Photochemical Transfer of an Electron and a Proton across the Interface in Microemulsions

Mikhail Khramov,† Georgii G. Lazarev,*,‡
Federico García J., and Arturo Zentella D.

Instituto de Química
Universidad Nacional Autónoma de México
Circuito Exterior, Ciudad Universitaria
Coyoacán, 04510 México, D.F., Mexico

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Microemulsions and lipid vesicles are widely used as models for the development of artificial photosynthetic systems.[1-3] It is generally accepted that the conversion of light energy into chemical form proceeds in two stages.[4] (1) photochemical charge separation at an interface with partition of the products of this reaction between different phases; and (2) "dark" reactions in the course of which the carriers of the separated charges, oxidant and reductant, evolve toward the target products.

There exist two problems which must be solved in the development of such systems: (1) the interface is electrically charged by the transport of electrons across it, which impedes further interfacial transport; and (2) the separation of charge into the aqueous and organic phases of the microemulsions means that oxidant and reductant are formed in different phases. (It is difficult to use oxidant or reductant in the organic phase for oxygen or hydrogen evolution.) The first problem can be solved by ensuring a cotransport of ions across the interface,[3,5] and the second one, by arranging for the process of O_2 and H_2 evolution to occur in different aqueous phases (water droplets) of a water-in-oil microemulsion[4] or in water phases inside and outside the cavities of a vesicle suspension.[6]

In the present study, an ESR method which has been shown to discriminate between electron and hydrogen atom transfer in doped crystals[7,8] and which has been used to study photochemical reactions in micelles[9,10] is used to investigate photochemical reactions in water-in-oil microemulsions. Transport of an electron and a proton from 2,6-di-*tert*-butyl-4-methylphenol (ionol) localized in the organic phase to the persulfate anion, confined in the water phase, is demonstrated. The coupled transfer of an electron and a proton prevents charging of the interface, thus solving the first problem. The only ions which may be transported, together with an electron, across water–organic interfaces in artificial water decomposition systems without altering the composition of these phases (thus permitting a cyclic performace of such systems) are H^+. Therefore, transport of a hydrogen atom across the microemulsion interface, equivalent to the concurrent transport of an electron and H^+, also overcomes the second problem encountered in development of artificial photosynthetic systems.

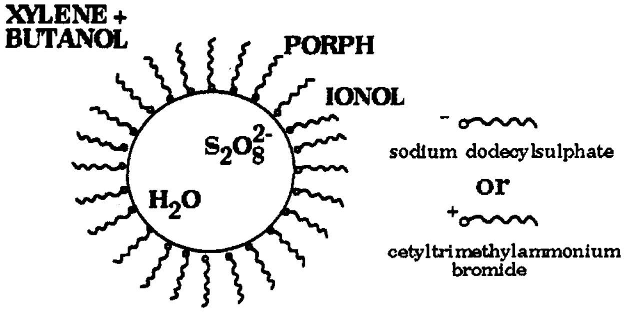

Figure 1. Schematic representation of microemulsions used in the present work.

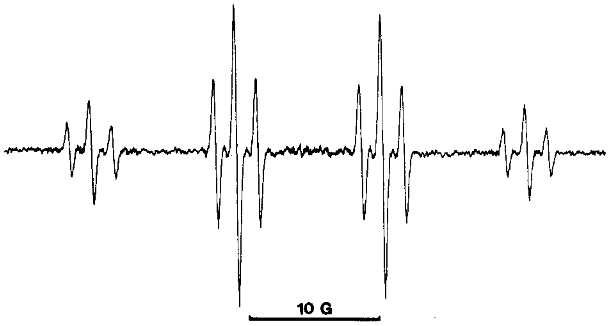

Figure 2. ESR spectrum of 2,6-di-*tert*-butyl-4-methylphenol in a SDS microemulsion.

In the present work, water-in-oil microemulsions with negatively (sodium dodecyl sulfate, SDS, as a surfactant) and positively (cetyltrimethylammonium bromide, CTMAB, as a surfactant) charged interfaces were studied; a schematic representation of the microemulsion is shown in Figure 1. *meso*-Tetraphenylporphyrin (porph) was used as a photocatalyst. Microemulsions were of the following compositions (in weight percent): mixture of xylenes 75.7%, butanol-1 17.8%, SDS 3.5%, water 3%; and mixture of xylenes 74.9%, butanol-1 17.6%, CTMAB 4.5%, water 3%. All of the reagents were of analytical grade. A 0.1 M solution of 2,6-di-*tert*-butyl-4-methylphenol (ionol) and *meso*-tetraphenylporphyrin (Fluka) (10^{-5} M) were dissolved in the xylene–butanol mixture, to which the solid surfactant was added. Water or a 0.25 M water solution of $(NH_4)_2S_2O_8$ was added with vigorous stirring until the mixture became transparent under transmitted light (clear solution) and opalescent under reflected light. Samples were deoxygenated by freezing and evacuating. Samples became turbid upon freezing but returned to their initial transparent and opalescent state upon warming to ambient temperature.

The samples were irradiated in the cavity of a Brucker ER 200D ESR spectrometer using a 300-W halogen lamp in the absorption band of *meso*-tetraphenylporphyrin. An OG-495 filter was used to cut off light at wavelengths shorter than 495 nm.

Illumination into the absorption band of the *meso*-tetraphenylporphyrin of the microemulsions (with both negatively and positively charged interfaces) containing the porphyrin and 0.1 M ionol in the organic phase and 0.25 M $(NH_4)_2S_2O_8$ in water droplets results in the appearance of the ESR signal shown in Figure 2. One sees four sets of lines with relative intensities 1:3:3:1 and characteristic hyperfine splitting (HFS) value $a = 11 \pm 0.2$ G. Each of these four sets of lines reveals a structure consisting of three lines with relative intensities 1:2:1 and HFS value $a_1 = 1.7 \pm 0.1$ G. ESR spectra of this type can be assigned

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* Address for correspondence: Prof. G. G. Lazarev, Instituto de Química, UNAM, Circuito Exterior, Ciudad Universitaria, Coyoacan, 04510 Mexico, D. F., Mexico.

† On leave from the Institute of Catalysis, Russian Academy of Science, Novosibirsk 630090, Russia.

‡ On leave from the Institute of Chemical Physics, Russian Academy of Science, Moscow 117334, Russia.

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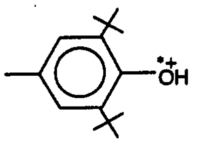
to the neutral radical of ionol (**2**).[11] The four sets of lines with relative intensities 1:3:3:1 and $a = 11 \pm 0.2$ G are due to the splitting by three equivalent protons of the CH_3 group in the para position. Additional splitting of each of these four sets of lines with $a_1 = 1.7 \pm 0.1$ G can be attributed to the interaction of an unpaired electron with two protons in the meta positions of the benzene ring.[11,12] The characteristic HFS values are $a = 14 \pm 0.2$ G for ionol cation radical (**1**)[11] and $a = 11 \pm 0.2$ G for the neutral phenoxy radical (**2**) of ionol.[11] The experimental value of HFS measured in the present work is $a = 11 \pm 0.2$ G, which allows us to conclude that the spectrum of Figure 2 is correctly assigned to the neutral radical (**2**) of ionol.



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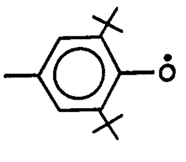

2

In the dark, no signal which could be assigned to the ionol radical was observed, either in SDS or in CTMAB microemulsions containing both ionol in the organic phase and $S_2O_8^{2-}$ in the aqueous phase. We conclude there is no "dark" reaction between ionol and $S_2O_8^{2-}$. Upon illumination ($\lambda > 495$ nm) of the SDS and CTMAB microemulsions containing only ionol (organic phase) or ionol and $S_2O_8^{2-}$ also no signal assignable to the ionol radical was observed. Illumination of the SDS and CTMAB microemulsions containing both porphyrin and ionol in the organic phase but no $S_2O_8^{2-}$ in the water phase leads to the formation of the ionol radical (**2**), the yield being 30 times lower than in the complete system containing ionol and porphyrin in the organic phase and $S_2O_8^{2-}$ in the aqueous phase. This may be explained by the porphyrin catalyzed oxidation of ionol by traces of O_2 present in the reaction system. These results demonstrate that the presence of all the components of the system is necessary for efficient formation of the neutral ionol radical. Two possible mechanisms may be proposed to explain the experimental results:

mechanism 1

$$\text{porph} \xrightarrow{k_{1\text{-}1}} {}^*\text{porph} \qquad (1\text{-}1)$$

$$^*\text{porph} \xrightarrow{k_{1\text{-}2}} \text{porph} \qquad (1\text{-}2)$$

$$^*\text{porph} + {}^1/{}_2S_2O_8^{2-} \xrightarrow{k_{1\text{-}3}} \text{porph}^+ + SO_4^{2-} \qquad (1\text{-}3)$$

$$\text{porph}^+ + \text{ionol} \xrightarrow{k_{1\text{-}4}} \text{porph} + \text{ionol}^{\bullet+} \qquad (1\text{-}4)$$

$$\text{ionol}^{\bullet+} \xrightarrow{k_{1\text{-}5}} \text{ionol}^{\bullet} + H^+ \text{ (organic)} \qquad (1\text{-}5)$$

$$H^+ \text{ (organic)} \xrightarrow{k_{1\text{-}6}} H^+ \text{ (aqueous)} \qquad (1\text{-}6)$$

mechanism 2

$$\text{porph} \xrightarrow{k_{2\text{-}1}} {}^*\text{porph} \qquad (2\text{-}1)$$

$$^*\text{porph} \xrightarrow{k_{2\text{-}2}} \text{porph} \qquad (2\text{-}2)$$

$$^*\text{porph} + \text{ionol} \xrightarrow{k_{2\text{-}3}} \text{porph}^- + \text{ionol}^{\bullet+} \qquad (2\text{-}3)$$

$$\text{porph}^- + \text{ionol}^{\bullet+} \xrightarrow{k_{2\text{-}4}} \text{porph} + \text{ionol} \qquad (2\text{-}4)$$

$$\text{porph}^- + S_2O_8^{2-} \xrightarrow{k_{2\text{-}5}} \text{porph} + {}^1/{}_2SO_4^{2-} \qquad (2\text{-}5)$$

$$\text{ionol}^{\bullet+} \xrightarrow{k_{2\text{-}6}} \text{ionol}^{\bullet} + H^+ \text{ (organic)} \qquad (2\text{-}6)$$

$$H^+ \text{ (organic)} \xrightarrow{k_{2\text{-}7}} H^+ \text{ (aqueous)} \qquad (2\text{-}7)$$

At the present stage it is difficult to make a definite conclusion about the mechanism of the process. However, a kinetic analysis of these mechanisms argues in favor of mechanism 1. The rates of ionol• formation, under steady-state conditions for *porph, porph+, porph−, and ionol•+ are as follows:

$$\frac{d[\text{ionol}^\bullet]}{dt} = \frac{k_{1\text{-}1}k_{1\text{-}3}[\text{porph}][S_2O_8^{2-}]}{k_{1\text{-}2} + k_{1\text{-}3}[S_2O_8^{2-}]} \qquad \text{(mechanism 1)}$$

$$\frac{d[\text{ionol}^\bullet]}{dt} = \frac{k_{2\text{-}1}k_{2\text{-}3}k_{2\text{-}5}[\text{porph}][\text{ionol}][S_2O_8^{2-}]}{(k_{2\text{-}4}[\text{ionol}^{\bullet+}] + k_{2\text{-}5}[S_2O_8^{2-}])(k_{2\text{-}2} + k_{2\text{-}3}[\text{ionol}])} \qquad \text{(mechanism 2)}$$

The constants which may depend strongly on the interfacial charge are those of the reactions which involve reagents from different phases, 1–3, 1–6, 2–5, and 2–7. However, only k_{1-3} and k_{2-5} appear in the velocity equation. In reaction 1–3 only $S_2O_8^{2-}$ is charged. This substance is present at a high concentration (0.2 M) within a very small (~n·10 Å) water droplet, so it is reasonable to suppose that the charge of the interface will not significantly affect the concentration of $S_2O_8^{2-}$ close to the interface (otherwise a large $S_2O_8^{2-}$ concentration gradient will develop across the droplet). In reaction 2–5 both reagents are charged molecules. The influence of the surface charge on the concentration of $S_2O_8^{2-}$ close to the interface will be the same as in mechanism 1. However, this charge will strongly influence the porph− concentration close to the interface (porph− is present at low concentration, and its repulsion from or attraction to the interface will not create a big concentration gradient). Consequently, the influence of the interfacial charge should be much more marked in mechanism 2. Since in the experiment no essential difference in the yield of ionol• was observed, we can suppose that the process occurs according to mechanism 1. However, the detailed mechanism of this process will be the subject of further studies.

This method may also be used to study photochemical reactions and discriminate between electron and coupled electron–H+ transfer in a range of various microheterogeneous systems like micelles, microemulsions, and lipid vesicles, including reactions of quinone complexes having biological importance,[13] and in the theoretical description of charge transfer.[14]

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