The effect of light on the thermodynamic equilibrium in the formation of the complex between viologen and the ferrocyanide ion

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The formation of the complex between *N,N'*-dibutyl-4,4'-dipyridilium dibromide and potassium ferrocyanide was studied in aqueous solutions. The charge transfer band was observed and the composition of the complex between the dipyridilium dication and the ferrocyanide ion (1 : 1) was established. The irradiation ($\lambda \leq 350$ nm) of deaerated solutions in the absorption region of individual components results in a shift of the thermodynamic equilibrium towards complex formation *via* the intermediate formation of an exciplex. Since the absorption maximum of the complex is located in the visible region ($\lambda = 528$ nm), its reversible formation and decomposition are accompanied by reversible coloring of the solution, *i.e.*, the system is photochromic.

Key words: viologens, complex formation; photochromism.

The formation of complexes involving *N,N'*-substituted 4,4'-dipyridilium cations (viologens) has been studied in detail.[1,2] Viologens are of interest due to their pronounced catalytic,[3] electrochromic,[4] and other specific properties.

It is known that in weakly polar media, in particular, in aqueous—alcoholic solutions, the viologen dication forms charge transfer complexes (CTC) with counterions (halide ions),[5] which, however, are completely dissociated in aqueous solutions. The characteristics of CTC between low-molecular[6,7] and polymeric[7] viologens and ferrocyanide ions have been studied in several works. The electrochromic properties of these complexes have also been studied. It has been shown[7] for the complexes of diheptylviologen dibromide and polypentamethyleneviologen dibromide with potassium ferrocyanide that in the electronic absorption spectra (EAS) the long-wave maxima of the charge transfer bands are at 545 and 553 nm, respectively.

We believed that these complexes possess photochromic properties. The stability of the states corresponding to the changed oxidation states, *i.e.*, ferrocyanide ions and viologen radical cations, respectively, and relatively high extinction coefficients of viologen radical cations in the visible spectral region[8] are prerequisites for this assumption.

We studied the formation of complexes of dibutylviologen dibromide with the ferrocyanide ion in aqueous solutions and the behavior of these complexes in photochemical processes.

Experimental

Dibutylviologen dibromide was synthesized according to the previously described procedure.[9] Electronic absorption spectra were recorded on a Beckman DU-7 spectrophotometer. An SVDSh-250 mercury lamp was used for irradiation of samples. The necessary spectral regions were picked out by light filters. Aqueous solutions of viologen and potassium ferrocyanide were mixed in a sealed quartz cuvette with special chambers for solutions of components. Solutions were evacuated in the course of several freezing—thawing cycles.

Results and Discussion

It was established that in aqueous solutions ferrocyanide ions interact with dibutylviologen dibromide to form CTC in which viologen acts as the electron acceptor. The charge transfer band of this complex is pronounced in the EAS and has an absorption maximum at 528 nm (Fig. 1).

The composition of the complex, which is close to 1 : 1, was determined by the method of isomolar series (Fig. 2). The asymmetry of the curve indicates the presence of complexes of higher orders. Since the charge of the ferrocyanide ion is twice the charge of the viologen dication, it is evident that the charge compensation is due to the additional number of K^+ cations.

No noticeable changes are observed in the EAS of this system after irradiation in the charge transfer region both in air and in an inert atmosphere. At the same

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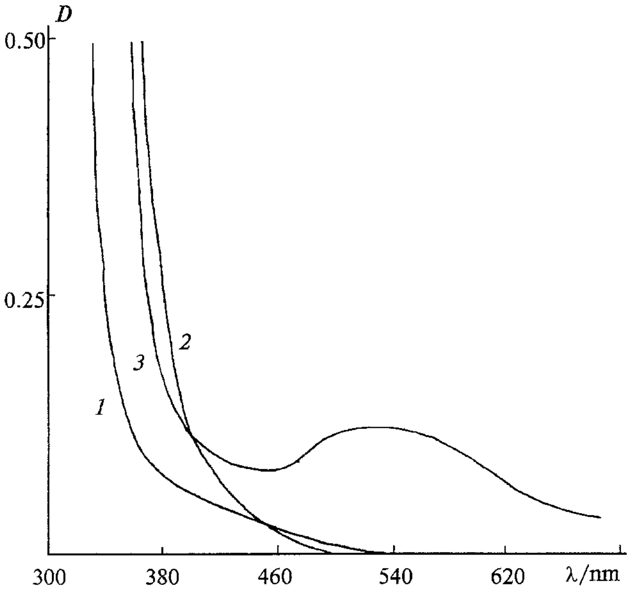


Fig. 1. Electronic absorption spectra of dibutylviologen dibromide (*1*), potassium ferrocyanide (*2*), and their equimolar mixture (*3*) in water (in all cases the concentration is 50 mmol L^{-1}).

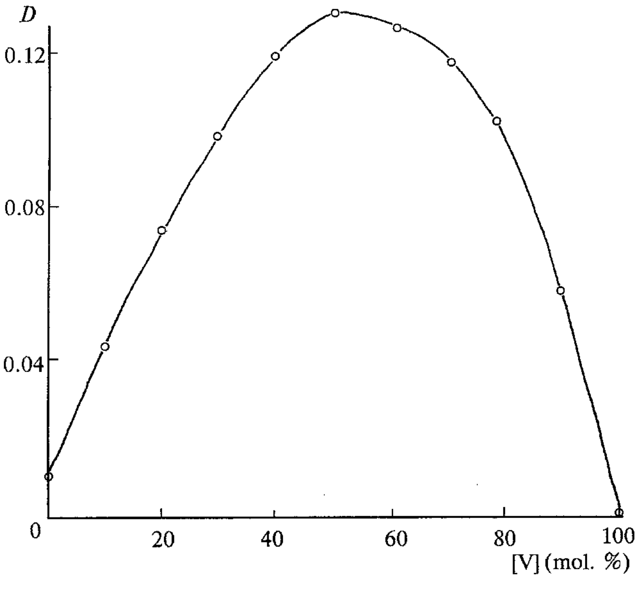


Fig. 2. Optical density at λ = 528 nm of isomolar solutions of a mixture of dibutylviologen dibromide (V) and potassium ferrocyanide in water (the total concentration of the components is 25 mmol L^{-1}).

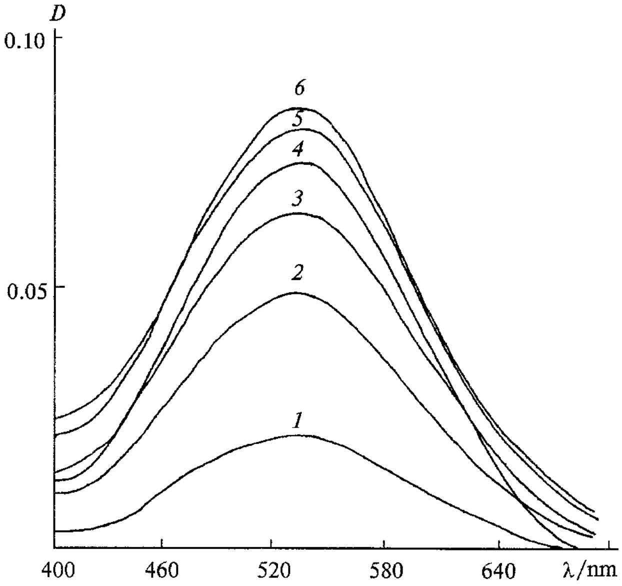


Fig. 3. Changes in the absorption spectra of solutions of the equimolar mixture of dibutylviologen dibromide (V) and potassium ferrocyanide due to irradiation with the light from a SVDSh-250 lamp (l = 5 cm) in the region of $\lambda \le 350$ nm (the total concentration of the components is 100 mmol L^{-1}). The duration of the irradiation/s: 15 (*1*); 30 (*2*); 45 (*3*); 60 (*4*); 120 (*5*); 180 (*6*).

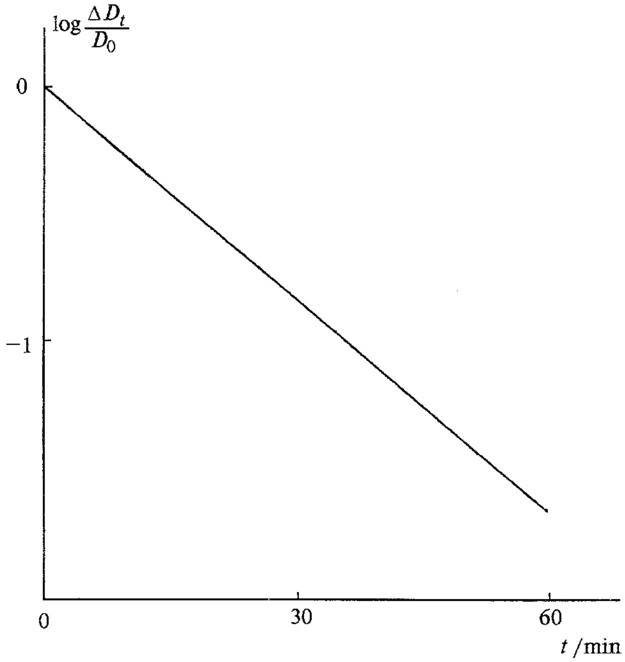


Fig. 4. Kinetics of the decrease in the optical density at $\lambda \approx 528$ nm of the solution of an equimolar mixture of dibutylviologen dibromide and potassium ferrocyanide under dark conditions after 5 min of irradiation by the light with $\lambda \le 350$ nm.

time, the irradiation of deaerated solutions with ultraviolet light ($\lambda \le 350$ nm), *i.e.*, in the excitation region of the initial components, results in an increase in the optical density in the region of the charge transfer band (Fig. 3). The shape of this band is almost unchanged during photogeneration (see Fig. 3). This probably indicates that the observed increase in the optical density is related only to an increase in the concentration of the CTC.

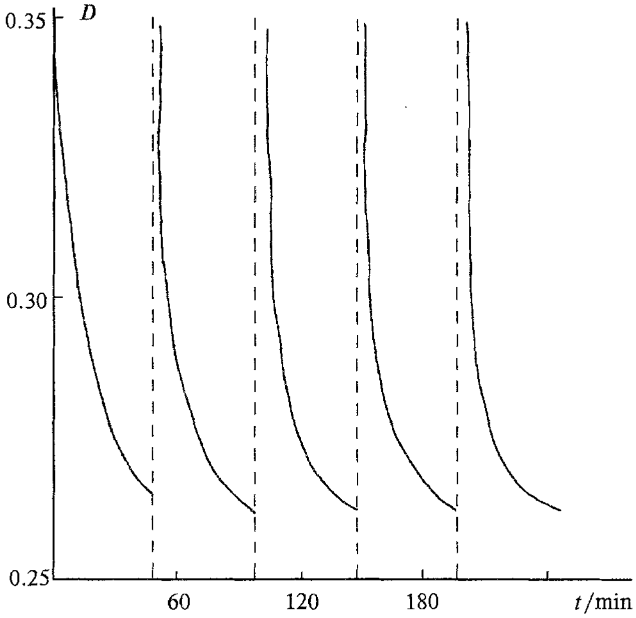
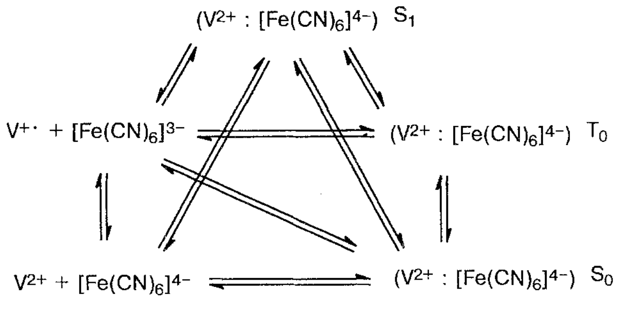


Fig. 5. Changes in the optical density at λ = 528 nm of an aqueous solution of an equimolar mixture of dibutylviologen dibromide and potassium ferrocyanide during irradiation—dark cycles (the total concentration of the components is 100 mmol L^{-1}).

As shown in Fig. 4, after the irradiation is stopped the optical density in the region of the charge transfer decreases. This decrease is described by a first-order equation. This process can be repeated many times without any noticeable changes (Fig. 5). The transformations considered are observed only in the absence of air.

The data presented attest to the unusual behavior of the donor-acceptor system considered: no products of the complete charge transfer are formed by the action of light in the region of the charge transfer, while the excitation of the initial components results in a reversible shift of the equilibrium of complex formation towards the formation of new complexes. The different states and the transformations between them possible in this system are presented in Scheme 1.

Scheme 1



(V is viologen)

The excitation of the initial components results in the formation of an exciplex, which is transformed to the unexcited CTC *via* different routes. The excess amount of the complex is accumulated, and this is manifested in the EAS. The thermodynamic equilibrium concentration of the complexes is reduced relatively slowly (see Fig. 4), which is probably caused by the high activation energy. At the same time, the CTC is formed rather rapidly *via* the stage of the exciplex, because the activation barrier is overcome due to the photoexcitation of the initial components by high-energy photons. It is likely that no products of the complete transfer are observed, because both the components in the free state and the CTC based on them have a significantly higher ionic character than the products of complete electron transfer. The values of the products of the ionic charges of the components (measured in charges of an electron), which give a first approximation of the force of the Coulomb interaction in the system, are 8 and 3, respectively. Therefore, the existence of ionic states in a strongly polar medium (water) is more thermodynamically favorable and, hence, the equilibrium is strongly shifted towards the initial components and the CTC based on them.

The effect of oxygen on this process can also be seen in its interaction either with the complexes in excited states, in which the degree of electron transfer from the donor to the acceptor must be high, or with the viologen radical cation, one of the components of the ionic pair formed by the dissociation of these excited states. In the first case, it is likely that the interaction of oxygen with the excited complex favors quenching of the excited states. In fact, the complete transfer of an electron from the donor (the ferrocyanide ion) to the acceptor (the viologen dication) occurs in the excited complex to form virtually the same viologen radical cation and then to transfer the electron from it to oxygen. As follows from the published data,[10] these processes are related to the formation of intermediate complexes of viologen radical cations with oxygen and to their further interactions.*

Thus, the data presented make it possible to draw the conclusion that the donor-acceptor system based on potassium ferrocyanide and dibutylviologen dibromide is photochromic due to the reversible formation of complexes between ferrocyanide ions and viologen dications in light and their decomposition in the dark. This is a significant difference between this system and the majority of photochromic systems, in which the reversible coloring is caused, as a rule, by the formation of either products of the complete transfer of electrons or of photoisomers with absorption spectra different from those of the initial components.[11] The principle characteristic of the system considered is that there is a noticeable shift of the thermodynamic equilibrium when it is irradiated with

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* The effect of oxygen can be related not only to electron transfer, but also to the transfer of energy from the triplet state of the excited complex[2] to oxygen.

weak light beams, which, judging from published data, has not yet been observed for donor-acceptor systems. It is evident that the reason for this is screening of the charge transfer band by other bands corresponding to the absorption of the individual components and products of the complete electron transfer. In addition, unlike the system studied, in other systems there are often many various irreversible side processes, which makes it impossible to speak about a shift of the initial equilibrium in the system.

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