© 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 2352—2355 (1982) [Vol. 55, No. 8

Dynamic Studies on Electron Transport Across Micellar Phase. Intermicellar Migration of Hydrated Electrons

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(Received February 20, 1982)

The dynamics of hydrated electrons generated by pulsed electron beams was studied for micellar systems with a series of halogenated naphthalenes as substrates exclusively dissolved in micellar phase. Time behavior of absorption for hydrated electrons, displayed as a curve consisting of two exponential decays, affords evidence that two different routes exist in advance of dissociative electron attachement: 1) direct penetration of electrons through micellar phase with substrates, and 2) migration of hydrated electrons between micells in the absence and presence of substrates, prior to the penetration of electrons into the reactive center in the micelle. Electrostatic interaction of hydrated electrons with positively charged surface of micelles is also discussed.

Knowledge of electron transfer mechanisms with donor–acceptor systems, separated from each other by hydrophobic compartments in aqueous micellar solution, is essential for constructing artificial photosynthetic devices.[1–3] Ionic micelles, like charged colloids and ion-exchange resins, have the property of being able to bind with oppositely charged ions.[4] This aspect of micelles has been used to study a variety of reactions in conjunction with their ability to solubilize hydrophobic molecules in aqueous solutions. In previous works, it has been reported that adsorbed metal ions on anionic micelles can act as efficient electron acceptors from excited micelle solubilized species,[5] and that they can promote the rate of phosphorescence in some aromatic hydrocarbons.[6] Recently, kinetic studies on the movement of metal ions in aqueous micellar solutions have also been reported.[4,7,8] The use of hydrated electrons, generated in bulk aqueous phase, as a source of electrons for redox reactions seems to provide information on the reactivity of electrons with micelle-bound substrate. Few kinetic studies, however, have been directed at studying the movement of hydrated electrons in aqueous micellar solutions.[6,9] Hydrated electrons in aqueous cationic micellar solutions are expected to act in the same manner as metal ions which accelerate or inhibit reactions with oppositely or commonly charged surface of micelles.[4,10] We report here results of dynamic studies on the movement of hydrated electrons in an aqueous cationic micellar solution. The reaction of dissociative electron attachment was utilized to determine the rate of electron transfer from the surface to core of micelles.

Experimental

1-Chloronaphthalene (CN) and 1-bromonaphthalene (BN), purchased from Nakarai Chemicals, were purified by repeated vacuum distillation. 1,4-Dibromonaphthalene (DBN, Wako) was purified by vacuum sublimation. Hexadecyltrimethylammonium bromide (HDTBr, Sigma Chemicals) was used as supplied. For solubilization of halonaphthalenes as substrates, HDTBr detergent in triply distilled water was shaken with the substrate overnight. Concentrations of the substrates in micellar solutions were determined by their absorbances.

Halogenated naphthalenes (XN) are frequently used as effective electron scavengers in radiolyses of various chemical substances. This is based on the fact that XNs are highly reactive toward electrons, and that when an electron attaches to XN, it will dissociate into a neutral radical and a halide ion:[11)

$$XN + e^- \longrightarrow X^-N \longrightarrow X^- + N\cdot. \qquad (1)$$

Reaction 1 is a so-called dissociative attachement. Since, however, kinetics between hydrated electrons (e_{aq}^-) and halogenated naphthalenes are not well known because of their low solubilities in water, the reactivity of reaction $e_{aq}^- + XN$ should be tested by monitoring the decay of hydrated electrons prior to running experiments on micellar systems. The decay curve for hydrated electron in an aqueous solution with EtOH (1.0 M) (1 M = 1 mol dm^{-3}) consisted of a single exponential component over the range of halonaphthalene concentrations examined (5×10^{-5}—5×10^{-6} M). From observed decay rates of hydrated electrons as a function of XN concentration, rate constants of the reactions of e_{aq}^- with DBN, BN, and CN were determined to be 3.0×10^{10}, 1.8×10^{10}, and 1.4×10^{10} M^{-1} s^{-1}, respectively. These values should represent the rate constant for the following reaction:

$$XN + e_{aq}^- \longrightarrow N\cdot + X^- + H_2O. \qquad (2)$$

By monitoring the decay rate for the absorption of hydrated electron after pulse irradiation, reaction kinetics of the electron transport from bulk aqueous phase to micellar phase could be examined if the rate changes with change in the concentration of substrates and/or micelles. Two series of micellar solutions were prepared by 1) changing the concentration of substrates (from 0 to 3×10^{-4} M) at a fixed HDTBr detergent concentration (0.05 M), and 2) changing both the concentrations of substrates [XN] and detergent [Det] at a fixed mean occupancy number ⟨XN⟩, which is the number of substrates bound per micelle. The substrates used are known to be exclusively micellized under the experimental conditions studied, since the binding constants between HDTBr micelle and halogenated naphthalenes are known to be 1.7×10^6 and 3.7×10^6 M^{-1} for BN and CN, respectively.[12,13]

Micellar solutions were deaerated by bubbling purified argon for 10 min through them.

Pulse radiolysis measurements were performed with electron pulses (45 MeV) from a linear accelerator (Mitsubishi) installed in Hokkaido University. The half-width of the electron pulse used was 20 ns. The dose per pulse was in a range of 9—12 krad. The design and performance of the optical detection system combined with the LINAC have been described in a previous paper.[14] The output signal from the detection system was displayed on a transient digitizer (IWATSU) with the shortest resolvable time of 10 ns.

Results and Discussion

Transient adsorption after pulse irradiation on micellar solution without substrate shows a broad spectrum around 400—750 nm, which is exclusively assigned to hydrated electron. With increase in detergent concentration, a little change in absorption decay of e_{aq}^- was observed. From the change in the decay rate of e_{aq}^-, rate constant for the reaction of e_{aq}^- with HDTBr micelle is approximately estimated to be less than 3×10^8 M^{-1} s^{-1}. Since the reaction of hydrated electrons with positively charged micelle does not occur,[6] though the attractive force of micelle for e_{aq}^- sometimes catalyzes reactions, the rate constant obtained in our experiment might be related partly to reactions of e_{aq}^- with some impurities contained in the micelle.

Variation in Absorption Decays of e_{aq}^- as a Function of Micelle and Substrate Concentrations at Fixed Mean Occupancy Number. The mean occupancy number of substrate in a micelle $\langle XN\rangle$ is defined as

$$\langle XN\rangle = \frac{[XN]}{[M]} = \frac{n}{[Det]-cmc}[XN], \qquad (3)$$

where [XN], [M], and [Det] are bulk concentrations of XN, micelle, and detergent, respectively, and n is the aggregation number of the detergent. Thus, [XN] may be changed by varying $\langle XN\rangle$, [Det], or n. All experiments were performed in concentration ranges of detergent for which n is not subject to significant variation.

Above the critical micelle concentration (*cmc*), dilution of a micellar solution with water does not significantly alter the value of $\langle XN\rangle$, *i.e.*, since the ratio [XN]/[Det] and n remain constant with aqueous dilution, $\langle XN\rangle$ also remains constant. Figure 1 shows the effect of aqueous dilution on absorption decays of e_{aq}^-, where a stock micellar solution with CN ([CN]$=1.4\times 10^{-4}$ M; [Det]$=$[HDTBr]$=5\times 10^{-2}$ M) was diluted with water by half, one fourth, and so on. From the literature values of $n=72$ and $cmc=8.5\times 10^{-4}$ M,[15] we obtained by calculation that $\langle XN\rangle$ will vary from 0.21 to 0.25 in our experimental conditions. The increase in total decay rate with increasing concentration of micelle-bound substrate implies that the hydrated electron will react effectively with halogenated naphthalenes *via* Reaction 2.

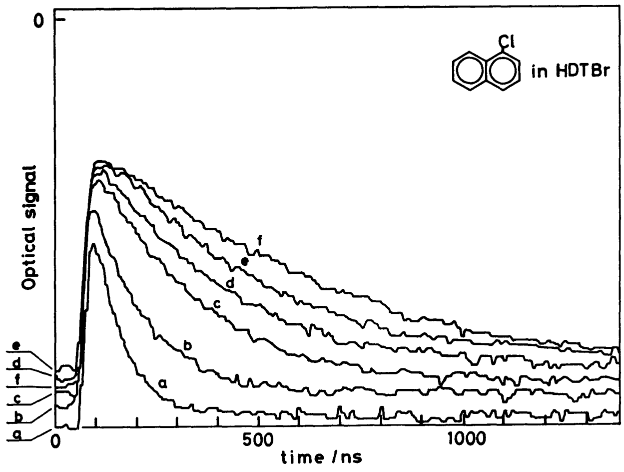

Fig. 1. The decay curves of e_{aq}^- after the pulse irradiation for the aqueous micellar solutions. The concentrations are a) [CN]$=1.4\times 10^{-4}$ M, [HDTBr]$=5\times 10^{-2}$ M, b) [CN]$=7\times 10^{-5}$ M, [HDTBr]$=2.5\times 10^{-2}$ M, c) [CN]$=3.5\times 10^{-5}$ M, [HDTBr]$=1.25\times 10^{-2}$ M, d) [CN]$=1.8\times 10^{-5}$ M, [HDTBr]$=6.3\times 10^{-3}$ M, and e) [CN]$=1.2\times 10^{-5}$ M, [HDTBr]$=4.2\times 10^{-3}$ M, respectively. The decay curve (f) is obtained for triply distilled water. The monitoring wavelength and the dose per pulse are 650 nm and 9 krad, respectively.

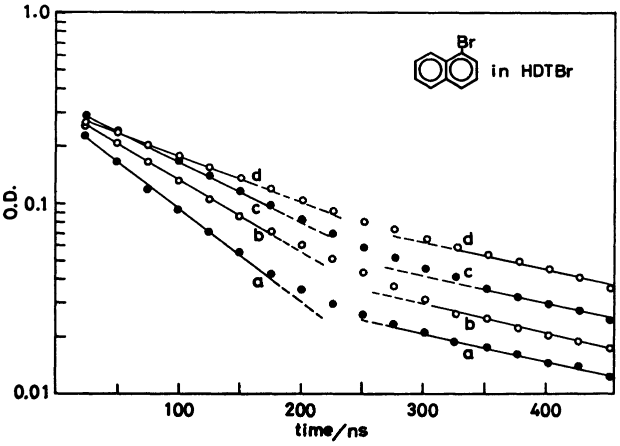

Fig. 2. First-order decay curves of the absorption of e_{aq}^- *vs.* time in aqueous solutions at different [BN] and [HDTBr]. The concentrations are a) [BN]$=2.9\times 10^{-4}$ M, [HDTBr]$=5\times 10^{-2}$ M, b) [BN]$=1.5\times 10^{-4}$ M, [HDTBr]$=2.5\times 10^{-2}$ M, c) [BN]$=7.3\times 10^{-5}$ M, [HDTBr]$=1.3\times 10^{-2}$ M, and d) [BN]$=3.7\times 10^{-5}$ M, [HDTBr]$=6.3\times 10^{-3}$ M, respectively. The monitoring wavelength and the dose per pulse are 650 nm and 9 krad, respectively.

The decay curves for the absorption of e_{aq}^-, however, do not fit a simple first-order decay, but consist of fast- and slow-decaying components. Figure 2 shows plots of log *O.D.* (e_{aq}^-) against time t as a function of [BN] and/or [M]. With increasing concentration of substrate, the fast-decaying component increases in decay rate, whereas the slow-decaying component remains constant, as shown in the figure. The plot of log *O.D.*(e_{aq}^-) *vs.* t for the time range far away from the time of pulse irradiation gives the first-order decay rate τ_s^{-1}, corresponding to the decay rate for the slow-decaying component. The decay rate for the fast-decaying component, τ_f^{-1}, can be obtained from the difference between the total decay curve and the first-order decay curve extrapolated toward shorter times by use of τ_s^{-1}. Apparent rate constants for the reaction of e_{aq}^{-1} with XN in micelles were then obtained from the slope of the linear plots of τ_f^{-1} *vs.* [XN]. Rate constants thus obtained are summarized in Table 1.

The constancy of rate for the slow-decaying component with the change in micelle concentration at constant $\langle XN\rangle$ may arise from a constant ratio in number of the micelles possessing one substrate M_{XN} to those possessing zero substrate M_0. Since multiple occupancy of the substrate per micelle is neglected from

Table 1. Rate constants/$M^{-1}\,s^{-1}$ of reaction of hydrated electron with halogenated naphthalenes

	DBN	BN	CN
Aqueous solution (+1 M EtOH)	3.0×10^{10}	1.8×10^{10}	1.4×10^{10}
HDTBr micellar solution[a]	2.9×10^{10}	2.0×10^{10}	2.2×10^{10}

a) Evaluated from fast-decaying components.

the Poisson statistics, hydrated electrons can encounter only those micelles with one or zero substrate.

It should be noted here that the initial intensity of absorption decay of e^-_{aq} after the pulse does not change with varying [XN] and/or [M], implying that only the reactions after the formation of hydrated electrons with micelles or substrates are observed.

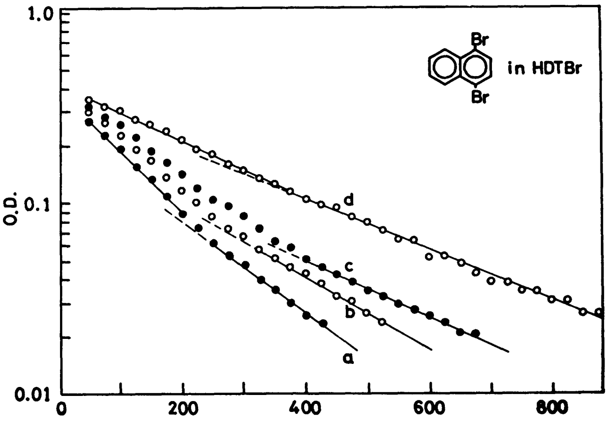

Fig. 3. First-order decay curves of the absorption of e^-_{aq} *vs.* time in 5×10^{-2} M HDTBr solutions at different [DBN]. The concentrations of DBN are a) 3.3×10^{-4} M, b) 9.8×10^{-5} M, c) 6.5×10^{-5} M, and d) 3.3×10^{-5} M, respectively. The monitoring wavelength and the dose per pulse are 650 nm and 9 krad, respectively.

Variation in Absorption Decays of e^-_{aq} as a Function of Substrate Concentration at Fixed Micelle Concentration. In a series of experiments with [HDTBr] fixed at $=5\times10^{-2}$ M, the concentration of [XN] was varied from 3.3×10^{-5} to 3.3×10^{-4} M. Figure 3 shows semilogarithmic plots of e^-_{aq} absorption against time as a function of [DBN] at fixed detergent concentration. The decay curves for the absorption of e^-_{aq} also consist of fast- and slow-decaying components. In this case, however, unlike the case of aqueous dilution experiments, both the fast- and slow-decaying components increase in decay rate with increasing concentration of substrate. Apparent rate constants for the reaction of e^-_{aq} with micelle-bound substrates were obtained from the slope of the plots of τ_f^{-1} *vs.* [XN] as in the case of aqueous dilution experiments. The rate constant values obtained are comparable with that obtained in the aqueous dilution experiment.

The rate of encounter between M_{XN} and M_0 is given by

$$k_e[M_{XN}][M_0] = k_e\cdot P_{XN}\cdot P_0[M]^2, \tag{4}$$

where k_e is the rate constant for encounter between M_{XN} and M_0. P_{XN} and P_0 represent respective probability distributions of M_{XN} and M_0, which are based on the Poisson statistics. With increasing ⟨XN⟩ value from 0.05 to 0.5 at constant [M] (6.8×10^{-4} M), the value for $P_{XN}\times P_0$ increases from 0.048 to 0.23. The increase in the slow reaction rate τ_s^{-1} with increasing rate of encounter between M_{XN} and M_0 (in consequence of increasing ⟨XN⟩) suggests that, in the absence of substrates, micelles play a mechanistic role in electron transport from hydrated electrons to micelle-bound substrates.

Mechanisms for Electron Transport in Micellar Systems. The large positive charge on micelle surface forms a Gouy-Chapman double layer which is spread over several hundred Å from the surface of micelle.[16,17] Along the electrostatic field which is produced by the double layer, hydreted electrons move toward the surface. The electrostatic interaction between hydrated electrons and positive charges on the surface, then may lead to formation of a complex $(M_0\cdots e^-_{aq})$ or $(M_{XN}\cdots e^-_{aq})$. Electron transfer reaction (*viz.*, $(M_{XN}\cdots e^-_{aq})\rightarrow M_{X-N}+H_2O$) will take place quickly for micelles in the presence of substrates. On the other hand, hydrated electrons may survive to form a complex $(M_0\cdots e^-_{aq})$, since the lifetime of hydrated electrons is practically unchanged by the addition of cationic detergent to aqueous solution. The following scheme represents the electron transport reaction relevant to our experimental data:

$$\begin{tikzcd}
{} & & M_{X\text{-}N} \\
(M_0\cdots\cdots e^-_{aq}) + M_{XN} \arrow[u] \arrow[d, shift left] \arrow[r, shift left] & M_0 + (M_{XN}\cdots\cdots e^-_{aq}). \arrow[l, shift left] \arrow[ur] & \\
M_0 + e^-_{aq} \arrow[u, shift left] & M_{XN} + e^-_{aq} \arrow[u] &
\end{tikzcd} \tag{5}$$

If a sizable percent of complex $(M_0\cdots e^-_{aq})$ is formed, migration of hydrated electrons from $(M_0\cdots e^-_{aq})$ to M_{XN} will occur on micelle surface before an electron penetrates the reactive center in micelle M_{XN}. This migration behavior of hydrated electron is similar to that of micelle-bound metal ion which moves through micelle-micelle collision, at which overlap of ionic charge clouds of micelles allows the ion to migrate from one micelle to another.[4,8] The migration of surface-bound hydrated electrons leads eventually to an electron transfer reaction from the surface to reactive halonaphthalenes. Qualitatively, this migration mechanism interprets the "slow" electron transport reaction which controls the slow-decaying component. Direct encounter between M_{XN} and e^-_{aq} leads to the "fast" electron transport reaction which controls the fast-decaying component. Collectively, the experimental results relating to the decay curves for e^-_{aq} absorption consisting of the slow- and fast-decaying components are consistent with Reaction Scheme 5 which would be expected from an electrostatic consideration.

A further kinetic and spectroscopic study was designed to investigate these systems and to evaluate exactly rate constants for the reaction scheme. Details of the kinetic analysis will appear in the successive paper.

Conclusion

This paper has described electron transport reactions between hydrated electrons and micelle-bound electron acceptors. Preliminary kinetic measurements indicate that, together with direct encounter between e_{aq}^- and M_{XN}, micelle plays a significant role in the reaction of electron transport from hydrated electron to micelle-bound substrate.

The authors wish to acknowledge Dr. Takeaki Enoto and Messrs. Hiroaki Tanida and Koichi Sato for their help in stabilizing and operating the LINAC.

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