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REDOX REACTIONS IN MICELLAR SYSTEMS. COMMUNICATION 1. REDUCTION OF METHYL VIOLOGEN BY KETYL RADICAL

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In the development of artificial converters of solar energy to the chemical fuel energy, using the principles of natural photosynthesis, a problem arises in preventing interaction between the primary oxidizing and reducing agents that are formed under the influence of the light quanta [1, 2]. In all of the reactions that have been used to store light energy, a significant positive change in the free energy is observed, such that the reverse reaction is always thermodynamically favorable and may proceed spontaneously with the evolution of heat unless special measures are taken to preserve the free energy obtained in the primary acts. One of the possible means for preventing the reverse reaction, in the case of electron phototransport, is to carry out the reaction at a boundary between two phases, with a certain electric potential at the interface [1-3].

Here we are reporting on the reaction of methyl viologen reduction by the ketyl radical, generated photochemically in homogeneous alcoholic media, and also in ultramicroheterogeneous systems containing inverse micelles with various polar "heads" [4]. Ketyl radicals formed by the photoreduction of benzophenone may lead to the release of hydrogen, both in photo-catalytic systems [5, 6] and in photoelectrochemical cells [7] upon oxidation at the electrode.

## EXPERIMENTAL

Benzophenone, pure grade, was recrystallized twice from benzene; mp 47.8°. The methyl viologen dichloride (MeVi<sup>2+</sup>), chemically pure grade, was used without further purification. Sodium dodecylsulfate (SDS), pure grade, and cetyltrimethylammonium bromide (CTAB), pure grade, were purified by two recrystallizations from methanol. The aqueous solutions were prepared with double-distilled water. The n-octyl alcohol was redistilled under vacuum, collecting the 100-101° fraction at 20 mm. The isopropyl alcohol (IPA) was purified by redistillation, bp 82°. The reaction medium was illuminated in sealed quartz cuvettes with a light path of 1 cm, by means of a DRSh-1000 superhigh-pressure mercury lamp. Before starting the illumination, the reaction mixture was degassed, either by purging with helium or by means of a threefold cycle of freezing, pumping down in a vacuum unit, and melting. The completeness of oxygen removal from the reactor was monitored on the basis of the absence of an induction period in the accumulation of the cation radical of methyl viologen MeVi<sup>+</sup> in the reaction medium. The 365-nm band was segregated from the radiation spectrum of the mercury lamp by means of interference light filters. The light flux intensity was determined by a ferrooxalate actinometer [8]. The concentration of MeVi<sup>+</sup> during the course of the reaction was determined spectrophotometrically in a Specord UV-Vis spectrometer in the same quartz cuvettes in which the photolysis was performed. The optical density was measured at  $\lambda$  605 nm ( $\varepsilon$  = 13,800 liters/mole.cm [9]). The quantum yield of MeVi<sup>+.</sup> was determined by dividing the initial rate of MeVi<sup>+</sup>. formation by the intensity of light absorbed by the benzophenone. The error in determining the quantum yields was ±10%. For the quantitative measurements, we determined the molar extinction coefficients of benzophenone in various solvents by dissolving accurately weighed samples in the required quantity of solvent. At  $\lambda$  365 nm, we obtained the following values of  $\varepsilon$  (liters/mole.cm): 61 in octyl alcohol, 62 in isopropyl alcohol, and 57 in a 9/1 mixture of isopropanol and water by volume. The critical micelle concentrations (CMC)

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Fig. 1. Timewise change in  $[MeVi^+ \cdot]$  in IPA/water mixture (1) and in octyl alcohol (2).  $[(C_6H_5)_2CO]_0 = 10^{-3} \text{ M}; [MeVi^{2+}]_0 = 10^{-4} \text{ M}; 22 \pm 2^\circ.$ 

Fig. 2. Initial rate of MeVi<sup>+</sup> formation as a function of benzophenone concentration in following media: 1) octyl alcohol; 2) same, with the addition of  $10^{-3}$  M SDS; 3) IPA/water (9/1 by volume). [MeVi<sup>2+</sup>]<sub>0</sub> =  $10^{-4}$  M; I<sub>0</sub> =  $6.9 \cdot 10^{16}$  quanta/sec; V = 3 ml.

were determined conductometrically [10]. In octyl alcohol, the CMC for the SDS is  $8.2 \cdot 10^{-4}$  M, and for the CTAB it is  $5.5 \cdot 10^{-3}$  M. In isopropanol, no micelles were formed, even at the highest concentrations of the detergents.

## DISCUSSION OF RESULTS

A study of the reaction of photosensitized reduction of MeVi<sup>2+</sup> in a mixture of IPA and water showed that, at first, the cation radical MeVi<sup>+</sup>. accumulates in the reaction mixture; then, as the illumination is continued, this species disappears as a result of interaction with the ketyl radical [11]. When this reaction is carried out in octyl alcohol, the same picture is observed for the timewise change in [MeVi<sup>+</sup>.] (Fig. 1). The initial rate of MeVi<sup>2+</sup> reduction is directly proportional to the concentration of benzophenone (B) when the reaction is carried out either in a mixture of IPA and water [11] or in octyl alcohol (Fig. 2). Careful measurements of the initial rate of MeVi<sup>2+</sup> reduction with small [B] and extrapolation of the straight line to zero value of [B] show that in the absence of benzophenone as well, photoreduction of MeVi<sup>2+</sup> in the nonsensitized reaction is observed; this is explained by electron transfer from the alcohol to the photoexcited molecule of MeVi<sup>2+</sup>. In our experiments, the rate of the nonsensitized reaction was found to be  $1,5\cdot10^{-6}$  mole/liter.sec in both media with  $[MeVi^{2+}]_{o} = 10^{-3}$  M. All these data are characteristic for the usual reaction of photoreduction of B by alcohols to the ketyl radical [12] with subsequent electron transfer from the radical to the MeVi<sup>2+</sup> [11]. However, our studies of the dependence of the initial rate of methyl viologen reduction on [MeVi<sup>2+</sup>] showed that with large [MeVi<sup>2+</sup>], the rate decreases both in octyl alcohol and in the IPA/water mixture (Fig. 3, curve 1). This is evidently related to quenching of the excited triplet state <sup>3</sup>B by the methyl viologen. And in fact, when we take the nonsensitized reaction into account (line 2 in Fig. 3), we observe a good rectification of the dependence of the quantum yield of MeVi<sup>+</sup>. on [MeVi<sup>2+</sup>] on the coordinates of Stern and Volmer, both in IPA/water medium (Fig. 3, curve 3) and in an octyl alcohol medium (Fig. 3, curve 4). Thus, the scheme of the process of photosensitized reduction of MeVi<sup>2+</sup> that was proposed in [11] should be supplemented with the reaction of quenching of <sup>3</sup>B by methyl viologen, whereupon it can be represented in the following form

> 1.  $B \xrightarrow{k_0} {}^{3}B$  rate equal to  $I_a = k_0[B]$ 2.  ${}^{3}B \rightarrow B$   $k_2 [{}^{3}B]$ 3.  ${}^{3}B \rightarrow HeVi^{2+} \rightarrow B + MeVi^{2+} k_t [{}^{3}B][MeVi^{2+}]$ 4.  ${}^{3}B + ROH \rightarrow BH + \dot{R}O k_v' [{}^{3}B]$ 5.  $B + \dot{R}O \rightarrow BH + A k_5[B][\dot{R}O]$



Fig. 3. Dependence, on  $[MeVi^{2+}]_0$ , of initial rate of MeVi<sup>+</sup> formation (1), rate of nonsensitized reaction (2), and reciprocal of quantum yield in IPA/water mixture (3) and in octyl alcohol (4).  $[(C_6H_5)_2CO]_0 = 10^{-3}$  M;  $I_0 = 8.3 \cdot 10^{16}$  quanta/sec; V = 3 ml, 22 ± 2°.

6. BH + MeVi<sup>2+</sup>  $\rightarrow$  B + MeVi<sup>+</sup>·  $k_{r}$  [BH][MeVi<sup>2+</sup>] 7. BH + MeVi<sup>+</sup>·  $\rightarrow$  B + P  $k_{g}$  [BH][MeVi<sup>+</sup>·1 8. BH + BH  $\rightarrow$  HBBH (pinacone)  $k_{n}$ [BH]<sup>2</sup>

In the scheme,  $I_{\alpha}$  is the intensity of absorbed light; BH is the ketyl radical;  $\hat{R}^0$  is the alcohol radical; A is the aldehyde corresponding to the alcohol (or acetone in the case of the IPA); P is the product of hydrogenation of the cation radical MeVi<sup>+</sup>, which does not absorb light in the 600-nm region.

From this scheme, under the condition of quasistationary concentrations of <sup>3</sup>B, BH, and RO, we can obtain an expression for the initial rate of reduction of MeVi<sup>2+</sup>,

$$W_{0} = \frac{2k_{v}'k_{0}[B]_{0}}{\frac{k_{2} + k_{v}' + k_{t}[MeVi^{2+}]_{0} + 2k_{v}'k_{0}/k_{t}[MeVi^{2+}]_{0}}{k_{2} + k_{v}' + k_{t}[MeVi^{2+}]_{0} + 2k_{v}'k_{0}/k_{t}[MeVi^{2+}]_{0}}},$$

which indicates a linear dependence of  $W_0$  on  $[B_0]$ . With very small  $[MeVi^{2+}]_0$ , a linear dependence of  $W_0$  on  $[MeVi^{2+}]_0$  is also observed; however, with sufficiently large  $[MeVi^{2+}]_0$ , the expression for the rate is simplified, since the last term in the denominator becomes insignificant. In this case, for the initial quantum yield of  $MeVi^+$ , we obtained the relationship

$$\frac{1}{\Phi_0} = \frac{1}{2} + \frac{k_2}{2k_y'} + \frac{k_t}{2k_y'} \, [\text{MeVi}^{2+}]_0 \, .$$

which is followed closely if the nonsensitized reaction of MeVi<sup>2+</sup> reduction is taken into account (see Fig. 3, lines 3 and 4). From these data, we can evaluate certain rate constants of the reactions included in the process scheme. For this purpose, we will assume for the quenching rate constant  $k_t$  the value 3.2·10° liters/mole.sec, calculated from the formula  $k_t = 8RT/3000n$  [13]. Let us note that a direct determination of  $k_t$  in a medium of acetonitrile with added water gave the value 2.6·10° liters/mole.sec [14], although lower values have also been reported [7]. The slope of line 3 in Fig. 3, which is equal to the ratio  $k_t/2k_v^i$ , together



Fig. 4. Initial rate of accumulation of MeVi<sup>+</sup>. as a function of SDS concentration in octyl alcohol.  $[MeVi^{2+}]_0 = [(C_6H_5)_2CO]_0 = 10^{-3}$  M;  $I_0 = 6.9 \cdot 10^{16}$  quanta/sec; V = 3 ml.

Fig. 5. Kinetics of formation of intermediate after exhaustion of  $MeVi^{2+}$  (1) and without  $MeVi^{2+}$  (2).  $[MeVi^{2+}]_{o} = 10^{-4}$  M;  $[(C_{o}H_{s})_{2}CO]_{o} = 10^{-3}$  M; V = 3 ml; IPA/water, 22 ± 2°.

with the value assumed for  $k_t$ , gives the following value for the rate constant of hydrogen abstraction by triplet benzophenone from isopropyl alcohol;  $k_V^1 = 10^6 \text{ sec}^{-1}$ . This is an effective value of the constant; and when it is divided by the concentration of isopropyl alcohol, the value of the "true" rate constant of the bimolecular reaction proves to be approximately an order of magnitude smaller than the value  $10^6$  liters/mole·sec that was reported in [15]. This sort of difference is to be expected, since our estimate was made with a very high concentration of one of the reactants (the alcohol); and it is known that as the reactant concentrations are increased, the rate constant of a bimolecular reaction generally decreases [16].

The rate constant thus estimated for the reduction of benzophenone in octyl alcohol (Fig. 3, line 4) coincides with the value obtained for the rate constant of hydrogen atom abstraction from isopropyl alcohol ( $\sim 10^5$  liters/mole·sec), in accordance with the identical H-donor properties of these alcohols [13]. The rate constant for deactivation of <sup>3</sup>B in octyl alcohol  $k_2 \approx 5 \cdot 10^4$  sec<sup>-1</sup>. For the constant  $k_2$  is aqueous IPA medium, also estimated from the intercept of the Stern-Volmer line on the vertical axis (Fig. 3), we obtained the value  $1 \cdot 10^5$  liters/mole·sec, coinciding with the value reported in the literature [13].

The accumulation of MeVi<sup>+</sup>. in the systems that we have studied proceeds with autoinhibition, since as the concentration of MeVi<sup>+</sup>. increases, we begin to see an "internal light filter effect," related to the absorption of light by not only the benzophenone, but also the MeVi<sup>+</sup>. that has been formed. After passage through a maximum on the kinetic curve (see Fig. 1), the reaction, in contrast, becomes autocatalytic, since the "internal light filter effect" decreases.

However, if as a zero approximation we consider this reaction as a sequence of pseudomonomolecular reactions  $\text{MeVi}^{2+} \xrightarrow{k'} \text{MeVi}^+ \cdot \xrightarrow{k''} P$ , and if the  $\text{MeVi}^+ \cdot$  is considered to be an intermediate product, then, on the basis of the time required to reach the maximum concentration of  $\text{MeVi}^+ \cdot$ ,  $t_{max} = [1n(k'/k'')]/(k' - k'')$  [16], we can determine the ratio of constants  $k_r/k_g$ . Since k' can readily be determined from the initial section of the kinetic curve (see Fig. 1), we can then determine k'', which proves to be practically equal to k' under the conditions of our experiments. Thus, the constant  $k_g$  (the same as  $k_t$ ) is 3,2·10° liters/mole·sec, which is entirely reasonable for the reaction of two radicals. For example, the rate constant for the interaction of BH with the radical obtained by abstraction of hydrogen from decane is 2·10° liters/mole·sec [17].

The addition of SDS to the IPA/water reaction medium, up to a concentration of  $10^{-2}$  M, has no effect wheatever on the rate of MeVi<sup>2+</sup> reduction; this is consistent with the fact that the SDS does not form micelles in this medium, according to the conductometric data, all

the way up to  $10^{-2}$  M SDS. In octyl alcohol, the addition of SDS up to a concentration of  $10^{-3}$  M increases the rate of reaction by a factor of approximately 3 (see Fig. 2). The dependence of the initial reaction rate on [SDS] is shown in Fig. 4. It will be noted that the reaction rate reaches a maximum at approximately the CMC of the SDS in octyl alcohol  $(8.2 \cdot 10^{-4} \text{ M})$  and then decreases with further increases in [SDS].

Contradictory data have been reported in the literature on the possible participation of a surfactant micelle as a hydrogen atom donor in the photoreduction of benzophenone. For example, it is stated in [18] that surfactant molecules are even better donors than alcohols, whereas in [19] it was found that these molecules have practically no H-donor capability in micellar solutions. Our data indicate that the CTAB in the micelles is at least 10 timess less reactive than alcohols as a hydrogen donor, and the SDS is less reactive by a factor of 2. Thus, the increase in the rate of MeVi<sup>2+</sup> reduction in the micellar solution (see Fig. 4) is not related to any better H-donor properties of the SDS molecules.

The formation of inverse micelles when CTAB is added to octyl alcohol has practically no effect on the rate of MeVi<sup>2+</sup> reduction. If we consider that all of the conclusions in [20] are applicable to inverse micelles, these conclusions having been obtained for normal micelles from the kinetic concept of micellar effects in a bimolecular reaction [21], the behavior that we have observed can be explained as follows. In the case in which no micelles are formed (10<sup>-2</sup> M SDS in the IPA/water mixture), the reaction naturally proceeds in accordance with the scheme shown above for homogeneous solutions. When a cationic surfactant (CTAB) is added to the octyl alcohol medium, we should expect that there will be no binding of the MeVi<sup>2+</sup> in the polar core of the inverse micelle, owing to repulsion of the like-charged particles. Thus, both reactants are located outside the micelles, and there should be no effect from the presence of the CTAB micelles; this is consistent with what is actually observed, The formation of SDS micelles effectively separates the MeVi<sup>2+</sup>, which is located primarily within the polar region of the inverse micelle and is bound to the negatively charged polar heads of the SDS, from the benzophenone, which remains in the alcohol medium. Nevertheless, under these conditions we observe an increase in the reaction rate for the photosensitized reduction of MeVi<sup>2+</sup>; this can be explained on the basis that there is a decrease in the quenching of the excited benzophenone by methyl viologen (reaction 3) and an increase in the stationary concentration of the ketyl radical. And indeed, the dependence of the initial quantum yield of the MeVi<sup>+</sup>, cation radical on  $[MeVi^{2+}]_0$  is rectified on Stern-Volmer coordinates in the same manner as is observed in homogeneous media (see Fig. 3), the slope of this line in the micellar medium being approximately one-third that in the octyl alcohol medium (Fig. 3, line 3). An analogous effect of micelles on the quenching rate was observed in [22].

Reactions (7) and (8) were not taken into account in working up the kinetic data, since these reactions do not occur in the early stages of the process, and consumption of the benzophenone begins only after complete decolorization of the solution (destruction of the MeVi+., which gives a dark blue color). Also, the pinaconization of benzophenone (reaction 8) is much slower than the main reaction (Fig. 5). Complete disappearance of B is observed only after an interval hundreds of times longer than the time of the reaction of MeVi<sup>2+</sup> reduction, as indicated by the kinetics of formation and destruction of the intermediate that is the predecessor of the benzopinacone (see Fig. 5).

In conclusion, let us note that our purpose in starting this research was to determine the feasibility of regulating the fast recombination of photogenerated oxidizing and reducing agents in two-phase systems; however, this reaction of MeVi<sup>2+</sup> reduction proceeds very well indeed without any special measures in this direction. The explanation is that in the first chemical stage in the interaction of <sup>3</sup>B with the alcohol, as a result of hydrogen atom abstraction, a triplet radical pair is formed, which cannot recombine because of Wigner spin prohibition [15]. This is apparently one of the most important physical means for preventing relatively fast recombination of the products from electron transfer (or transfer of a hydrogen atom). Effective performance of this reaction in a homogeneous medium is also favored by the circumstance that an alcohol radical that has left the cage is a rather strong reducing agent that is capable of reducing both the MeVi<sup>2+</sup> and the benzophenone that are present in significant quantities in the reaction medium. When it is necessary to use other compounds as the donor (for example, water in the photocatalytic decomposition of water into its elements), we cannot count on such "joint action" for the desired reaction path.

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## CONCLUSIONS

1. A study has been made of the reaction of benzophenone-photosensitized reduction of methyl viologen in octyl alcohol and in a mixture of isopropyl alcohol and water,

2. For a complete explanation of the relationships observed in the occurrence of the reaction, consideration must be given to the stage of benzophenone triplet quenching by methyl viologen.

3. Extraction of methyl viologen by inverse micelles of sodium dodecylsulfate leads to an increase in the rate of photoreduction of methyl viologen, owing to a reduction of the rate of benzophenone triplet quenching.

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