KINETICS OF ELECTRON TRANSFER IN QUENCHING OF TRIPLET STATE OF XANTHENE DYES BY CYANIDE COMPLEXES OF TRANSITION METALS

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It is known that electron transfer is one of the basic mechanisms of quenching of the triplet state (TS) of dyes by organic compounds and inorganic ions [1].

In the work reported here, we investigated the kinetics of electron transfer between molecules of dyes in the TS (eosin, Bengal rose) and cyanide complexes of Fe(II), Fe(III), Mo(IV), W(IV), Ru(II), and Co(III) in aqueous solutions.

EXPERIMENTAL

The spectral-kinetic measurements were performed in a microsecond pulse photolysis unit [2]. The measurements were performed at ~20°C in buffer solutions (double-distilled water, borate buffer, pH 9.18, ionic strength 0.01 M). The concentration of dye ranged from 1·10^{-7} to 5·10^{-6} M. The absorption spectra were measured in a Specord M-40 spectrophotometer.

The dyes were purified by recrystallization from ethanol; the purity was checked by measuring absorption and fluorescence excitation spectra. The cyanide complexes K_{6}Fe(CN)_{6}·3H_{2}O and K_{2}Fe(CN)_{6}, Grade kh.ch. ("chemically pure") were further purified by recrystallization; the K_{6}Mo(CN)_{6}·2H_{2}O, K_{6}W(CN)_{6}·2H_{2}O, K_{6}Ru(CN)_{6} and K_{3}Co(CN)_{6} were obtained by methods described in [3].

The experimental results on TS quenching were worked up by the least squares method in a Silex microcomputer. The dependences of the quenching rate constants on the free energy change in the reactions were calculated in the Silex microcomputer, printing out the results on a graph plotter. When aqueous solutions of eosin (EO) and Bengal rose (BR) were exposed to pulse radiation, triplet-triplet (T-T) absorption of the dyes was observed.

From the kinetic measurements, it was established that the rate of TS deactivation of the EO and BR (C_{0} = 5·10^{-7} M) is described by a first-order equation. In the presence of the ions Fe(CN)_{6}^{4-}, Mo(CN)_{6}^{4-}, W(CN)_{6}^{4-}, Ru(CN)_{6}^{4-}, Fe(CN)_{6}^{3-}, and Co(CN)_{6}^{3-} (C =5·10^{-6} to 4·10^{-3} M), the lifetime of the dye molecules in the TS is shortened as a result of quenching. From a comparison of the dye TS deactivation rates, measured in the absence and in the presence of the quenching ions, the values of the TS quenching rate constant k_{q} were determined.

Quenching of the triplet state of the EO and BR by the ions Fe(CN)_{6}^{4-}, Mo(CN)_{6}^{4-}, W(CN)_{6}^{4-}, and Ru(CN)_{6}^{4-} leads to the formation of the semireduced form of the dyes; quenching by the Fe(CN)_{6}^{3-} ion leads to the formation of the semioxidized form. In quenching of the TS by the Co(CN)_{6}^{3-} ion, we did not observe any significant increase in the yield of the semioxidized form of the dyes in comparison with the yield determined in the absence of the quenching agent. In the present work, we determined the rate constants for the formation of the semioxidized and semireduced forms of the dyes k_{r} from a comparison of the rate of decrease in T-T absorption with the rate of accumulation of the semioxidized (or semireduced) form of the dyes.

DISCUSSION OF RESULTS

In general, the quenching of the TS of dye molecules by inorganic ions in solutions may proceed through the following mechanisms: electron transfer (e), energy transfer (E), and as a result of the action of an "external" heavy atom [1, 4-6]. In TS quenching through the
electron transfer mechanism, the change in free energy of the reaction $\Delta G_e < 0$ and $\Delta G_E > 0$, whereas in quenching through the energy transfer mechanism, $\Delta G_E < 0$ and $\Delta G_e > 0$. In the present work, values of $\Delta G_e$ and $\Delta G_E$ have been found for pairs consisting of a dye and a quenching-agent ion. The values of $\Delta G_e$ and $\Delta G_E$ were found from the expressions

$$\Delta G_e = E_{v1}(D/D^+) - E_{v1}(A^-/A) - E_T + w_p - w_r$$

(1)

$$\Delta G_E = E_Q - E_T$$

(2)

where $E_{v1}(D/D^+)$ and $E_{v1}(A^-/A)$ are the respective potentials for polarographic oxidation of the donor and reduction of the acceptor; $E_T$ is the energy of triplet excitation of the dye molecule; $E_Q$ is the energy of the lowest excited state of the quenching-agent ion; $w_r$ and $w_p$ are the amounts of work required for approach of the reacting particles and the reaction products, respectively. For aqueous solutions, the expressions for $w_r$ and $w_p$ have the form

$$w_r = 17.81 \frac{2z_2}{r} \left(\frac{1}{1 + \kappa r}\right), \text{ kJ/mole}$$

(3)

$$w_p = 17.81 \frac{(z_1 + 1)(z_2 + 1)}{r} \left(\frac{1}{1 + \kappa r}\right), \text{ kJ/mole}$$

(4)

where $r$ is the distance between reactants with charges $z_1$ and $z_2$ in an encounter complex; $\kappa = 0.329 \sqrt{T} \text{ A}^{-1}$ (T is the ionic strength of the solution) at 298°K. At pH 9.18, the EO and BR exist in the dianion form [7]. Values of $w_r$ and $w_p$ were obtained from (3) and (4) for $r = 10$ Å (radii of cyanide complexes 4.5 Å [8], EO 4.9 Å, BR 5.2 Å [9]) and zero ionic strength.

In Table 1 we have listed values of $\Delta G_e$ and $\Delta G_E$, as well as values of the redox potentials of the ions and the position of their energy levels. For all of the dye-ion pairs, energy transfer is a considerably endothermic process, whereas electron transfer is exothermic. The only exceptions are the pairs EO-Co(CN)₆³⁻, BR-Co(CN)₆³⁻, and BR-Ru(CN)₅⁴⁻. It should be noted that for these pairs, the energy transfer process is more endothermic in comparison with electron transfer.

In general, electron transfer in quenching the TS of dye molecules by inorganic ions can be represented by scheme (I) [4]

$$\begin{array}{c}
M_r^{z_1} + Q^{z_2} \xrightarrow{k_{21}} M_r^{z_1+} + Q^{z_2+} \\
M_r^{z_1} + Q^{z_2} \xrightarrow{k_{21}} M_r^{z_1+} + Q^{z_2+}
\end{array}$$

(1)

where $M_r^{z_1}$ and $M_r^{z_1}$ are the dye molecule in the triplet and ground (unexcited) states, respectively; $Q^{z_2}$ is the quenching-agent ion (electron donor or acceptor); $M_r^{z_1}...Q^{z_2}$ and $M_r^{z_1}...Q^{z_2}$ are encounter complexes; $M_r^{z_1+}...Q^{z_2+}$ is an ion-radical pair; $M_r^{z_1+}$ and $Q^{z_2+}$ are ion-radicals of the dye and quenching agent, respectively. From scheme (I), we obtain the following expression for the quenching rate constant $k_q$:

$$k_q = \frac{k_{21}}{1 + \frac{k_{21}}{k_{20}} \exp \frac{\Delta G_{23}^{\text{ad}}}{RT} + \frac{k_{21}}{k_{20}} + \frac{k_{21}}{k_{20}} \exp \frac{\Delta G_{23}^d}{RT}}$$

(5)

where $\Delta G_{23}^{\text{ad}}$ and $\Delta G_{23}$ are the free energy of activation and the change in free energy of the electron transfer reaction; $k_{20}^{0}$ is the frequency factor. Equation (5) was used in describing the experimental dependence of $k_q$ on $\Delta G_{23}$. The experimental values of $k_q$ were recalculated from zero ionic strength by using the Brønsted-Bjerrum equation

$$\lg k_q^{I=0} = \lg k_q^I - \frac{1.02z_1z_2 \sqrt{T}}{1 + 0.329r \sqrt{T}}$$

(6)