]$ S L is the number of colloidal particles that fall to the light beam.

Experimental peculiarities of the photocatalytic action of ultradispersed CdS colloids under steady-state irradiation

The typical experimental kinetic curve of MOr decolorization consists of three regions (Fig. 4): AB, a rapid initial decrease in [MOr]; BC, a linear region (observed nearly until the complete consumption of MOr); and CH, a fast retardation of the reaction rate. This kinetic dependence becomes more obvious, taking a characteristic stepped form, if the "quantum yield φ—current concentration of MOr" coordinates are used (by formulas (1)—(3)) instead of the "optical density D ([MOr])—time t" coordinates. The kinetic curve for the initial $[MOr]_0 = 10^{-4}$ mol L^{-1} is presented in Fig. 5 as an example. In these coordinates, the change in [MOr] (from the initial $[MOr]_0 = 10^{-4}$ mol L^{-1} to $[MOr] = 0.6 \cdot 10^{-4}$ mol L^{-1}) is accompanied by a twofold change in the quantum yield of the reaction system (from the initial $\varphi_0 = 0.03$ to the steady-state $\varphi_{st} \approx 0.015$), the stabilization of the quantum yield at the level of $\varphi_{st} \approx 0.015$ (from $0.6 \cdot 10^{-4}$ to $0.1 \cdot 10^{-4}$ mol L^{-1} for [MOr]), and finally, a sharp decrease in φ to 0 as [MOr] decreases from $0.1 \cdot 10^{-4}$ mol L^{-1} to 0.

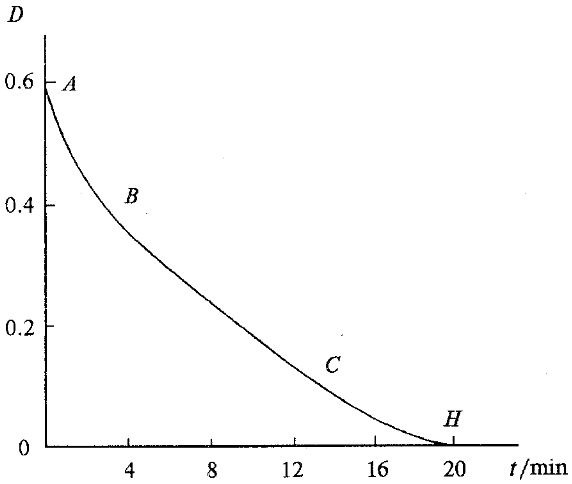


Fig. 4. Kinetics of the photoreduction of MOr in the presence of the CdS colloid in the system containing Na_2S as the electron donor. $[CdS] = 0.4 \cdot 10^{-3}$, $[PAA] = 2.4 \cdot 10^{-3}$, $[Na_2S]_0 = 10^{-2}$, $[Na_2SO_3]_0 = 10^{-2}$, $[MOr]_0 = 10^{-4}$ mol L^{-1}, $I_0 = 0.8 \cdot 10^{-8}$ E s^{-1} L^{-2}.

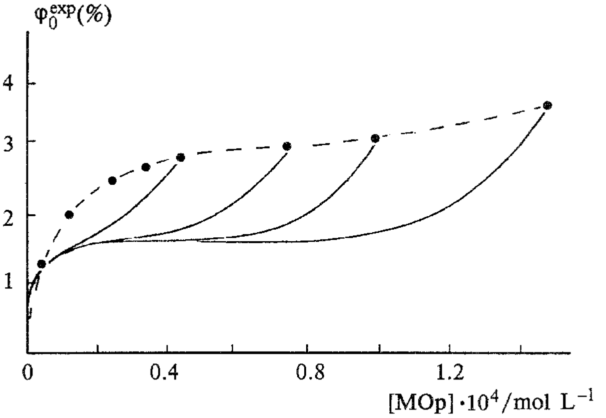


Fig. 5. Dependence of the initial quantum yield ($\varphi_0{}^{exp}$) on the initial concentration ($[MOr]_0$) (dotted line) and typical kinetic curves (solid lines) obtained for different values of $[MOr]_0$ in the system with Na_2S as the donor. For conditions see Fig. 4.

We found that the experimental initial reaction rate (w_0) is proportional to I_0 (Fig. 6), *i.e.*, the initial quantum yield of the reaction ($\varphi_0{}^{exp}$) is independent of I_0, for all light intensities used (E s^{-1} cm^{-2}): $0.2 \cdot 10^{-8} < I_0 < 1.6 \cdot 10^{-8}$.

The comparison of the experimental dependence of $\varphi_0{}^{exp}$ on [MOr] (see Fig. 5) and the adsorption isotherm of MOr in the aqueous suspension of CdS with the corresponding additives (see Fig. 3) shows a qualitative analogy in the shapes of these curves. The characteristic increase in of $\varphi_0{}^{exp}$ after the horizontal region is more pronounced when $K_2C_2O_4$ is used as an electron donor instead of sulfide ions (Fig. 7). This coincidence indicates that adsorbed MOr particles react first.

It is noteworthy that all of the kinetic curves reach the same value of φ_{st} independently of the initial MOr concentration ($[MOr]_0$) (see Fig. 5). The φ_{st}/φ_0 ratio depends on the nature of the polymeric surfactant used to stabilize the CdS colloid. For example, this ratio is equal to ~0.5 in the case of PAA and 0.6 in the case of PVA.

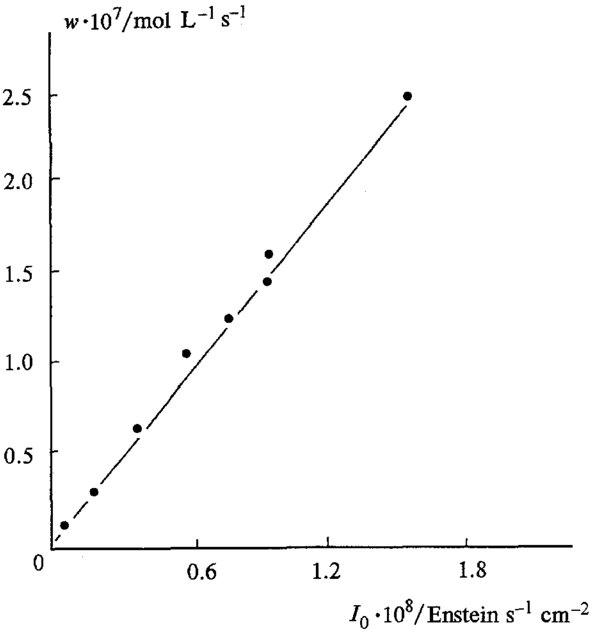


Fig. 6. Dependence of the initial rate (w_0) of the overall reaction (4) on the light intensity (I_0) at λ = 365 nm. ($[MOr]_0$ = 10^{-4} mol L^{-1}).

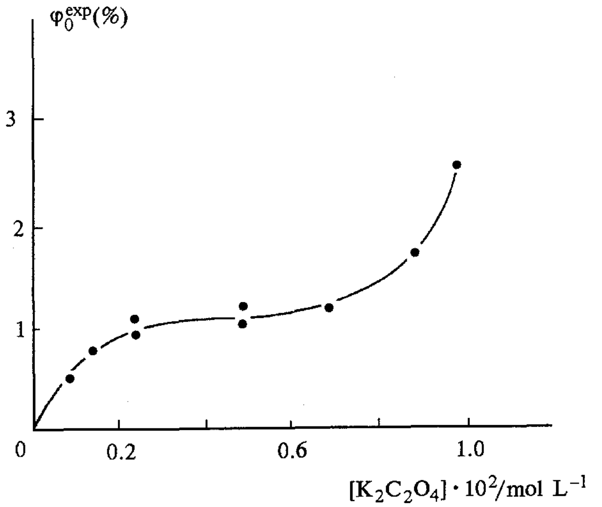


Fig. 7. Dependence of the initial quantum yield ($\varphi_0{}^{exp}$) on $[MOr]_0$ in the system with $K_2C_2O_4$ as the electron donor. For conditions see Fig. 4.

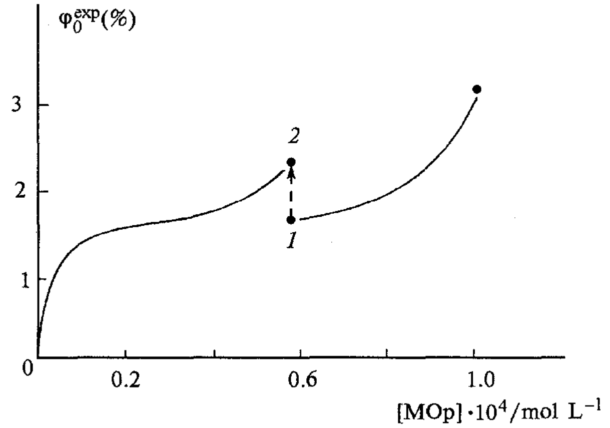


Fig. 8. Effect of interrupting the irradiation on the change in the quantum yield of the overall reaction (φ^{exp}): *1*, interrupting the irradiation; *2*, renewal of the irradiation after 1 h. For conditions see Fig. 4.

It is also interesting to note that some slow relaxation processes are occur in the reaction studied. When the irradiation of the sample is stopped, φ reaches a steady-state value (for example, point *1* in Fig. 8). Then, if the irradiation is started again after ~1 h, φ immediately becomes higher than φ_{st} and again tends to φ_{st} with time.

The experiments with "rough" noncolloidal CdS suspensions show that this peculiarity of the behavior of the systems studied and the establishment of φ_{st} are observed only in the presence of the macromolecular surfactant stabilizer (PAA). In fact, one can assume that slow conformational transformations in macromolecules of the surfactant can significantly affect the adsorption-desorption equilibria on the surface of the semiconducting particles studied and thus influence the course of the redox processes that are photogenerated by these particles.

We attempted to semiquantitatively describe the processes observed in the system studied.

Semiquantitative description of the photocatalytic action of CdS colloids taking in to account adsorption-desorption processes

It is convenient to distinguish three states of the photocatalyst particle to describe the photocatalytic action of semiconducting particles in the transfer of an electron from a donor to an acceptor: *1*, the semiconducting particle does not contain excess photogenerated electrons or holes; *2*, the semiconducting particle simultaneously contains one excess electron and one excess hole; and *3*, excess charge carriers reach the semiconductor—electrolyte interface to be "captured" by the surface levels of the semiconductor.

It is important for further discussion to estimate the characteristic time scales for the transitions of the ~5-nm CdS colloidal particles from one state to another.

The transition from state *1* to state *2* occurs with probability close to unity each time a colloidal particle absorbs a photon, *i.e.*, with the frequency ν ~ 25 s^{-1}. In other words, the transition from state *1* to state *2* occurs every $\tau_{1,2}$ ~0.04 s.

The transition from state *2* to state *3* occurs *via* the transfer of the excess charge carriers generated to the surface of the colloidal particle. The characteristic time of this transfer ($\tau_{2,3}$) can be estimated on the basis of the concepts of the diffusion motion of nonequilibrium charge carriers:

$$\tau_{2,3} \approx r^2/\chi \approx 10^{-13}\ \text{s}, \qquad (5)$$

where χ ~0.4 $\text{cm}^2\ \text{s}^{-2}$ is the diffusion coefficient for the charges in CdS [7] and $r \approx 2.5$ nm is the radius of the colloidal particle. The internal quantum yield (φ_{in}) is determined as the ratio of the excess electrons (holes) escaped to the surface of the colloidal particles to the number of excess electrons (holes) formed in the volume of the colloidal particle. It is likely that φ_{in} for the colloidal particles of the size discussed is close to unity.

The transition from state *3* to state *1* corresponds to the recombination of excess charge carriers on the surface of the semiconducting particle or to their transfer through the interface. This transition is completed in $\tau_{3,1} < 10^{-6}$ s (see Refs. 8 and 10).

Note that the quantum yield of the reactions that require the simultaneous presence of two excess electrons (holes) in the colloidal particle is extremely low (for the light intensities used, $I_0 < 1.8 \cdot 10^{-8}$ E s^{-1} cm^{-2}, and the characteristic size of the colloid, $2r \approx 5$ nm). Indeed, this value cannot exceed the probability of the absorption of a photon by the colloidal particle in the presence of an excess electron (hole). Under the conditions of the experiment performed, this probability is equal to 10^{-5}, which is considerably lower than the typical quantum yield (0.03) of the reaction studied. Then the photocatalytic reduction of MOr can be considered as a monoquantum process. In the process of the photocatalytic action, the colloidal particle continuously passes through the following stages:

$$\begin{tikzcd}1 \arrow[r] & 2 \arrow[r] & 3 \arrow[ll, bend left]\end{tikzcd}$$

Reaction (4) occurs in the *3*→*1* transition, and its probability is given by the quantum yield φ. Changing the light intensity causes a proportional change in the number of cycles that each colloidal particle performs in a unit of time; however, it does not affect (for the specified composition of the particle surface) the quantum yield of the reaction on a separate colloidal particle and, hence, in the whole reaction mixture.

Effect of the adsorption of an electron acceptor on the reaction quantum yield. Let us consider probable ways for the transition from state *3* to state *1* to occur in order to determine the dependence of φ on the concentration of ions of the A_{ad} acceptor (in our case, MOr_{ad}) or the D_{ad} donor (in our case, HS^-) on the surface of the colloidal particle. Let us consider that the transition from state *3* to state *1* can be performed *via* three channels (Fig. 9): first, by the recombination of the excess electron and the excess hole, with the effective first-order rate constant k_{r} (hereinafter effective rate constants are measured in s^{-1}); second, by the initial oxidation of the donor by the excess hole, with rate constant k_{D}, followed by the reduction of the MOr molecule by the excess electron (the rate constant k'_{MOr}) or that of the secondary acceptor (*e.g.*, O_2, H_2O), with rate constant k'_{s}; third, by the initial reduction of MOr and the secondary acceptor with the characteristic rate constants k_{MOr} and k_{s}, respectively, followed by the oxidation of the electron donor by the hole (the rate constant k'_{D}).

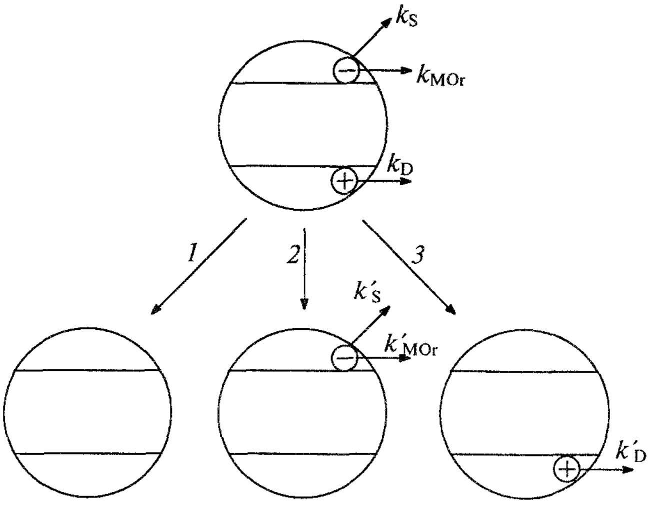


Fig. 9. Scheme of possible channels for the transition of the photocatalyst particle from state *3* to state *1*.

In this case, the time evolution of the transition of the colloidal particle from state *3* to state *1* is described by the following system of differential equations:

$$\frac{\mathrm{d}P_{\text{h-e}}}{\mathrm{d}t} = P_{\text{h-e}} \cdot k_{\Sigma}\ ;$$

$$\frac{\mathrm{d}P_{\text{h}}}{\mathrm{d}t} = P_{\text{h-e}} \cdot (k_{\text{MOr}} + k_{\text{s}}) - P_{\text{h}} \cdot k'_{\text{D}}\ ;$$

$$\frac{\mathrm{d}P_{\text{e}}}{\mathrm{d}t} = P_{\text{h-e}} \cdot k_{\text{D}} - P_{\text{e}} \cdot (k'_{\text{MOr}} + k'_{\text{s}})\ ;$$

$$\frac{\mathrm{d}P_{\text{MOr}}}{\mathrm{d}t} = P_{\text{h-e}} \cdot k_{\text{MOr}} + P_{\text{e}} \cdot k'_{\text{MOr}}\ ;$$

$$\frac{\mathrm{d}P_{\text{D}}}{\mathrm{d}t} = P_{\text{h-e}} \cdot k_{\text{D}} + P_{\text{h}} \cdot k'_{\text{D}}. \qquad (6)$$

Here $P_{\text{h-e}}$, P_{h}, and P_{e} are the probabilities of finding an electron-hole pair, a single hole, and a single electron, respectively, in the semiconducting particle at time t; P_{MOr} and P_{D} are the probabilities of finding a reduced ion of the acceptor and an oxidized ion of the donor, respectively, on the surface of the colloidal particle at the same moment; $k_{\Sigma} = k_{\text{r}} + k_{\text{D}} + k_{\text{MOr}} + k_{\text{s}}$.

One can assume that $P_{\text{h-e}} = 1$ and P_{e}, P_{h}, P_{MOr}, and P_{D} equal 0 at the initial moment $t = 0$. When the process generated by one photon ceases, *i.e.*, at $t \gg 10^{-6}$ s, one can observe: $P_{\text{h-e}}$, P_{e}, P_{h} equal 0, $P_{\text{MOr}} = \Delta P_{\text{MOr}}$, and $P_{\text{D}} = \Delta P_{\text{D}}$.

The theoretical surface quantum yield φ^t determined as the ratio of the probability of finding a reduced ion of MOr to the initial number of electron-hole pairs on the surface of the semiconducting particle is given by the expression:

$$\varphi^t = \frac{k_{MOr}}{k_\Sigma} + \frac{k_D}{k_\Sigma\left[1 + \dfrac{k'_s}{k'_{MOr}}\right]} . \quad (7)$$

The first term of the sum gives the probability of MOr reduction *via* the second channel of the process (see above), and the second term describes the probability of the reduction of MOr *via* the third channel.

Since $\varphi_{in} \approx 1$ (see Eq. (7)) describes the total theoretical quantum yield of the process studied on a single semiconducting particle, φ^t should be averaged over all colloidal particles to determine the theoretical quantum yield of the process for the whole sample studied. Assuming that this averaging does not significantly change the form of function (7) and that in place of the effective rate constants (k) their average over all colloidal particles can be used, we find:

$$\varphi^t = \frac{1}{k_r}\left[{}''K_{MOr}MOr_{ad} + \frac{K_D D_{ad}}{1 + \dfrac{V'_s}{{}''K'_{MOr}MOr_{ad}}}\right], \quad (8)$$

where $''K_{MOr}$, $''K_D$, $''K'_{MOr}$ are the heterogeneous rate constants of the corresponding reactions. In Eq. (8) the observed quantum yield of the reaction (φ^{exp}) is considered to be fairly small (≈ 0.03), suggesting that $k_\Sigma \approx k_r$.

Equation (8) describes qualitatively the dependence of $\varphi_0{}^{exp}$ on [MOr] observed in the experiment.

In fact, the number (concentration) of ions of MOr_{ad} dye adsorbed on the surface of one colloidal particle before the irradiation of the system is a function of [MOr] in the solution and is similar to the MOr adsorption isotherm on the same surface.* Since MOr_{ad} increases as [MOr] increases, the $k'_s/(''K'_{MOr} \cdot MOr_{ad})$ ratio can be significantly lower than 1 when some [MOr]′ concentration is exceeded. If the D_{ad} value is constant, the second term of the sum in (8) becomes constant, resulting in the following expression:

$$\varphi^t_0 = \frac{1}{k_r}\left[{}''K_{MOr}MOr_{ad} + \text{const}\right]. \quad (9)$$

For $[MOr]_0 > [MOr]'$, $\varphi_0{}^t$ really copies the adsorption isotherm of MOr on the CdS colloid with the accuracy of an additive constant and a numerical factor. This point satisfactorily explains the parallelism between the $\varphi_0{}^{exp}$ *vs.* [MOr] dependence after its horizontal region and the adsorption isotherm of MOr on the CdS suspension when $[MOr] > 0.6 \cdot 10^{-4}$ mol L^{-1} (it is likely that the latter value corresponds to the [MOr]′ value).

Let us mention, without a detailed analysis of the $\varphi_0{}^t$ *vs.* [MOr] dependence for $[MOr] \le [MOr]'$, that $\varphi_0{}^t$ also equals to zero when [MOr] = 0. Therefore, the dependences of $\varphi_0{}^{exp}$, $\varphi_0{}^t$, and MOr_{ad} on $[MOr]_0$ must be qualitatively similar over the whole [MOr] range.

Analysis of the kinetic regularities of the system studied. Let us try to correlate the concentration dependence of the observed quantum yield for the whole reaction system with the analogous dependence for a single colloidal particle.

We assume in the calculation of the initial quantum yield that before the reaction, the surface composition is nearly the same for all colloidal particles of the sample. However, distinctions in the surface composition can considerably increase in the course of the reaction. In fact, nonuniform irradiation across the cell results in faster consumption of reagents to form more reaction products on the surface of strongly irradiated colloidal particles than those on the surface of weakly irradiated colloidal particles. In addition, possible distinctions in rate constants may also result in faster consumption of reagents and the formation of reaction products on the surface of more active colloidal particles than on those of less active particles.

Let us show that the composition of the surface of a colloidal particle is not significantly changed during its stay within a light spot (~5 s) at the velocity used for stirring the solution. In fact, based on the adsorption isotherms (see the adsorption isotherm of MOr with additives of PAA and sodium sulfide in Fig. 3 and the adsorption isotherm of Na_2S on the CdS surface),[8] the total numbers of MOr ions and hydrosulfide anions adsorbed on a colloidal CdS particle with the characteristic size (d ~ 5 nm) can be estimated as MOr_{ad} ~100 and $HS^-{}_{ad}$ ~300. Thus, the composition of the surface of the colloidal particle is changed by ≤ 4 % if φ ~0.03 and the number of photons absorbed by the colloidal particle in one second averages ~25 quantum s^{-1} during its stay within the light spot. Note that dynamic adsorption-desorption processes on the surface of the CdS particle give additional inertia to the processes that change the composition of the surface of colloidal particles due to the capacity of the surrounding solution to decrease the given numerical value.

All of the above means that the movement of colloidal particles from strongly irradiated places to weakly irradiated or nonirradiated places and the opposite movement, which occur as the solution is being stirred, are fairly fast. Therefore, spatial nonuniformity of irradiation within the cell cannot be a reason for the substantial distinction in the compositions of the surfaces of different colloidal CdS particles.

Considering the different reactivities of colloidal particles, it is quite correct to assume that the rate constants

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* Unfortunately, since the surfaces of suspended particles of industrial CdS can considerably differ from those of colloidal particles (for example, due to different methods of preparation and/or the prehistory of CdS samples studied), only qualitative similarity of MOr adsorption isotherms should be expected for CdS colloids and an aqueous suspension of industrial CdS in the presence of the corresponding additives.

of the electron transfer through the colloidal particle—electrolyte interface are approximately the same for all colloidal particles and their scattering in the course of the reaction cannot result in any significant variation of the surface composition of the photocatalyst particles. Note that we can speak confidently about the approximate equality of rate constants only for CdS particles with $2r \geq 5$ nm, *i.e.,* in the case when the properties of the colloidal particles are close to those of a large semiconductor. At the same time, a substantial dependence of the rate constants on particle size is quite probable for CdS particles with $2r \leq 5$ nm; this can result in complex "polychromatic" kinetics.[14]

Thus, in the course of the reaction all of the photocatalyst particles in the sample are assumed to have the same surface composition and to be characterized by equal rate constants of the reactions discussed. Since the reaction quantum yield on a single colloidal particle is independent of the light intensity, all colloidal particles in the sample "work" with equal quantum yields despite the nonuniform irradiation within the cell. In this case, the quantum yield calculated by formula (2) for the whole sample corresponds to the quantum yield of the reaction occurring on any of the colloidal particles in the sample. In particular, the kinetic dependences of φ([MOr]) obtained by Eq. (2) copy the φ([MOr]) dependences for each single arbitrarily chosen colloidal CdS particle.

As already mentioned, elemental sulfur is formed on the surface of a colloidal particle in the oxidation of the hydrosulfide anion:

$$\mathrm{HS_{ad}^{-}} + 2h \longrightarrow \mathrm{H^{+}} + \mathrm{S_{ad}}.$$

Some part of the sulfur atoms are easily accessible to sulfite anions from the solution and are rapidly removed from the surface in the course of the reaction

$$\mathrm{S_{ad}} + \mathrm{SO_3^{2-}} \longrightarrow \mathrm{S_2O_3^{2-}}.$$

followed by rapid adsorption of the new hydrodulfide anion. However, others of the sulfur atoms can be "blocked" by a unit or several units of the polymeric molecule of the stabilizer, for example, PAA. It is possible that the process of "blocking" the sulfur is actually the adsorption of the surfactant above the sulfur atoms of the near-surface layer of the colloidal particle. The latter gives rise to steric hindrances to the approach of the $\mathrm{SO_3}^{2-}$ anion to the $\mathrm{S_{ad}}$ particle. In fact, this means the passivation of the "working" (active) surface of the colloidal particle, which eventually may decrease the quantum yield of the reaction.

If the number of PAA units that "block" the sulfur formed from $\mathrm{SO_3}^{2-}$ ions is limited and the surface area "blocked" by these units is less than the working surface of the colloidal particle at the beginning of the reaction, a decrease in φ in the initial region of the kinetic curve occurs up to the value of φ_{st}. This value is due to some stationary state of the working surface not blocked with PAA, which agrees with the experimental data. The fraction of the surface blocked by the polymeric surfactant and, hence, the $\varphi_{\mathrm{st}}/\varphi_0$ value must depend on the nature of the surfactant used.

The slow "dark" relaxation process can be reasonably explained in terms of the model suggested by blocking out the sulfur atoms shut off from interaction with $\mathrm{SO_3}^{2-}$ in the course of some dark process followed by the removal of the sulfur from the surface of the colloidal particle in the form of the thiosulfate anion and the adsorption of the new hydrosulfide anion.

The large size of the surfactant polymeric molecules and the interaction of separate units of these macromolecules considerably decrease the conformational mobility of both the whole molecule and the discrete parts of its chain. Due to this effect, the times of adsorption-desorption of sulfur atoms and other particles can increase to 1 h and more, *i.e.,* to times characteristic of the dark relaxation process observed.

Finally, the mentioned relationship between some of the kinetic peculiarities discussed and the presence of macromolecular stabilizers gives direct evidence for the fact that the decrease in φ within the initial region of the kinetic curve and the dark relaxation process are caused by the presence of surfactant macromolecules in the reaction system.

To semiquantitatively describe the initial region of the experimental kinetic curve, let us consider the data presented in Fig. 10. It can be seen that the kinetic dependences in the "rate (w)—current MOr concentration" coordinates determined for different light intensities (I_0) at constant initial concentrations of reagents are

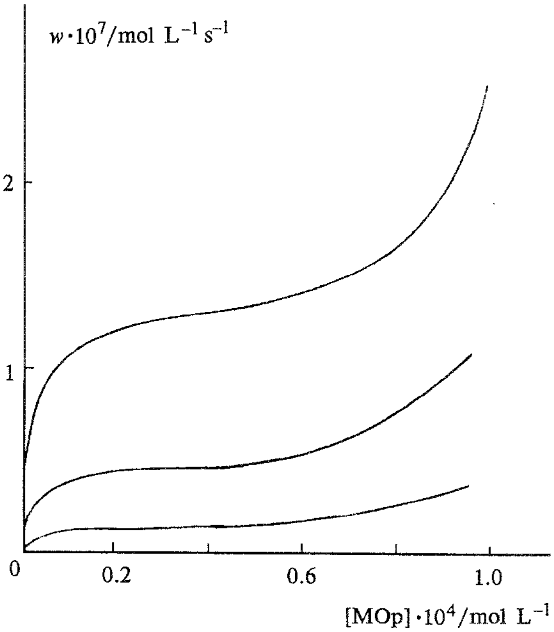

Fig. 10. Kinetics of MOr reduction ($[\mathrm{MOr}]_0 = 10^{-4}$ mol L^{-1}) in the system with $\mathrm{Na_2S}$ as the electron donor for $I_0 \cdot 10^8$, E s^{-1} cm^{-2}: 0.2 (*1*); 0.6 (*2*); and 1.6 (*3*). For conditions see Fig. 4.

similar, *i.e.*, any curve can be transformed into another by multiplying it by a numerical coefficient. Since the similarity factor is equal to I_0, the reaction quantum yield calculated by formulas (2) and (3) and, hence, the composition of the adsorption layer on the surface of the colloidal particle are functions of [MOr] in the sample and explicitly independent of the time required for achieving a given [MOr].

For a specified light intensity within the range studied ($I_{\min} < I_0 < I_{\max}$) at constant initial concentrations of the reagents ($[\mathrm{reag}]_0$), the composition of the adsorption layer on the surface of the colloidal particle during the reduction of MOr can be determined by its current concentration in two limiting cases. First, in the event of fast (compared to the rate of the overall reaction) desorption of the reaction products from the surface of the colloidal particle and fast adsorption of the reagents on its surface when a further decrease in the characteristic time of establishing the adsorption-desorption equilibrium exerts no effect on the $\varphi^{\mathrm{exp}}([\mathrm{reag}]_0, [\mathrm{MOr}])$ dependence. Second, in the event of slow (compared to the rate of the overall reaction) desorption of reaction products or slow adsorption of reagents when a further increase in the time of the adsorption-desorption process also does not affect the $\varphi^{\mathrm{exp}}([\mathrm{reag}]_0, [\mathrm{MOr}])$ dependence.

In the first case, the chemical reaction virtually does not disturb the adsorption-desorption equilibrium of the adsorption layer of the colloidal particle with the solution. The composition of the adsorption layer in the course of MOr reduction can be expressed by the initial concentrations of reagents and the current value of [MOr]. In the second case, the reaction volume of the colloidal particle is restricted by its adsorption layer, whose composition in the course of the reduction of MOr can be also found from $[\mathrm{reag}]_0$ and [MOr]. In the intermediate case, the current composition of the adsorption layer of the surface of the colloidal particle and, hence, the value of $\varphi^{\mathrm{exp}}([\mathrm{reag}]_0, [\mathrm{MOr}])$ depend on I_0.

The aforesaid can be schematically displayed as a hierarchic temporal scale in which the characteristic times of the overall reactions (τ_{p}) and those of establishing adsorption-desorption equilibria ($\tau_{\mathrm{ad\text{-}des}}$) are marked. Let us estimate these times for the reaction system studied.

Let us define τ_{p} as the time necessary to basically change the composition of the adsorption layer in the absence of adsorption-desorption processes. The value of τ_{p} can be easily found by dividing the total number of reagent ions ($\mathrm{MOr}_{\mathrm{ad}}$, $\mathrm{HS^-}_{\mathrm{ad}}$) adsorbed on the surface of the colloidal particle by the total rate of the photoinduced process ($w = \varphi\ \nu$). Taking into account that $\varphi^{\mathrm{exp}} \approx 0.03$ and the value of ν, *i.e.*, the number of quanta absorbed by one colloidal particle in one second, is within the range of $6 < \nu < 45$ (quantum s^{-1}) for $I_{\min} \approx 0.2 \cdot 10^{-8} < I_0 < I_{\max} \approx 1.6 \cdot 10^{-8}$ (E s^{-1}), we obtain that $\tau_{\mathrm{p}} \approx \mathrm{MOr}_{\mathrm{ad}}/\varphi\ \nu$ is within the range from 70 to 500 s.

The characteristic time for establishing the adsorption-desorption equilibrium of PAA is given by the following equality: $\tau^{\mathrm{PAA}}_{\mathrm{ad\text{-}des}} \approx 4000$ s (~1 h).

Let us also estimate the time of establishing the adsorption-desorption equilibrium for low-molecular components of the $\mathrm{MOr{-}HS^-{-}SO_3^{2-}}$ system ($\tau^{\mathrm{low}}_{\mathrm{ad\text{-}des}}$). The collision frequency (ν_{c}) of an arbitrary colloidal particle with ions of the low-molecular component, *e.g.*, MOr ions, is given by the known formula:

$$\nu_{\mathrm{c}} = 4\pi(R_{\mathrm{c}} + R_{\mathrm{MOr}})(\chi_{\mathrm{c}} + \chi_{\mathrm{MOr}})[\mathrm{MOr}],$$

where R_{c} and R_{MOr} are the sizes and χ_{c} and χ_{MOr} are the diffusion coefficients of the colloidal particle and MOr ions, respectively. Assuming that $R_{\mathrm{c}} + R_{\mathrm{MOr}} \approx r \approx 2$ nm, $\chi_{\mathrm{c}} + \chi_{\mathrm{MOr}} \approx \chi_{\mathrm{MOr}} \approx 0.3 \cdot 10^{-5}$ $\mathrm{cm^2\ s^{-1}}$, and $[\mathrm{MOr}] = 10^{-4}$ $\mathrm{mol\ L^{-1}}$, we find that each particle of the colloid undergoes more than 10^5 collisions with MOr ions in 1 s. Assuming that the adhesion coefficient in the collision is equal to unity and considering that ~100 MOr anions are adsorbed on the surface of the colloidal particle in the stationary state, we obtain the characteristic time of the change in the composition of the adsorption layer of the surface of the colloidal particle as a result of adsorption: $\tau_{\mathrm{ad}} \approx 100/10^5 \approx 10^{-3}$ s.

It follows from the experimental data (see, *e.g.*, Fig. 5) that the steady-state value of the quantum yield ($\varphi_{\mathrm{st}}{}^{\mathrm{exp}}$) is only half as much as the initial value ($\varphi_0{}^{\mathrm{exp}}$). Since the rates of adsorption and desorption are the same for the stationary state, the characteristic time of the change in the composition of the surface of a colloidal particle due to desorption of low-molecular components is of the same order of magnitude as the time of adsorption, *i.e.*, $\tau_{\mathrm{des}} \approx \tau_{\mathrm{ad}} \approx 10^{-3}$ s.

Thus, we obtain the following hierarchic scale of characteristic times in the system studied: $\tau^{\mathrm{PAA}}_{\mathrm{ad\text{-}des}} = 4000\ \mathrm{s} \gg \tau_{\mathrm{p}}{}^{\max} = 500\ \mathrm{s} > \tau_{\mathrm{p}}{}^{\min} = 70\ \mathrm{s} \gg \tau^{\mathrm{low}}_{\mathrm{ad\text{-}des}} = 10^{-3}$ s.

Based on these data, one can propose that the adsorption layer on the surface of the colloidal particle is represented by regions of at least two types, which differ drastically in the time of establishing adsorption-desorption equilibria with respect to the characteristic times of the overall photocatalytic reaction. For the part of the surface that is free of PAA molecules, $\tau_{\mathrm{ad\text{-}des}} = \tau^{\mathrm{low}}_{\mathrm{ad\text{-}des}} \ll \tau_{\mathrm{p}}{}^{\min}$. This part should be assigned to case *1* described above. The other part of the adsorption layer of the surface is established in the course of the reaction as the result of blockage of the elemental sulfur formed by PAA units. For this part of the surface, $\tau_{\mathrm{ad\text{-}des}} \approx \tau^{\mathrm{PAA}}_{\mathrm{ad\text{-}des}} \gg \tau_{\mathrm{p}}{}^{\max}$ (case *2*). The composition of the adsorption layer on the regions of different types in the τ_{p} interval studied ($\tau^{\mathrm{low}}_{\mathrm{ad\text{-}des}} \ll \tau_{\mathrm{p}} \ll \tau^{\mathrm{PAA}}_{\mathrm{ad\text{-}des}}$) is still determined by the initial concentration of the reagents ($[\mathrm{reag}]_0$) and the current [MOr], but it is explicitly independent of the time of establishing the specified [MOr]. Thus, the dependence of φ^{exp} on [MOr] remains unchanged for any light intensities (I_0) in the range of $I_{\min} < I_0 < I_{\max}$, which is confirmed by the similarity of the kinetic curves in Fig. 10.

One can quantitatively describe the initial region of the kinetic curves in terms of the model of a semiconducting particle with regions of different ("active" and "inactive") types of adsorption layers. Let us denote the total surface area of the colloidal particle as Ω and the surface area of the colloidal particle covered with PAA as Ω_{PAA}. Let us call the surface area of the colloidal particle that is free of PAA the "working" surface, denoting it as Ω_w: $\Omega_w = \Omega - \Omega_{PAA}$. Let the surface area of the "working" surface before irradiation be denoted as $\Omega^0{}_w$.

If it is assumed that the reaction products formed ($MOrH_2$ and $S_2O_3{}^{2-}$) weakly affect the composition of the adsorption layer that is free of PAA the number of ions of the reagents adsorbed on the surface of the colloidal particle and the effective rate constant k'_s (neglecting the consumption of the secondary acceptors of nonequilibrium charges, H_2O and O_2) are proportional to Ω_w, and are determined by the current concentrations of the reagents ([reag]). Thus,

$$\frac{MOr_{ad}}{MOr_{ad}^{kin}} = \frac{D_{ad}}{D_{ad}^{kin}} = \frac{k'_s}{k'^{kin}_s} = \frac{\Omega_w}{\Omega_w^0} , \tag{10}$$

where $MOr_{ad}{}^{kin}$ ($D_{ad}{}^{kin}$) corresponds to the number of MOr_{ad} ions (D_{ad}) adsorbed on the surface of the colloidal particle (k'^{kin}_s corresponds to the rate of this process) for the working surface area equal to $\Omega^0{}_w$ and the current reagent concentration in the solution. Replacing MOr_{ad}^{kin}, D_{ad}^{kin}, and k'^{kin}_s in Eq. (10), we obtain:

$$\varphi^t([reag]) = \varphi_0^t([reag]) \cdot \frac{\Omega_w([reag])}{\Omega_w^0([reag])} . \tag{11}$$

It can be seen that the decrease in the quantum yield in the course of the catalytic reaction is caused by two cofactors: the first is a decrease in the quantum yield due to a decrease in the total concentration of reagents (predominantly, MOr) in the sample, while the second cofactor is the decrease in the working surface area of the colloidal particle due to blockage of part of the surface by PAA macromolecules. The dependence of the initial quantum yield of the overall reaction on the MOr concentration is experimentally measured (see Fig. 5) and can be used as a function of $\varphi^t{}_0$ in Eq. (11).

Let us consider the change in Ω_w during the reaction. Elemental sulfur is formed in the course of the reaction on the surface of the colloidal particle. Let us denote the fraction of newly formed sulfur atoms that are "blocked" by the surfactant as P_{bl}. The P_{bl} value can be determined by the expression:

$$P_{bl} = \frac{k_{PAA}(PAA)'}{k_{PAA}(PAA)' + k_S[SO_3^{2-}]} ,$$

where $k_{PAA}(PAA)'$ is the rate at which the sulfur atoms formed are blocked, $k_S[SO_3{}^{2-}]$ is the rate of the reaction of sulfur with the $SO_3{}^{2-}$ anion. Here (PAA)′ is the average (calculated per colloidal particle) current number of PAA units that are capable of blocking the sulfur formed, and k_{PAA} is the rate constant of the blocking.

When $SO_3{}^{2-}$ concentrations are sufficiently high, it can turn out that the rate at which the formed sulfur is blocked by PAA molecules is significantly lower than the rate of the reaction with $SO_3{}^{2-}$. In this case, the fraction of the blocked sulfur atoms is small and is proportional to (PAA)′:

$$P_{bl} = \frac{k_{PAA} \cdot (PAA)'}{k_D[SO_3^{2-}]} = \eta \cdot (PAA)', \text{ where } \eta = \frac{k_{PAA}}{k_D[SO_3^{2-}]} .$$

The number of sulfur atoms formed in the reaction is equal to the number of reduced MOr molecules:

$$C \cdot dS_{ad} = C \cdot (-dMOr_{ad}) = -dMOr.$$

From here it follows:

$$dS_{ad} = -dMOr/C = d[MOr]/[C], \tag{12}$$

where MOr and C are the numbers of MOr molecules and colloidal particles in the system, respectively, [MOr] and [C] are average volume concentrations of MOr and colloidal particles, and the differentially small values of dS_{ad} and $dMOr_{ad}$ are the changes in the numbers of sulfur atoms and MOr ions adsorbed on average by one particle of the colloid.

Assuming that the surface area blocked by PAA when one adsorbed sulfur atom is covered is equal to ω, it is easy to find that when dS_{ad} sulfur atoms are formed, the working surface area of the colloidal particle (Ω_w) is decreased by the value:

$$d\Omega_w = -\omega P_{bl} dS_{ad} = \omega P_{bl} \frac{d[MOr]}{[C]} =$$

$$= \omega\eta(PAA)' \frac{d[MOr]}{[C]} = (\Omega_w - \Omega_w^{st})\eta \frac{d[MOr]}{[C]} . \tag{13}$$

Here $\Omega_w{}^{st}$ is some stationary value of the working surface area of the colloid. Integrating Eq. (13), we find:

$$\Omega_w = \Omega_w^{st} + (\Omega_w{}^0 - \Omega_w^{st}) \cdot \exp(-\eta \frac{[MOr]_0 - [MOr]}{[C]}) . \tag{14}$$

Thus, the working surface area of the colloidal particle exponentially decreases as the current concentration of MOr decreases from $\Omega^0{}_w$ to $\Omega_w{}^{st}$.

The result obtained agrees with the experiment. Let us consider as an example the kinetic dependence of the quantum yield for the system with $[MOr]_0 = 10^{-4}$ and $[Na_2S]_0 = 10^{-2}$, $[Na_2SO_3]_0 = 10^{-2}$ mol L^{-1} (see Fig. 5). Since $\varphi^{exp}{}_0$ weakly depends on the concentration of MOr (mol L^{-1}) in the range of $0.5 \cdot 10^{-4} < [MOr] < 10^{-4}$, according to Eq. (11) the change in the quantum yield for this region follows the change in the working surface area of the colloidal particle and, according to Eq. (14), depends exponentially on the $[MOr]_0 - [MOr]$ difference. This conclusion is confirmed by the analysis of the shape of the initial region of the curve presented in Fig. 5.

The results obtained in the present work attest to the considerable effect of adsorption-desorption processes, including their dynamic parameters, on the course of photocatalytic redox reactions that occur during steady-state irradiation of the reaction mixture in the presence of colloidal semiconductors stabilized by surfactant molecules. The observed linear dependence of the rate of the model catalytic reaction studied on the light intensity testifies that photocatalytic processes sensitized by colloidal semiconductors are efficient monoquantum processes. The fact that the dependence of the initial quantum yield of the reaction on the concentration of MOr in the solution is identical to the isotherm of MOr adsorption on the aqueous CdS suspension demonstrates the participation of adsorbed MOr molecules in the reaction. The regularities of the process observed under continuous irradiation of the system suggest that at least two regions coexist on the surface of the colloidal particle: a region of the surface free of stabilizing surfactant molecules, which is characterized by a small ($\leq 10^{-3}$ s) time for establishing an adsorption-desorption equilibrium with the solution, and a region of the surfactant-blocked surface, which is characterized by the large (~1 h) time of establishing adsorption-desorption equilibria. In the course of the photocatalytic reaction the surfactant molecules are likely to reversibly block a part of the photocatalyst surface, which significantly decreases the steady-state quantum yield of the process due to photoinduced inhibition.

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