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EOSIN Y SENSITIZED REDUCTION OF QUINONES TO THEIR PERSISTENT RADICAL ANIONS

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Eosin Y sensitized efficiently the reduction of duroquinone and anthraquinone-2-sulfonate to their persistent radical anions in aqueous 2-propanol in the presence of triethanolamine.

Recently many attempts have been made to construct photochemical electron transfer systems to reduce quinones by excitation of dyes by mimicking natural photosynthetic systems$^{1)}$ in which photoexcitation of chlorophyll induces electron transfer to plastoquinone followed by regeneration of chlorophyll through electron transfer from other electron donors. However, in most cases examined, the resulting radical anions were very short-lived.$^{1)}$

We now wish to report that on irradiation with visible light in a 2-propanol water mixture in the presence of triethanolamine (TEOA) Eosin Y (EY^{2-}) sensitizes efficiently the reduction of quinones like duroquinone (DQ) and sodium anthraquinone-2-sulfonate (AQS) into their almost persistent radical anions.

In a typical run, when EY^{2-} (1.5×10^{-5} mol/l) was irradiated with light of wavelengths longer than 500 nm from a 500 W xenon lamp in the presence of DQ (1.0×10^{-4} mol/l) in an equivolume mixture of 2-propanol and water containing sodium hydroxide (0.1 mol/l) and TEOA (1.9×10^{-3} mol/l) under argon atmosphere, DQ was reduced to give duroquinone radical anion ($DQ^{\bar{\cdot}}$). On the contrary, in the absence of EY^{2-} under otherwise the same conditions DQ was not reduced. The production of $DQ^{\bar{\cdot}}$ was easily detected by the growth of its characteristic absorption bands with the maxima around 416 and 440 nm$^{2)}$ (Fig. 1) and by its characteristic ESR spectrum having thirteen lines with a hyperfine splitting constant about 0.16 mT.$^{3)}$ The resulting radical anions were still alive on standing overnight.$^{4)}$ The quantum yield for $DQ^{\bar{\cdot}}$ formation was determined to be 0.47 by irradiating with 480 ± 10 nm light from a 500 W xenon lamp.$^{5)}$

Under the similar conditions, AQS was reduced to its radical anion ($AQS^{\bar{\cdot}}$) through EY^{2-} sensitization.$^{6)}$ $AQS^{\bar{\cdot}}$ was also characterized by its absorption$^{7)}$ (Fig. 2) and ESR spectra.$^{4)}$

In both cases introduction of air to the irradiated solutions eliminated completely the absorption of quinone radical anions and recovered the original absorption of EY^{2-} without any decrease in intensity. This shows that EY^{2-} was quite durable for visible light irradiation under the conditions examined.

In contrast, in the absence of quinones under otherwise the same conditions, irradiation of EY^{2-} led to photobleaching of EY^{2-} through formation of $EY^{3\bar{\cdot}}$.$^{8)}$

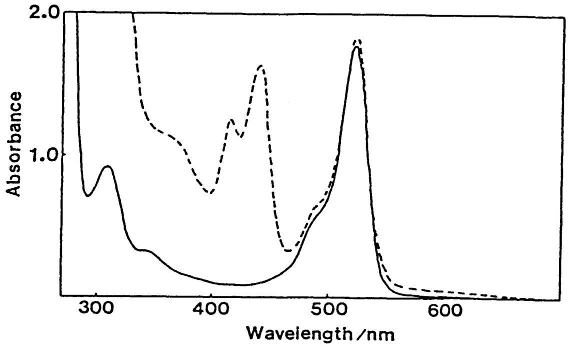

Fig.1. The spectral change of an EY^{2-}/DQ system on irradiation with visible light (>500 nm). —— : before irradiation, ---: after irradiation.

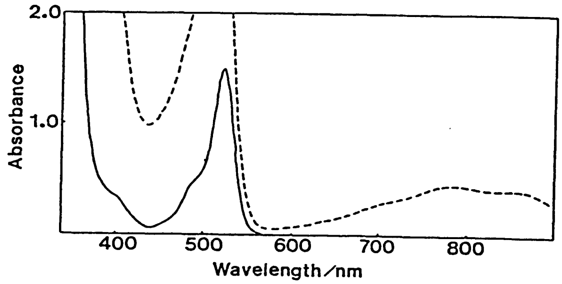

Fig.2. The spectral change of an EY^{2-}/AQS system on irradiation with visible light (>500 nm). —— : before irradiation, ---: after irradiation.

On the other hand, in the absence of TEOA under otherwise the same conditions, irradiation of EY^{2-} did not lead to formation of $DQ^{\cdot-}$ and $AQS^{\cdot-}$.

Finally, it should be noted that the present system comprised of EY^{2-} , TEOA, and quinones could be used as a potential electron transferring system through formation of almost persistent radical anions of quinones. The mechanism will be discussed in a full paper.

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5) The quantum yield was determined in the following concentrations: $[EY^{2-}]= 1.2 \times 10^{-4}$, $[DQ]= 1.0 \times 10^{-4}$, $[TEOA]= 1.9 \times 10^{-3}$ mol/l.

6) The reduction of AQS was performed in the following concentrations: $[EY^{2-}]= 1.5 \times 10^{-5}$, $[AQS]= 2.0 \times 10^{-3}$, $[TEOA]= 5.6 \times 10^{-3}$ mol/l.

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