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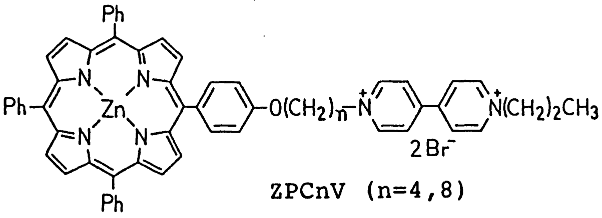
Counterion Effects on the Photoinduced Electron-Transfer and the Reverse Process in Porphyrin-Viologen Linked Compounds [1)]

Akira MITSUI, Akihiro UEHATA, Hiroshi NAKAMURA, and Taku MATSUO*
Department of Organic Synthesis, Faculty of Engineering,
Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

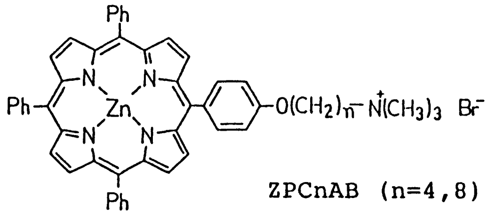
In porphyrin-viologen linked compounds, photoinduced electron-transfer from porphyrin to viologen was suppressed by Br^-, while the decay of the resulting triplet radical pair was accelerated by the same counterion. Contribution of heavy atom effects and CT interaction was suggested to explain the observed counterion effects.

Photochemical behavior of donor-acceptor linked compounds has intensively been investigated as a model photoreaction center for artificial photosynthesis.[2)] For a given donor-acceptor pair, the electron-transfer (abbreviated to ET hereafter) rates have been found to decrease exponentially with the donor-acceptor distance of the pair in the singlet state.[3)] As to the photogenerated radical pair, the reverse ET rates have been proved to depend on the spin multiplicities as verified by the external magnetic field effects (abbreviated to EMFES hereafter) on the decay rate of porphyrin-viologen linked radical pair.[4)] Stereochemical factors also play very important roles in the photogeneration of radical pairs and the decay process as in the case of phenothiazine-viologen linked compounds.[5)] The present paper reports a new finding that both the forward- and reverse ET-processes could be remarkably affected by the choice of the counter ion for the viologen units in porphyrin-viologen linked compounds.

The following porphyrin-viologen linked compounds and the reference were prepared according to the standard procedures,[6)] and the counter ion effects on the ET reactions were examined in three different types of microenvironment: *aqueous acetonitrile (50:50 by volume), micelles, and molecular bilayers of cationic surfactants in water.*



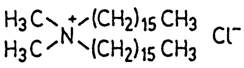
ZPCnV (n=4,8)



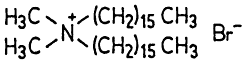
ZPCnAB (n=4,8)

$(H_3C)_3\overset{+}{N}(CH_2)_{15}CH_3$ Cl^- CTAC

$(H_3C)_3\overset{+}{N}(CH_2)_{15}CH_3$ Br^- CTAB


$(H_3C)_2\overset{+}{N}((CH_2)_{15}CH_3)_2$ Cl^-

DHDAC


$(H_3C)_2\overset{+}{N}((CH_2)_{15}CH_3)_2$ Br^-

DHDAB

The Study of Radical Pairs in Aqueous Acetonitrile: Sample solutions containing appropriate amount of linked compounds (2×10^{-5} M; 1 M=1 mol dm^{-3}) and sodium salts of various ions (0-0.4 M) were irradiated with an excimer laser beam at 351 nm (Lambda Physik EMG-100, 5 mJ, and 15 ns pulse duration), and the transient absorption of the radical pair was detected at the absorption maximum (640 nm). The sample solutions were degassed and photolyzed in Ar atmosphere at 25 °C. The measurements were made in the presence of external magnetic fields (0.5 T), where the radical decay rates have been known to decrease to asymptotic values.4)

The transient absorption quickly decayed to constant values within 10 microseconds after laser pulsing as previously reported.4) After subtracting the constant value, which is ascribed to radicals as generated via intermolecular ET in the secondary process,4) one can isolate the component due to the linked radical pair. The time profile of this rapidly decaying component followed first-order reaction kinetics in agreement with the following scheme, where a triplet radical pair decays via intersystem crossing. The first order decay rate constants for ZPC_8V are plotted against the sodium salts concentration in Fig. 1.

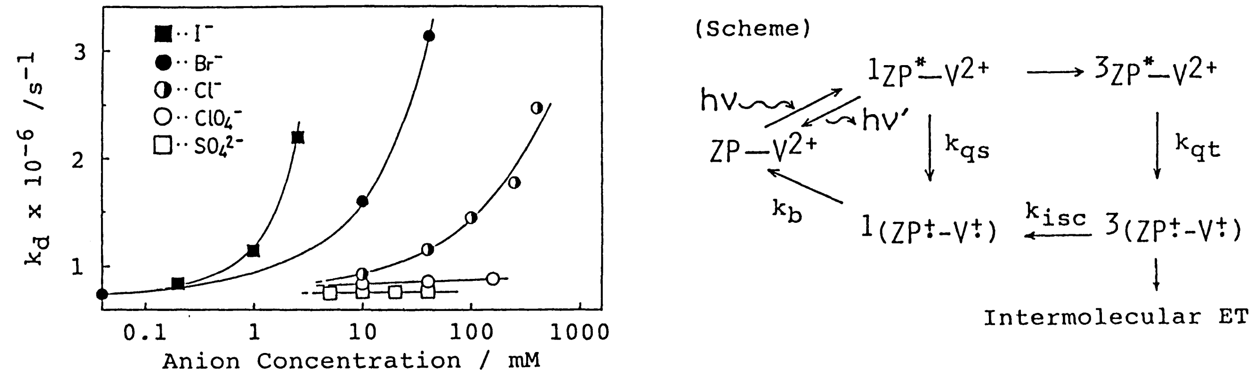


Fig. 1. Effects of counterion on the decay rate constant of the photoinduced radical pair $^3(ZP^{\dot{+}}C_8V^{\dot{+}})$ in aqueous acetonitrile and the reaction scheme.

It is clearly observed that halide ions have much more pronounced effects on accelerating the radical decay than either perchlorate or sulfate. Previous studies of EMFES on the decay rate of the linked radical pairs under discussion have confirmed that the radical pairs are in the triplet state and the decay rates are determined by the triplet-singlet intersystem crossing.4) In the presence of external magnetic fields above 0.3 T, Zeeman splitting of the triplet sublevels becomes important and electron spin relaxation from T_+ and T_- sublevels to T_0 appears to be the rate-determining factor in the intersystem crossing process, and the radical decay is accelerated in the presence of paramagnetic lanthanide ions.7) The effects of halide ions in the present study are also in good agreement with the electron-spin relaxation mechanism as one would expect of the general trend in the heavy atom effects associated with the spin-orbit coupling constants ($I^- > Br^- > Cl^-$). The extremely small dependence on sulfate concentration may indicate that the electronic charge of the counter ion itself does not play important roles in determining the lifetime of the radical pairs.

The counterions can not be expected to reside on the viologen moieties all the time, as it is obvious from the fact that the radical decay rates increase with the concentration of halide ions. Attempts have been made to enrich the counterions by the use of cationic surfactant molecular assemblies, which are capable of incorporating the porphyrin-viologen linked pairs.

The Counterion Effects on ET Properties of the Linked Compounds in Surfactant Molecular Assemblies: In order to understand the finer details of the heavy atom effects, the linked compounds were incorporated into comicelles of CTAC and CTAB. The total concentration of the surfactants was kept constant (10 mM), but the molar ratios were systematically varied: [CTAC]+[CTAB]=10 mM. The radical pairs decayed with first-order reaction kinetics and the decay rate increased with the increase of bromide ions as it is clear from the time profile of the transient absorption (Fig. 2). These trends are in good agreement with the reported heavy atom effects of halides on the triplet yields and lifetimes of anthracene in micellar systems of CTAC homologues.[8) Surfactant molecular bilayers afford much more stable sites for incorporating amphiphilic guest molecules than micellar systems. The counter ion of dihexadecyldimethylammonium (DHDA) bilayer membrane was changed from chloride to bromide ion by increasing the molar ratio between DHDAC to DHDAB: [DHDAC]+[DHDAB]=10 mM. The concentration of the linked compounds was reduced to 10 μM because of the solubility problems. To be a surprise, the transient absorption due to the radical pair was observed only in the absence of DHDAB.

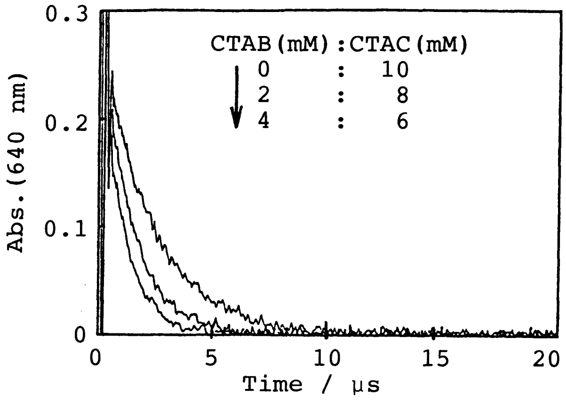


Fig. 2. Effects of bromide/chloride ion ratios on time profile of the absorption due to the radical pair $^3(ZP^{+\cdot}C_4V^{+\cdot})$ in CTAC/CTAB comicelles.

In addition, the quenching rate of the porphyrin triplet for ZPC_4V also was remarkably affected by the ratio between DHDAC and DHDAB (Fig. 3). The triplet lifetime of the reference compound with ammonium head group (ZPC_4AB) was beyond 1 ms even in DHDAB membranes. Thus, it is clear that the rapid decay of the triplet absorption (470 nm) in Fig. 3 is due to ET quenching of the triplet. The quenching rate increased with the DHDAC concentration, and an abrupt change was observed in the neighborhood of pure DHDAC membrane.

Quenching efficiency (Eq) of the fluorescence from the porphyrin moiety of ZPC_4V also gave a sigmoidal curve, when the bilayer composition was changed from pure DHDAB to DHDAC (Fig. 4). The fluorescence quenching is also ascribed to intramolecular ET from the porphyrin to the viologen moieties in linked compounds.6) These results strongly suggest that the photoinduced ET rates are considerably reduced when the counterion of the viologen moiety is changed from chloride to bromide ion. Charge transfer interaction between viologen moiety and bromide ion may be responsible to the reduction of photoinduced ET rates.9)

Essentially the same phenomena as described above were also observed with ZPC_8V incorporated into DHDAC-DHDAB mixed bilayers. It may reasonably be assumed that the molar ratio of these two surfactants represent the ratio of the

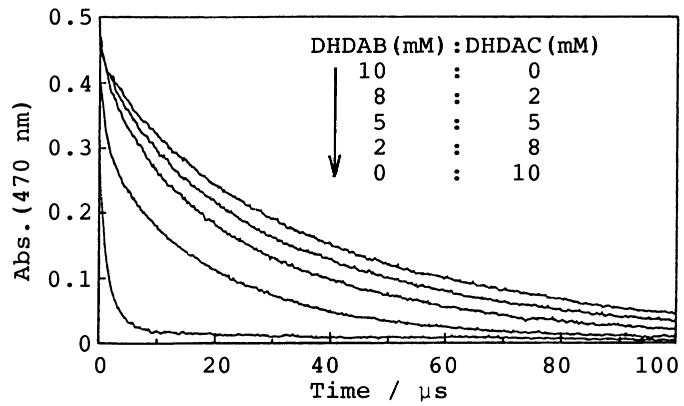


Fig. 3. Effects of bromide/chloride ion ratios on the triplet quenching of ZPC$_4$V in DHDAB/DHDAC mixed bilayers in various molar ratios.

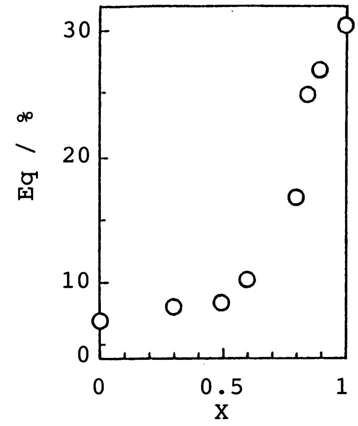


Fig. 4. Effects of the mole fractions, X=[DHDAC]/([DHDAC]+[DHDAB]), on the Eq-value for ZPC$_4$V.

counterion of the viologen unit in the linked compound. In the presence of bromide ions in the vicinity of viologen units, the photoinduced ET reaction is retarded while the reverse process is enhanced. As a consequence, the photogenerated radical pair will disappear immediately and do not reach to a detectable concentration as previously described.

In a summary, both the photoinduced ET rate and the reverse process are considerably modified by the choice of counterion of the viologen unit in the linked compounds. The counterion appears to affect the ET processes via two types of perturbation: (1) reduction of the electron accepting properties of viologen units through charge-transfer interaction, and (2) enhancement of inter-system crossing of the photogenerated radical pair via spin-orbit interaction.

References

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