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Photoinduced Electron and Hydrogen-Transfer Reaction in Micellar-Promoted Reduction of *vic*-Styrene Dibromide with 1-Benzyl-1,4-dihydronicotinamide

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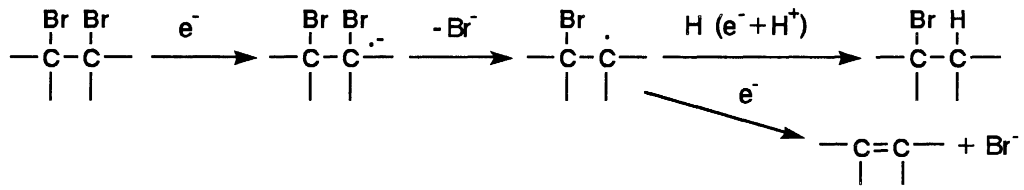
The photoreduction of *vic*-styrene dibromide by 1-benzyl-1,4-dihydronicotinamide (BNAH) gave (1-bromoethyl)benzene (StyHBr) in addition to styrene (Sty); Among the both products, StyHBr formation was found to include a direct hydrogen migration from BNAH by isotopic experiments with [$^2H_2$]BNAH. The remarkable acceleration of such a characteristic photoreaction became possible by the presence of ionic micelles.

Multi-electron-transfer reaction including proton transfer is very important in chemical, photochemical, and biological reaction systems. In this connection, the reduction of *vic*-dibromides is of interest because they are debrominated by two-electron transfer processes.[1,2] Although *vic*-dibromides are reduced to corresponding alkenes by two-electron transfer reaction (Eq. 1b), the monobromide



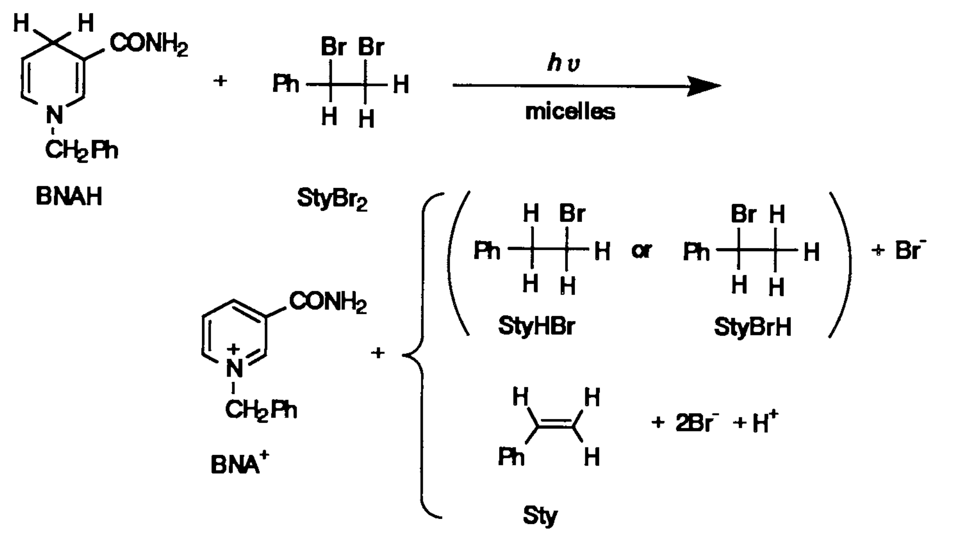
(1a)

(1b)

production by multi-step electron-hydrogen (or electron-proton-electron) transfer reaction (Eq. 1a) have not yet been reported. Since 1,4-dihydropyridine derivatives are characterized by their reducing ability as two-electron and one-proton donors,[3,4] the reduction of *vic*-dibromides by 1,4-dihydropyridines might give monobromides *via* multi-step electron-hydrogen transfer reactions. However, the only one report on the thermal reduction of *vic*-dibromides by 1,4-dihydropyridines did not deal with the production of monobromides.[5]

This letter concerned with the photoinduced multi-step electron-hydrogen transfer reduction of *vic*-dibromides by 1,4-dihydropyridine derivatives in the micellar-promoted reduction of styrene dibromide ((1,2-dibromoethyl)benzene, $StyBr_2$) by 1-benzyl-1,4-dihydronicotinamide (BNAH) with surfactants of sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium chloride (DTAC) (Eq. 2).

The photoirradiation ($340 < \lambda < 410$ nm) of the solution containing BNAH (5.0×10^{-4} M (1M = 1 mol dm^{-3})) and $StyBr_2$ (5.0×10^{-4} M) with or without surfactants ($0\text{-}6.0 \times 10^{-2}$ M) in 4-20%(v/v)CH_3CN-borate buffer (pH 9.0) at 30°C under an aerobic or a nitrogen atmosphere resulted in the appreciable decrease of BNAH. GLC analysis of the reaction mixtures indicated the production of both (2-



(2a)

(2b)

bromoethyl)benzene (StyHBr) and styrene (Sty). The hydrogen transfer to $StyBr_2$ from BNAH can also produce the another product of (1-bromoethyl)benzene (StyBrH). But StyBrH was not obtained for the present reaction probably because the intermediate C_2 radical of the substrate can not be stabilized by the absence of conjugation with a phenyl group. The instability of the radical at C_2 position was supported by the fact that the further reduction of StyHBr to ethylbenzene was not observed even in the presence of large excess of BNAH.

The rate of Sty or StyHBr formation during the photoreaction was remarkably accelerated by micelles. As listed in Table 1, the quantum yields of Sty and StyHBr (Φ_{Sty} and Φ_{StyHBr}, respectively) were enhanced by the presence of the micelles.[6)]

The Φ_{Sty} and Φ_{StyHBr} values increased with increasing the $StyBr_2$ concentration, while the concentration change of BNAH did not affect the quantum yield values under aerobic conditions. Therefore, the present reaction proceeds *via* the photoexcitation of BNAH (Eqs. 3a-c).

Table 1. Quantum Yields of Sty and StyHBr Production for the Photoreduction of $StyBr_2$ by BNAH in 20%(v/v)CH_3CN-Borate Buffer Solution under Air

[BNAH] mM	[$StyBr_2$] mM	Φ_{StyHBr} 10^{-3}	Φ_{Sty} 10^{-3}	Φ_{StyHBr}/Φ_{Sty}
0.5	0.4	0.21	0.38	0.57
0.5	0.5	0.26	0.45	0.59
0.5[a)]	0.5	2.48	8.16	0.30
0.5[b)]	0.5	1.54	8.50	0.18
0.5	0.6	0.31	0.68	0.46
0.5	0.8	0.42	0.80	0.53
0.5	1.0	0.55	0.92	0.59
0.25	0.5	0.25	0.44	0.56
0.75	0.5	0.27	0.54	0.50
1.0	0.5	0.26	0.54	0.49
0.5[c)]	0.5	0.25	1.00	0.25
1.0[c)]	0.5	0.27	3.21	0.08
0.5[d)]	0.5	0.29	0.50	0.59
0.5[c,d)]	0.5	0.29	1.24	0.24

a) In 4%(v/v)CH_3CN-borate buffer with 20 mM SDS. b) In 4%(v/v)CH_3CN-borate buffer with 30 mM DTAC. c) Under N_2 atmosphere. d) [$^2H_2$]BNAH was used.

$$\mathrm{BNAH}^* + \mathrm{StyBr_2} \xrightarrow{k_e} [\mathrm{BNAH}^{\cdot +}\,\mathrm{StyBr_2}^{\cdot -}] \qquad (3a)$$

$$[\mathrm{BNAH}^{\cdot +}\,\mathrm{StyBr_2}^{\cdot -}] \xrightarrow{k_b} \mathrm{BNAH} + \mathrm{StyBr_2} \qquad (3b)$$

$$[\mathrm{BNAH}^{\cdot +}\,\mathrm{StyBr_2}^{\cdot -}] \xrightarrow{k_d} [\mathrm{BNAH}^{\cdot +}\,\mathrm{StyBr}^{\cdot}] + \mathrm{Br}^- \qquad (3c)$$

According to the reaction mechanism indicated by Eqs. 3a-c, the following relationships between the quantum yields and $StyBr_2$ concentration were derived by the stationary-state assumption of the intermediate concentrations:

$$\frac{1}{\Phi_{total}} = \frac{k_b + k_d}{k_d} \left(\frac{1}{k_e \tau} \frac{1}{[StyBr_2]} + 1 \right) \quad (4)$$

where τ = lifetime of BNAH* in the absence of the substrates and $\Phi_{total} = \Phi_{StyHBr} + \Phi_{Sty}$.
Since the observed quantum yields satisfied the linear relationship expressed by Eq. 4, the proposed reaction mechanism seems reliable.[8)]

From the experimental results, it was found that the micelles accelerated the present reaction mainly by promoting the encounter complex formation (Eq. 3a) and partly by suppressing the reverse electron transfer in the encounter complex (Eq. 3b). Namely, the k_e values (2.6×10^{11} and 2.9×10^{11} $M^{-1}\ s^{-1}$ for SDS and DTAC, respectively), τ values (0.62 ns for both SDS and DTAC) and the $k_d/(k_d + k_b)$ values (0.12 for both SDS and DTAC) estimated for the photoreaction between BNAH and $StyBr_2$ with the micelles were larger than those (ca. 4.0×10^{10} $M^{-1}\ s^{-1}$, 0.52 ns, and ca. 0.05, respectively) without the micelles. Such micellar effects on the encounter-complex formation resulted from the concentration of BNAH and $StyBr_2$ through hydrophobic forces and from the lengthened lifetime of BNAH* in the micellar phase.[9)]

The present reaction under N_2 provided the noticeable information about the product formation. The remarkably large Φ_{Sty} values were observed for the reduction of $StyBr_2$ by BNAH under N_2, and the Φ_{Sty} values obtained for the reaction under N_2 were enhanced by increasing BNAH concentration (Table 1). These facts suggest that the process of Sty formation included free radical intermediates which initiate the radical chain reactions through the hydrogen abstraction from BNAH under N_2 (Eq. 5a-f). Under aerobic conditions, such radical chain reactions are suppressed because BNA˙ radicals are easily oxidized

$$[BNAH^{\cdot +}\ StyBr^{\cdot}] \longrightarrow BNAH^{\cdot +} + StyBr^{\cdot} \longrightarrow BNA^{\cdot} + Sty + Br^{\cdot} + H^{+} \quad (5a)$$

$$Br^{\cdot} + BNAH \longrightarrow HBr + BNA^{\cdot} \quad (5b) \qquad BNA^{\cdot} + StyBr_2 \longrightarrow BNA^{+} + StyBr_2^{\cdot -} \quad (5c)$$

$$StyBr_2^{\cdot -} \longrightarrow StyBr^{\cdot} + Br^{-} \quad (5d) \qquad StyBr^{\cdot} \longrightarrow Sty + Br^{\cdot} \quad (5e)$$

$$Br^{\cdot} + BNA^{\cdot} \longrightarrow Br^{-} + BNA^{+} \quad (5f)$$

by O_2. While the Φ_{StyHBr} values obtained under N_2 were essentially the same as those under aerobic conditions. The independence of Φ_{StyHBr} values on the BNAH concentration under both air and N_2 indicates that StyHBr was produced through hydrogen abstraction from $BNAH^{\cdot +}$ without the partition of the radical chain mechanism (Eq.6). The reaction path shown by Eq. 6 was also supported by the

$$[BNAH^{\cdot +}\ StyBr^{\cdot}] \longrightarrow [BNA^{+}\ StyHBr] \longrightarrow BNA^{+} + StyHBr \quad (6)$$

following fact: the NMR spectra of StyHBr produced by the reduction of $StyBr_2$ with deuterated BNAH ($[^2H_2]$BNAH) clearly indicated that the hydrogen (deuterium) of BNAH was directly transferred to the substrate without replacement by a hydrogen from the other hydrogen sources. Since the quantum yields obtained for the reaction with $[^2H_2]$BNAH were essentially the same as those estimated for non-deuterated BNAH (Table 1), a hydrogen transfer step does not participate in the rate-determining step.

In connection with Eqs. 5 and 6, it was noteworthy that the product selectivity (Φ_{StyHBr} / Φ_{Sty}) was affected by the polarity of the solvent (Table 2); the lowering of acetonitrile content resulted in the enhancementof the Φ_{StyHBr} value in addition to the diminution of the Φ_{Sty} value. In the higher polar media (*viz.* low aceto-nitrile content), the suppressed deprotonation process of $BNAH^{\cdot +}$ (and/or the intensified hydrophobic interaction between $BNAH^{\cdot +}$ and $StyBr^{\cdot}$) retards the Sty formation *via* Eq. 5a-f (and/or promotes the StyHBr formation *via* Eq. 6), so as to increase StyHBr selectivity .

Table 2. Φ_{Sty} and Φ_{StyHBr} Values for the Photoreduction of $StyBr_2$ by BNAH in 20%(v/v)CH_3CN-Borate Buffer Solution under Air

	CH_3CN / vol.%			
	20	40	60	80
$\Phi_{Sty} / 10^{-3}$	0.45	0.92	0.91	1.75
$\Phi_{StyHBr} / 10^{-3}$	0.26	0.26	0.16	0.15
$\Phi_{StyHBr} / \Phi_{Sty}$	0.59	0.28	0.17	0.08

Thus, the photoexcited 1,4-dihydronicotinamide in the photoreduction of $StyBr_2$ was found to act as an excellent electron and hydrogen donor *via* two different reaction processes (an electron-hydrogen transfer mechanism and a two electron transfer mechanism). The yields of StyHBr and Sty were enhanced remarkably by the surfactant micelles through the promotion of the encounter-complex formation.

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