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Pyrene-cation Formation on Reactions of Pyrene Triplet State with Metal Ions in Caffeine-solubilized Aqueous Solution

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Synopsis. Quenching of triplet states of pyrene and other aromatic hydrocarbons by metal ions in caffeine-solubilized aqueous solution was investigated. The concomitant formation of aromatic cations was observed on quenching of triplet pyrene by Hg^{2+} and Fe^{3+} and triplet phenanthrene and benz[*a*]anthracene by Hg^{2+}.

To the reactions between excited states of aromatic hydrocarbons and metal ions have been paid attention from the viewpoint of their application to solar energy conversion based on the photo-induced electron transfer reactions. However, such charge separation with metal ions was known only for the triplet states of thiazine dyes.[1-4] Recently, we have reported reduction of metal ions with the excited singlet state of pyrene solubilized in aqueous solution of caffeine.[5] The experiments performed in aqueous solution are of greater advantage than those in organic solvents in regard to dissolving various metal ions. In the present paper, we report a study on quenching of triplet states of pyrene and other aromatic hydrocarbons by metal ions in caffeine-solubilized aqueous solution. The results indicate that electron transfer occurs from the triplet state of pyrene to Hg^{2+} and Fe^{3+} whose reduction potentials are rather low. Other metal ions were not reduced, although they quenched the triplet state of pyrene to a certain extent.

The apparatus using a frequency doubled Q-switched ruby laser and experimental procedures have been described in the previous paper.[5] Figure 1 exhibits oscilloscope profiles representing the decay of the pyrene triplet state and concomitant growth of pyrene cations on quenching by Hg^{2+}. The assignment of the growing species to the pyrene cation was based on its absorption spectrum.[6] The concentrations of pyrene cations and pyrene triplet states were estimated from the absorbances at 450 and 414 nm using reported values of extinction coefficient.[7,8] The yields of the cation originating in the excited singlet state, which also contribute to the observed cation yields in the time region of Fig. 1, were given in the previous report.[5]

The bimolecular rate constant for triplet-quenching (k_q) was obtained from the observed pseudo-first-order rate constants;

$$k_{obsd} = k_o + k_q[M^{n+}],$$

where $[M^{n+}]$ is the concentration of metal ions. The reaction of the triplet state (^3P) with metal ions is expressed by Reactions 1 and 2.

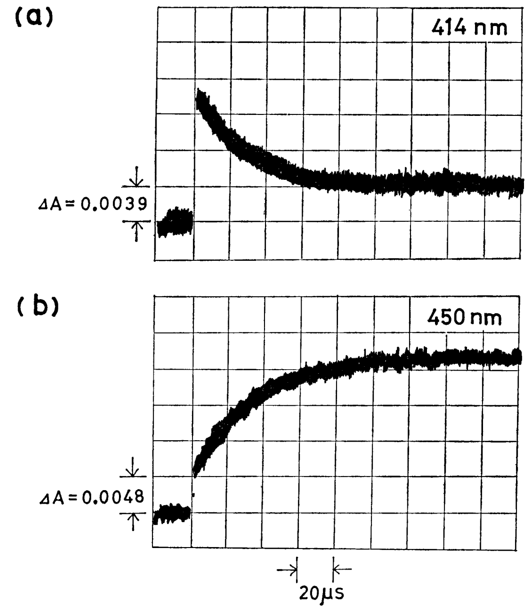

Fig. 1. Oscilloscope traces after laser excitation observed at 414 and 450 nm, which correspond to absorption peaks for pyrene triplet state and pyrene cation, respectively. [Pyrene]=0.04 mM, [Hg$(NO_3)_2$]=1.0 mM, and [caffeine]=60 mM.

$$^3P + M^{n+} \xrightarrow{k_{1q}} P + M^{n+}, \tag{1}$$

$$^3P + M^{n+} \xrightarrow{k_{2q}} P^+ + M^{(n-1)+}, \tag{2}$$

for which

$$k_q = k_{1q} + k_{2q}.$$

Quenching rate constants k_q measured for the reactions of the triplet state of pyrene with some metal ions and for the reactions of the triplet states of phenanthrene (^{3}Phe) and benz[*a*]anthracene (^{3}BA) with Hg^{2+} are shown in Fig. 2 as a function of the free-energy change (ΔG°)[5,9] of the charge transfer reaction (Eq. 2). For Eu^{3+}, Zn^{2+}, Cd^{2+}, Tl^+, and Tb^{3+}, the experimental values for k_q were less than $10^6\ M^{-1}\ s^{-1}$. Rate constants for pyrene fluorescence quenching as well as a theoretical curve which has been discussed in the previous report[5] are also shown in Fig. 2. The theoretical curve implies that electron transfer occurs with an activation energy of 0.75 eV in the case of $\Delta G^\circ = 0$ eV.[9]

The fraction of charge transfer, which is expressed by the ratio of the rate constants, k_{2q}/k_q, is calculated as the ratio of an increment of the pyrene cations to a decrement of the triplet state in the quenching process. The charge transfer fractions were more than 0.9 for Hg^{2+} and Fe^{3+}, and less than 0.1 for Cu^{2+},

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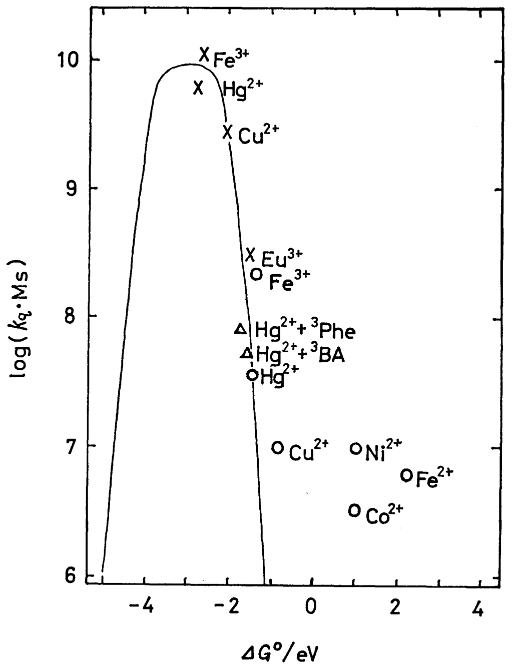

Fig. 2. Plot of log k_q as a function of the free energy change($\Delta G°$) for electron transfer reaction from excited states of pyrene to metal ions. Open circles and crosses show the reaction rates for triplet state and excited singlet state[5] of pyrene, respectively. ^{3}Phe and ^{3}BA are triplet states of phenanthrene and benz[*a*]anthracene.

Ni^{2+}, Fe^{2+}, and Co^{2+}. For metal ions by which hydrocarbon cations were formed, the experimental points for triplet excited states are located on the theoretical curve presented for singlet excitated states.[5] For the other metal ions, the experimental points are not located on the curve but above it, indicating existence of some efficient quenching mechanisms other than the electron transfer mechanism. The mechanism presented previously[5] for triplet state formation on fluorescence quenching may also be applicable to the mechanism of singlet state formation on phosphorescence quenching in this case. Further experiments for various metal ions will afford much information concerning the quenching mechanism which is applicable to both singlet and triplet excited states.

References

1) S. A. Alkaitis, R. Beck, and M. Grätzel, *J. Am. Chem. Soc.*, **97**, 5723 (1975).

2) Y. Moroi, A. M. Braun, and M. Grätzel, *J. Am. Chem. Soc.*, **101**, 567 (1979).

3) E. Pelizzetti and E. Pramauro, *Ber. Bunsenges. Phys. Chem.*, **83**, 996 (1979).

4) T. Ohno and N. N. Lichtin, *J. Am. Chem. Soc.*, **102**, 4636 (1980).

5) Y. Nosaka, A. Kira, and M. Imamura, *J. Phys. Chem.*, **85**, 1353 (1981).

6) T. Shida and S. Iwata, *J. Am. Chem. Soc.*, **95**, 3473 (1973).

7) G. E. Hall and G. A. Kenny-Wallace, *Chem. Phys.*, **32**, 313 (1978).

8) W. Heinzelmann and H. Labhart, *Chem. Phys. Lett.*, **4**, 20 (1969).

9) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).