Tris(bipyridyl)ruthenium(II)-photosensitized Reaction of 1-Benzyl-1,4-dihydronicotinamide with Benzyl Bromide

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An NADH model compound, 1-benzyl-1,4-dihydronicotinamide (BNAH), reduces benzyl bromide to yield toluene as the main product under irradiation of the absorption band of BNAH in the presence of pyridine in acetonitrile, while the addition of a sensitizer tris(bipyridyl)ruthenium(II) {$[Ru(bpy)_3]^{2+}$} to the BNAH–benzyl bromide system results in a drastic change in the photoreduced products, yielding 1,2-diphenylethane as the main product. Photosensitization by $[Ru(bpy)_3]^{2+}$ has been shown to change the mechanism of the photochemical reaction of BNAH with benzyl bromide; reaction in the absence of $[Ru(bpy)_3]^{2+}$ proceeds by a radical chain mechanism involving benzyl radicals as the chain carrier which is formed by electron transfer from the excited state of BNAH to benzyl bromide. However, the $[Ru(bpy)_3]^{2+}$-mediated photoreduction of benzyl bromide with BNAH occurs in the presence of $[Ru(bpy)_3]^{2+}$, where benzyl bromide is subject to two-electron reduction by $[Ru(bpy)_3]^{+}$ which is formed by an electron transfer from BNAH to the excited state of $[Ru(bpy)_3]^{2+}$.

There have been extensive studies on the mechanisms of thermal redox reactions involving NADH model compounds in relation with biological redox processes.[1] Photoredox reactions of NADH model compounds, in spite of their irrelevance to biological redox processes, have recently received increased attention[2–10] since they offer the possibility of increasing the number of reducible substrates and thereby some mechanistic problems concerning redox reactions of NADH model compounds may be resolved. Indeed, NADH model compounds have been shown to reduce a variety of organic substrates either by direct irradiation of NADH model compound–substrate systems,[2–8] or by photosensitization using tris(bipyridyl)ruthenium(II) {$[Ru(bpy)_3]^{2+}$}.[9,10] It has been accepted that photoredox reactions of NADH model compounds both in the absence and in the presence of a sensitizer involve one-electron-transfer pathways,[2–10] but the exact sequence of steps still remains uncertain. Moreover, no mechanistic comparison between the absence and presence of a sensitizer has so far been reported for photochemical reactions of NADH model compounds with the same substrate.

We have previously reported that an NADH model compound, 1-benzyl-1,4-dihydronicotinamide (BNAH), can reduce benzyl bromide to yield toluene as the main product by electron transfer radical chain reaction under direct irradiation of the absorption band of BNAH in the presence of pyridine in acetonitrile.[11] In this work, we found that the addition of $[Ru(bpy)_3]^{2+}$ to the BNAH–benzyl bromide system causes an alteration of the product distribution with 1,2-diphenylethane as the main product with a negligible amount of toluene. Thus, the photochemical reaction of BNAH with benzyl bromide in the absence and presence of $[Ru(bpy)_3]^{2+}$ provides an opportunity to compare the reaction mechanisms in the absence and presence of a sensitizer. The change of product distribution will be discussed in terms of the effect of $[Ru(bpy)_3]^{2+}$ on the mechanism of the photochemical reactions of BNAH with benzyl bromide, utilizing the effect of a radical scavenger isopentyl nitrite as well as the rate law of the photochemical reaction.

Experimental

Materials.—Tris(2,2′-bipyridyl)ruthenium(II) dichloride hexahydrate {$[Ru(bpy)_3]Cl_2 6H_2O$} was prepared according to the literature,[12] and purified by recrystallization from water. Preparation of 1-benzyl-1,4-dihydronicotinamide (BNAH) and purification of benzyl bromide were described previously.[11] Isopentyl nitrite obtained commercially was purified by the standard method[13] prior to use. Potassium ferrioxalate used as an actinometer was prepared according to the literature,[14] and purified by recrystallization from hot water. Acetonitrile and pyridine were purified and dried with calcium hydride by the standard procedure.[13]

$[Ru(bpy)_3]^{2+}$-*Photosensitized Reaction of BNAH with Benzyl Bromide.*—Typically, a purified sample of benzyl bromide (0.84 mmol) and an MeCN (1 cm^3) solution of $[Ru(bpy)_3]Cl_2 6H_2O$ (2.67×10^{-5} mmol), BNAH (4.67×10^{-3} mmol), and pyridine (0.12 mmol) were separately placed in two side arms of a Schlenk tube fused to a square quartz cuvette (1 mm i.d.). After thorough degassing under vacuum by the successive freeze–pump–thaw cycles, the reactants in the two side arms were mixed and transferred to a quartz cuvette, which was then irradiated for a few hours with the visible light from an Ushio model U1-501 xenon lamp through a Toshiba glass filter Y-43 transmitting light of $\lambda > 400$ nm. The rate of the photochemical reaction was determined from the decay of the absorption band due to BNAH, $\lambda_{max.}$ 350 nm (ε 6.00×10^4 mol^{-1} dm^2)[11] by using a Union SM-401 spectrophotometer. All the resulting products were analysed by g.l.c.

The quantum yield of the $[Ru(bpy)_3]^{2+}$ photosensitized reaction of BNAH with benzyl bromide was determined in the region of visible light through the filter transmitting light of $\lambda > 400$ nm, where only the absorption band due to $[Ru(bpy)_3]^{2+}$ ($\lambda_{max.}$ 452 nm) was irradiated, since the use of monochromatized light was too weak to measure the rate of the photochemical reactions accurately. The procedure for the quantum yield determination was similar to that described previously.[11]

Luminescence Quenching of $[Ru(bpy)_3]^{2+}$.—Quenching experiments of the $[Ru(bpy)_3]^{2+}$ luminescence were carried out by using a Hitachi 650-10S fluorescence spectrophotometer. The excitation wavelength was 450 nm and the relative emission intensities of $[Ru(bpy)_3]^{2+}$ at 600 nm were measured for MeCN solutions of $[Ru(bpy)_3]^{2+}$ (1.34×10^{-5} mol dm^{-3}) containing $Bu^n_4NClO_4$ (0.10 mol dm^{-3}) in the presence of a quencher at various concentrations; the solutions were degassed and replaced with nitrogen prior to the measurements. The Stern–Volmer relationship (1) was obtained between the ratio of the emission intensity in the absence and presence of a

Table 1. Yields of the products in the photoreduction of $PhCH_2Br$ (8.44×10^{-1} mmol) by BNAH (4.76×10^{-3} mmol) in 1 cm^3 MeCN containing pyridine (1.24×10^{-1} mmol) in the absence and presence of $[Ru(bpy)_3]^{2+}$ under irradiation, $\lambda > 360$ and >400 nm, respectively

Amount of $[Ru(bpy)_3]^{2+}$ (mmol)	Time (h)	Conversion of BNAH (%)	Yield of products (mmol)	
			$PhCH_3$	$PhCH_2CH_2Ph$
0[a]	2.6	87	3.8×10^{-3}	9.3×10^{-5}
6.7×10^{-6}	2.5	100	3.4×10^{-3}	1.1×10^{-3}
1.3×10^{-5}	2.0	100	0.5×10^{-3}	1.5×10^{-3}
2.7×10^{-5}	2.0	100	Trace	2.2×10^{-3}
6.7×10^{-5}	0.8	95	Trace	2.4×10^{-3}
2.7×10^{-4}	0.5	98	Trace	2.6×10^{-3}

[a] In the presence of 7.42×10^{-2} mmol pyridine.

Table 2. Quantum yields Φ for the photochemical reaction of BNAH with benzyl bromide (7.60×10^{-1} mol dm^{-3}) in MeCN containing pyridine (1.11×10^{-1} mol dm^{-3}) in the absence and presence of $[Ru(bpy)_3]^{2+}$ under irradiation at $\lambda > 360$ and >400 nm, respectively

Concentration of $[Ru(bpy)_3]^{2+}$ (mol dm^{-3})	[BNAH]/ mol dm^{-3}	In[a]/ einstein dm^{-3} s^{-1}	Φ
0	8.42×10^{-3}	9.7×10^{-7} [b]	1.61
2.67×10^{-5}	8.42×10^{-3}	2.6×10^{-6}	0.65
2.67×10^{-5}	4.21×10^{-3}	2.6×10^{-6}	0.48
2.67×10^{-5}	2.10×10^{-3}	2.6×10^{-6}	0.40
2.67×10^{-5}	1.09×10^{-3}	2.6×10^{-6}	0.26
6.68×10^{-5}	4.21×10^{-3}	6.0×10^{-6}	0.44
1.34×10^{-4}	4.21×10^{-3}	1.1×10^{-5}	0.36
2.67×10^{-4}	4.21×10^{-3}	1.9×10^{-5}	0.37

[a] Light intensity absorbed by $[Ru(bpy)_3]^{2+}$ unless otherwise noted. [b] Light intensity absorbed by BNAH.

quencher I_0/I to the quencher concentration [Q]. The quenching rate constant k_q was obtained from the slope of the Stern–Volmer relationship and the luminescence lifetime τ (850 ns in MeCN).[15]

$$I_0/I = 1 + k_q\tau[Q] \qquad (1)$$

Results and Discussion

Products of Photoreduction.—Irradiation of a degassed MeCN solution containing BNAH (4.76×10^{-3} mmol) and benzyl bromide (8.44×10^{-1} mmol) together with pyridine (1.24×10^{-1} mmol) for 2.6 h with light of $\lambda > 360$ nm consumed 87% of BNAH to yield toluene (80% based on the initial amount of BNAH) as the main product [equation (2)] and a small amount of 1,2-diphenylethane (Table 1). The addition of $[Ru(bpy)_3]^{2+}$ to the BNAH–benzyl bromide system and selective irradiation of the absorption band due to $[Ru(bpy)_3]^{2+}$ ($\lambda_{max.}$452 nm) instead of the BNAH band ($\lambda_{max.}$350 nm) with light of $\lambda > 400$ nm also resulted in the consumption of BNAH. However, the yield of toluene decreased, while that of 1,2-diphenylethane increased with increasing amounts of $[Ru(bpy)_3]^{2+}$; 1,2-diphenylethane became almost the only photoreduced product in the presence of more than 2.7×10^{-5} mmol $[Ru(bpy)_3]^{2+}$ (Table 1). During the photochemical reaction of BNAH with benzyl bromide in the presence of $[Ru(bpy)_3]^{2+}$, the concentration of $[Ru(bpy)_3]^{2+}$ measured from the electronic spectrum remained almost unchanged and no photochemical reaction between $[Ru(bpy)_3]^{2+}$ and benzyl bromide was observed in the absence of BNAH. Thus, $[Ru(bpy)_3]^{2+}$ functions as a sensitizer in the photoreduction of benzyl bromide by BNAH in MeCN containing pyridine to cause the change of the main product from toluene to 1,2-diphenylethane.

$$BNAH + PhCH_2Br \xrightarrow[\text{MeCN-pyridine}]{h\nu(>360\text{ nm})} BNA^+ + Br^- + PhCH_3 \qquad (2)$$

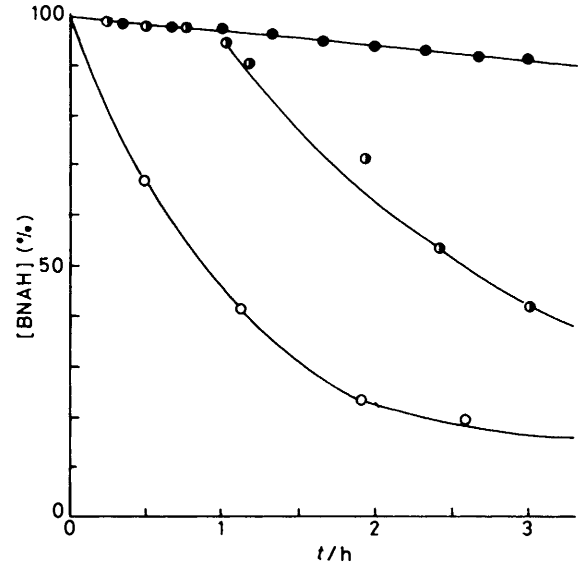


Figure 1. Inhibition effect of a radical scavenger isopentyl nitrite on the photochemical reaction of BNAH (4.21×10^{-2} mol dm^{-3}) with benzyl bromide (7.60×10^{-1} mol dm^{-3}) in MeCN containing pyridine (1.11×10^{-1} mol dm^{-3}); (○) no scavenger, (●) 7.44×10^{-2} mmol isopentyl nitrite, (◑) 1.49×10^{-3} mmol isopentyl nitrite

In the absence of pyridine, yields of the photoreduced products both in the absence and in the presence of $[Ru(bpy)_3]^{2+}$ were significantly lower than those in the presence of pyridine, suggesting that the presence of pyridine is essential for obtaining high yields of photoreduced products.

Quantum Yields.—Quantum yields Φ for the photochemical reaction of BNAH with benzyl bromide in the absence and presence of $[Ru(bpy)_3]^{2+}$ under various conditions are listed in Table 2. In the absence of $[Ru(bpy)_3]^{2+}$, a Φ value higher than unity (Φ 1.6) was obtained for a mixture of 8.42×10^{-3} mol dm^{-3} BNAH and 7.60×10^{-1} mol dm^{-3} benzyl bromide, indicating that a chain process is involved in the photochemical reaction.[11] In the presence of $[Ru(bpy)_3]^{2+}$, however, the quantum yield Φ is less than unity (Φ 0.65) under the same conditions as in the absence of $[Ru(bpy)_3]^{2+}$ and decreases with decreasing concentration of BNAH, but is approximately constant with a change in the concentration of $[Ru(bpy)_3]^{2+}$ (Table 2).

Effect of a Radical Scavenger.—Figures 1 and 2 show the effect of the addition of isopentyl nitrite, a strong radical scavenger,[16] on the rates of the photochemical reaction of BNAH with benzyl bromide in the absence and presence of $[Ru(bpy)_3]^{2+}$. In the absence of $[Ru(bpy)_3]^{2+}$, the addition of 7.44×10^{-2} mmol isopentyl nitrite suppresses the photochemical reaction significantly. The addition of a much smaller amount of isopentyl nitrite (1.49×10^{-3} mol dm^{-3}) similarly suppresses the photochemical reaction for an initial 1 h, which is considered to be an induction period, followed by the rapid consumption of BNAH at approximately the same rate as that in the absence of isopentyl nitrite (Figure 1). In the case of

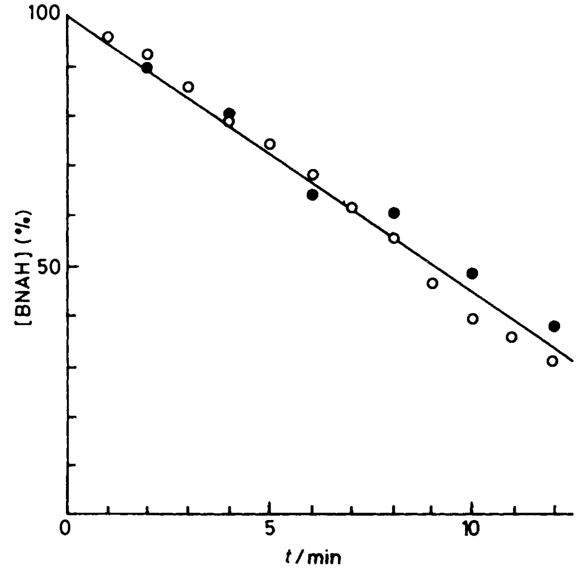


Figure 2. Effect of a radical scavenger isopentyl nitrite on the $[Ru(bpy)_3]^{2+}$-photosensitized reaction of BNAH (4.21×10^{-3} mol dm^{-3}) with benzyl bromide (7.60×10^{-1} mol dm^{-3}) in MeCN containing pyridine (1.11×10^{-1} mol dm^{-3}); (○) no scavenger, (●) 3.72×10^{-2} mmol isopentyl nitrite

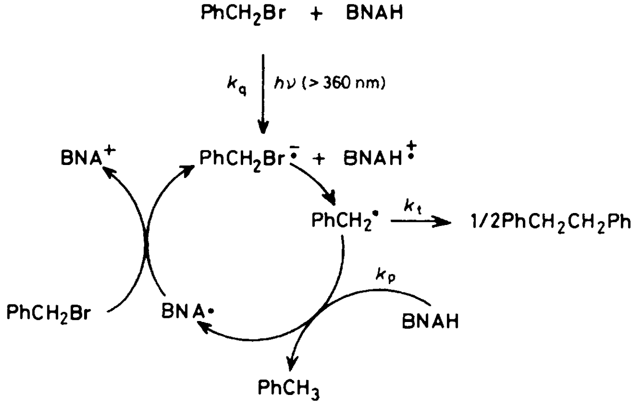
$[Ru(bpy)_3]^{2+}$-photosensitized reaction of BNAH with benzyl bromide, however, the addition of isopentyl nitrite (3.72×10^{-2} mmol) shows essentially no effect on the reaction rate (Figure 2), suggesting that no radical chain reaction is involved in the $[Ru(bpy)_3]^{2+}$-photosensitized reaction of BNAH with benzyl bromide.

Quenching of $[Ru(bpy)_3]^{2+}$ *Luminescence*.—The luminescence of $[Ru(bpy)_3]^{2+*}$ ($\lambda_{max.}$ 608 nm; τ 850 ns)[15] was efficiently quenched by electron transfer from BNAH to $[Ru(bpy)_3]^{2+*}$ [equation (3)]. The quenching rate constant k_q in deoxygenated

$$[Ru(bpy)_3]^{2+*} + BNAH \xrightarrow{k_q} [Ru(bpy)_3]^{+} + BNAH\cdot^{+} \qquad (3)$$

MeCN containing 0.10 mol dm^{-3} $Bu^n{}_4NClO_4$ has been determined as 4.1×10^8 mol^{-1} dm^3 s^{-1} from the Stern–Volmer plot (see Experimental section). Such a large rate constant for electron transfer from BNAH to $[Ru(bpy)_3]^{2+*}$ is consistent with the Gibb's free energy change of electron transfer which is evaluated as −0.17 V from the oxidation potential of BNAH (E_{ox}^0 +0.60 V *versus* s.c.e.)[17] and the reduction potential of $[Ru(bpy)_3]^{2+*}$ (E_{red}^0 +0.77 V *versus* s.c.e).[15] On the other hand, the luminescence of $[Ru(bpy)_3]^{2+*}$ is not quenched by benzyl bromide, suggesting that $[Ru(bpy)_3]^{2+*}$ cannot transfer electrons to benzyl bromide. This is in contrast to the case of the electron transfer from the excited state of BNAH to benzyl bromide in the absence of $[Ru(bpy)_3]^{2+}$.[11] Thus, the irradiation of an MeCN solution of $[Ru(bpy)_3]^{2+}$ containing BNAH and benzyl bromide results in the formation of a strong reductant $[Ru(bpy)_3]^{+}$, the oxidation potential of which is known to be highly negative, *i.e.*, E_{ox}^0 −1.33 V *versus* s.c.e.[15]

Kinetics and Mechanism.—We have recently proposed that the photochemical reaction of BNAH with benzyl bromide in the absence of $[Ru(bpy)_3]^{2+}$ proceeds by a photoinduced electron-transfer radical chain mechanism (Scheme 1).[11] The excited state of BNAH acts as an excellent electron donor that can transfer an electron to benzyl bromide (k_q' 4.9×10^9 mol^{-1} dm^3 s^{-1}), resulting in the formation of benzyl radical. The benzyl radical acting as a chain carrier abstracts hydrogen from BNAH (k_p 1.6×10^4 mol^{-1} dm^3 s^{-1}) to yield a product $PhCH_3$ and a radical intermediate BNA·, the latter of which can transfer an electron to regenerate benzyl radical. According to Scheme 1, the kinetic form of the photochemical reaction in the absence of $[Ru(bpy)_3]^{2+}$ is given by equations (4) and (5),[11]



Scheme 1.

$$r = k_p(R_i/2k_t)^{\frac{1}{2}}[BNAH] \qquad (4)$$

$$R_i = In\Phi_f^0\, k_q'\tau'[PhCH_2Br]/(1 + k_q'\tau'[PhCH_2Br]) \qquad (5)$$

where r is the rate of the disappearance of BNAH, R_i is the initiation rate, Φ_f^0 is the fluorescence quantum yield (Φ_f^0 0.11), and τ' is the lifetime of the excited state of BNAH (τ' 0.76 ns).[11] Based on the inhibitory effect of isopentyl nitrite in the absence of $[Ru(bpy)_3]^{2+}$ in Figure 1, the chain length of the radical chain reaction (r/R_i) has been evaluated as *ca.* 20.[11]

In the presence of $[Ru(bpy)_3]^{2+}$, the irradiation of an MeCN solution of BNAH and benzyl bromide produces a strong reductant $[Ru(bpy)_3]^{+}$ (E_{ox}^0 −1.33V *versus* s.c.e.) as described above. It is known that a strong reductant (RED) such as sodium naphthalenide can reduce benzyl halide by succesive two-electron transfer from RED to benzyl halide, resulting in the formation of the carbanion $PhCH_2^-$ [equations (6) and (7)].[18] The electrochemical reduction of benzyl bromide at

$$PhCH_2X + RED \longrightarrow PhCH_2\cdot + X^- + RED^+ \qquad (6)$$

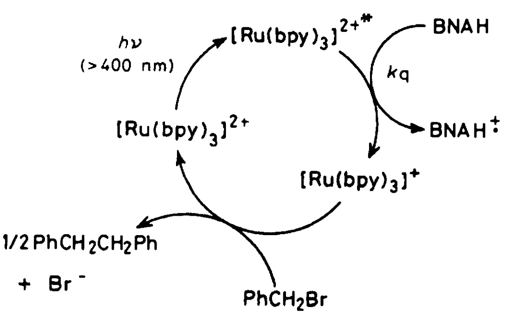
$$PhCH_2\cdot + RED \longrightarrow PhCH_2^- + RED^+ \qquad (7)$$

−1.2 V *versus* s.c.e. is also known to produce the carbanion.[19–21] Thus, in the presence of a strong reductant $[Ru(bpy)_3]^{+}$ (E_{ox}^0 −1.33 V *versus* s.c.e.) produced by electron transfer from BNAH to $[Ru(bpy)_3]^{2+*}$ [equation (3)], the reduction of benzyl bromide may proceed *via* two-electron reduction of benzyl bromide by $[Ru(bpy)_3]^{+}$ as in equations (8) and (9) where the benzyl radical formed by the electron transfer

$$[Ru(bpy)_3]^{+} + PhCH_2Br \longrightarrow PhCH_2\cdot + Br^- + [Ru(bpy)_3]^{2+} \qquad (8)$$

$$[Ru(bpy)_3]^{+} + PhCH_2\cdot \longrightarrow PhCH_2^- + [Ru(bpy)_3]^{2+} \qquad (9)$$

from $[Ru(bpy)_3]^{+}$ to benzyl bromide [equation (8)] is further reduced by $[Ru(bpy)^3]^{+}$ [equation (9)] before abstracting hydrogen from BNAH (Scheme 1). Thus, no radical chain reaction is involved as demonstrated by no inhibitory effect of a



Scheme 2.

radical scavenger, isopentyl nitrite, on the photochemical reaction of BNAH with benzyl bromide in the presence of $[Ru(bpy)_3]^{2+}$ (Figure 2). In an aprotic solvent such as MeCN employed in this study, the $PhCH_2^-$ carbanion may react with benzyl bromide in a nucleophilic fashion to yield 1,2-diphenylethane [equation (10)] without abstracting a proton

$$PhCH_2^- + PhCH_2Br \longrightarrow PhCH_2CH_2Ph + Br^- \quad (10)$$

from the solvent to yield toluene, in agreement with the product of the $[Ru(bpy)_3]^{2+}$-photosensitized reduction of benzyl bromide (Table 1). Thus, the mechanism of the $[Ru(bpy)_3]^{2+}$-photosensitized reaction of BNAH with benzyl bromide may be summarized as shown in Scheme 2. The radical cation $BNAH^{+\bullet}$ formed by electron transfer from BNAH to $[Ru(bpy)_3]^{2+*}$ in Scheme 2 is known to disproportionate [equation (11)].[22] In the absence of pyridine, the $(BNAH)H^+$

$$2BNAH^{+\bullet} \longrightarrow BNA^+ + (BNAH)H^+ \quad (11)$$

species may cause acid-catalysed decomposition of BNAH,[23] resulting in a decrease in the yield of photoreduced products of benzyl bromide.

The dependence of the quantum yield Φ on the concentration of benzyl bromide at fixed concentrations of BNAH and $[Ru(bpy)_3]^{2+}$ is shown in Figure 3. The quantum yield Φ is approximately constant when the concentration of benzyl bromide is larger than 0.40 mol dm^{-3}, suggesting that electron transfer from $[Ru(bpy)_3]^+$ to benzyl bromide in Scheme 2 is not rate determining under such conditions. Thus, on the basis of Scheme 2, the quantum yield Φ at 0.76 mol dm^{-3} benzyl bromide may depend only on the efficacy of the electron-transfer quenching of $[Ru(bpy)_3]^{2+*}$ by BNAH [equation (3)] and thereby may be expressed by equation (12), where Φ_0 is the

$$\Phi = \Phi_0 \frac{k_q\tau[BNAH]}{1 + k_q\tau[BNAH]} \quad (12)$$

quantum yield for the formation of $[Ru(bpy)_3]^{2+*}$. Equation (12) is rewritten as (13), which is obeyed as shown by the linear

$$\frac{1}{\Phi} = \frac{1}{\Phi_0}\left(1 + \frac{1}{k_q\tau[BNAH]}\right) \quad (13)$$

plot of $1/\Phi$ *versus* $1/[BNAH]$ in Figure 4. From the intercept of the plot, the Φ_0 value is obtained as 0.83, which agrees well with the quantum yield of the formation of $[Ru(bpy)_3]^{2+*}$ reported in the literature (Φ_0 0.8—1.0).[24-26] Moreover, the $k_q\tau$ value obtained from the ratio of the intercept to the slope of the plot in Figure 4 ($k_q\tau$ 4.2×10^2 mol^{-1} dm^3), is in reasonable agreement with that determined from the quenching of $[Ru(bpy)_3]^{2+*}$ emission by BNAH ($k_q\tau$ 3.5×10^2 mol^{-1} dm^3).

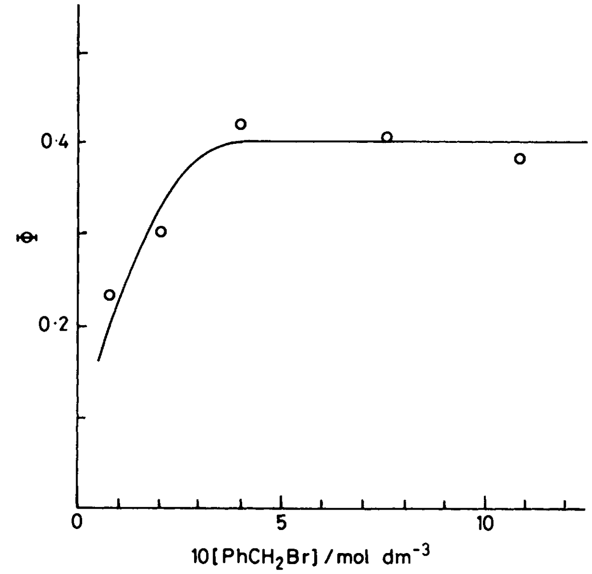


Figure 3. Dependence of the quantum yield Φ on the concentration of benzyl bromide for the photosensitized reaction of BNAH (4.21×10^{-3} mol dm^{-3}) with benzyl bromide in the presence of $[Ru(bpy)_3]^{2+}$ (6.68×10^{-5} mol dm^{-3}) in MeCN containing pyridine (1.11×10^{-1} mol dm^{-3})

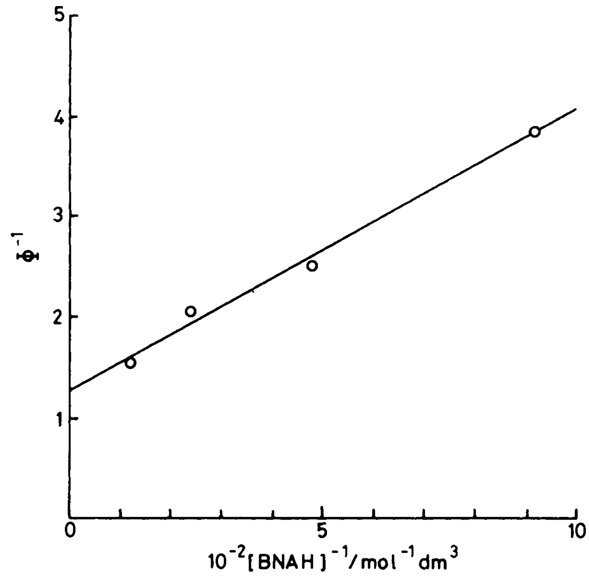


Figure 4. Plot of Φ^{-1} *versus* $[BNAH]^{-1}$ for the photosensitized reaction of BNAH with benzyl bromide (7.60×10^{-1} mol dm^{-3}) in the presence of $[Ru(bpy)_3]^{2+}$ (2.67×10^{-5} mol dm^{-3}) in MeCN containing pyridine (1.11×10^{-1} mol dm^{-3})

In conclusion, a drastic change in the product distribution in the photochemical reaction of BNAH with benzyl bromide in the presence of $[Ru(bpy)_3]^{2+}$ from that in its absence (Table 1) is caused by the presence of a strong reductant $[Ru(bpy)_3]^+$ which reduces benzyl radical to the carbanion [equation (9)], yielding 1,2-diphenylethane [equation (10)]. Thus, the occurrence of a radical chain process which yields toluene is suppressed.

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