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ENDOERGIC PHOTOINDUCED REDOX REACTIONS IN WATER-IN-OIL MICROEMULSIONS;
THE PHOTOSENSITIZED REDUCTION OF VILOGENS BY THIOPHENOL

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Abstract. The photosensitized reduction of methyl viologen (MV$^{2+}$) by thiophenol using Ru(bipy)$_3^{2+}$ or a water soluble Zn-porphyrin as sensitizer is described. The electron-transfer process is accomplished in a water-in-oil microemulsion. The oxidized donor, diphenyl disulfide, is extracted from the water-oil interface into the continuous organic phase. Consequently, the redox products are separated and back reactions are prevented. The net reactions performed are energy storing by 5-7 Kcal/mole of thiophenol. A structurally modified viologen, propyl viologen sulfonate (PVS$^0$) could similarly act as an electron-acceptor. Comparison of quantum yields of viologen radical production shows that reduction of PVS$^0$ is four times more efficient than that of MV$^+$ when the water soluble Zn-porphyrins are used as sensitizers.
The photoinduced electron-transfer resulting in the formation of an oxidized and reduced species along an uphill gradient of free energy is the basic principle for the construction of an artificial photosynthetic device (1-3). However, this principle suffers from a basic limitation that the photoproduced intermediates back-react (eq. 1). Thus, the energy stored in the photochemical event is degraded. Hence, in order to accomplish such an endoergic process, separation of products to prevent back reaction is a fundamental requirement (3). Detergent micelles (4,5), and bilipid vesicles (6) have been suggested as a means of separating redox products. Recently, we proposed the use of water-in-oil micro-emulsion systems as a means of retarding back-reactions, and a photosensitized electron-transfer across the water-oil interface was accomplished (7). In this system, phase-transfer of one of the photoproducts (reduced acceptor or oxidized donor) into the continuous organic phase provides for the separation of products.

\[
A + D \quad \text{hv, quenching} \quad A^- + D^+ \quad \text{(eqn. 1)}
\]

We now report that the construction of the reducing half-cell of the general model (7) has been accomplished. In the previous system (6), the donor, EDTA, was decomposed in the electron-transfer process. Here instead, non-destructible electron-donor was coupled to the photoinduced electron-transfer reaction. Water-soluble Zn-porphyrins and Ru(bipy)$_3^{2+}$ photosensitized the redox reactions, and structural modifications in the electron-acceptor of the system improved quantum efficiencies.

In the present microemulsion systems thiophenol (RSH) was used as electron-donor. We anticipate that a significant fraction of the thiophenol would be located at the water-oil boundary due to its amphiphilic character,
but that its oxidized product, the corresponding disulfide \((RSSR)\) (8), would be extracted to the continuous organic phase. Previously, the use of thiol compounds as electron-donors [cysteine (9), thioethanol (10)] in photoinduced redox reactions has been reported. However, examination of pH-conditions of these systems and concentrations of products shows that these reactions were essentially exoergic (downhill) reactions catalyzed by light. In our system the phase-transfer of the oxidized electron-donor into the continuous organic phase provides the separation of the redox products and facilitates the electron transfer along an endoergic (uphill) pathway.

A water-in-oil microemulsion was prepared by adding 0.1 ml of an aqueous phosphate buffer solution \((\text{pH} = 4.3)\) containing methylviologen, \(\text{MV}^{2+}\), \((6 \times 10^{-3} \text{ M})\) to 2.9 ml of toluene using 160 mg of dodecylammonium propionate as a surfactant. The photosensitizer, \(\text{Ru(bipy)}^2_3\) \((5 \times 10^{-5} \text{ M})\), and 33 \(\mu\text{l}\) of thiophenol \((0.1 \text{ M})\) were solubilized in the microemulsion. The deaerated solution (under argon) was illuminated with blue light \((440 \text{ nm} - 550 \text{ nm})\). The production of methylviologen radical \((\text{MV}^+)\) was observed and followed spectroscopically \((\lambda_{\text{max}} = 603 \text{ nm}, \epsilon = 12400 \text{ cm}^{-1} \text{ M}^{-1})\) (11). The maximal (initial) quantum yield for \(\text{MV}^+\) production was calculated to be \(\Phi_{\text{max}} = 0.005\). The amount of \(\text{MV}^+\) produced photochemically \((17 \times 10^{-5} \text{ M})\) implied that the sensitizer was recycled during the process. When either thiophenol or \(\text{Ru(bipy)}^2_3\) was excluded from the system, no \(\text{MV}^+\) formation was observed.

The results are accounted for by an electron-transfer from the photoexcited sensitizer to \(\text{MV}^{2+}\). The oxidized ruthenium complex is reduced by the thiol at the interface, thereby recycling the photosensitizer. In turn, the disulfide product is extracted into the continuous organic phase.
and separation of the active products is achieved (Fig. 1). The net reaction performed in this cycle represents the photoinduced reduction of MV$^{2+}$ by thiophenol (eq. 2). Based on the reduction potentials of the components, $E^0(\text{thiophenol}) = 0.11 \text{ V}$ (12), $E^0(\text{MV}^{2+/\text{MV}^+}) = -0.45 \text{ V}$ (13), and taking into account the pH-dependence of thiol oxidation and the concentrations used, the thermodynamic balance of the reaction is energy storing by ca. 7 Kcal per mole of thiol. The possibility of conducting the process along an uphill gradient of free energy is attributed to the separation of products by the phase transfer principle.

$$2 \text{MV}^{2+} + 2 \text{RSH} \rightarrow 2 \text{MV}^+ + \text{R-S-S-R} + 2 \text{H}^+ \quad \text{(eqn. 2)}$$

Recalling our original model (7), where a donor solubilized in the aqueous phase has been oxidized, the present system represents the complementary reducing half-cell. Since MV$^+$ is capable of reducing water to hydrogen at pH <7 in the presence of solid catalysts (14-16), the precursor for the hydrogen-evolving site has been constructed. Furthermore, the donor, thiophenol, is not consumed irreversibly during its oxidation. Thus, it is possible to regenerate the electron donor by coupling this system with a further redox cycle in the complementary half-cell (8).

The sensitizer utilized in the system, Ru(bipy)$_3^{2+}$, could be replaced by either of two water-soluble Zn-porphyrins: Zn-tetraphenylporphyrin sulfonate (Zn-TPPS, 1) or Zn-tetramethylpyridiniumporphyrin (Zn-TMPyP, 2). The
absorption patterns of the porphyrins (1) and (2) enables utilization of a broader region of the visible spectrum for inducing the electron-transfer process than is possible with Ru(bipy)$_3^{2+}$. Illumination of the previously described microemulsion, including (1) or (2) as sensitizers, with blue light (440-550 nm) resulted in the formation of MV$^+$(Fig. 2). It can be seen that (1) is more efficient ($\phi_{\text{max}} = 0.0067$) than (2) ($\phi_{\text{max}} = 0.0025$) in inducing the redox reaction. This difference is in line with the recently described electron-transfer properties of the two sensitizers (17).

The electron acceptor in the system, MV$^{2+}$, was replaced by propyl viologen sulfonate, PVS$^0$ (3). This zwitterionic viologen is neutral in its oxidized form and yields a negatively charged reduced product.

\[
\begin{align*}
\text{SO}_3^- & \quad \text{SO}_3^- \\
\text{(3)} & 
\end{align*}
\]

Water-in-oil microemulsions composed of (3) as electron-acceptor, thiophenol as electron-donor and (1) or (2) as sensitizer were illuminated. The production of the viologen radical (PSV$^-$) was ca. four times more efficient than that obtained in the corresponding experiments with MV$^{2+}$ as acceptor (Fig. 2). With (1) as sensitizer the maximal quantum yield of PVS$^-$ production was 0.03 vs. 0.0067 for MV$^+$ production. With (2) as sensitizer, the quantum yield of PVS$^-$ formation was improved by a similar factor ($\phi_{\text{max}} = 0.01$). The origin of the enhanced efficiency of electron-transfer using PVS$^0$ as acceptor is currently being investigated. The different charge properties of PVS$^0$ and MV$^{2+}$ suggest that electrostatic interactions have an important effect on the electron-transfer process.

In conclusion, we have demonstrated the use of thiophenol as a non-destructible electron-donor and accomplished an electron-transfer along
an endoergic pathway. The water-in-oil microemulsion provides a means of separating the redox products and retarding back-reactions. Metallo-porphyrins, in particular Zn-porphyrins, seem to be efficient sensitizers for photoinducing redox reactions. The enhanced efficiency of PVS\(^0\) as acceptor encourages its utilization as a mediator in water decomposition.

Acknowledgements

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References

Figure Captions

Fig. 1. Photosensitized reduction of MV$^{2+}$ by thiophenol: separation of products in the water-in-oil microemulsion.

Fig. 2. Quantum yield for the photosensitized reduction of viologens by Zn-porphyrins: (A) [Zn-TMPyP]; MV$^{2+}$ (6 x $10^{-3}$ M) (B) [Zn-TPPS]; MV$^{2+}$ (6 x $10^{-3}$ M) (C) [Zn-TMPyP]; PVS$^0$ (6 x $10^{-3}$ M) (D) [Zn-TPPS]; PVS$^0$ (6 x $10^{-3}$ M). In all experiments thiophenol, RSH, (0.1 M) used as electron-donor.
Figure 1
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Figure 2
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