CHEMISTRY LETTERS, pp. 1583-1586, 1982.

PHOTOREDUCTION OF ALKYL HALIDES BY AN NADH MODEL. EVIDENCE FOR ONE-ELECTRON TRANSFER MECHANISM

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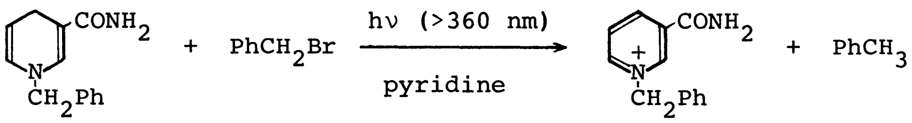
A model of NADH, 1-benzyl-1,4-dihydronicotinamide (BzlNH), reduces benzyl bromide and methyl iodide in the presence of pyridine in MeCN under irradiation of the visible light (λ > 360 nm), yielding toluene and methane as main products, respectively. Evidence is presented for occurrence of one-electron transfer from the excited state of BzlNH to benzyl bromide or methyl iodide in the primary process of the photoreduction.

There have been extensive studies on nonenzymatic reductions of various substrates with 1,4-dihydronicotinamides as models for dihydronicotinamide coenzymes.[1,2] It still, however, remains uncertain whether the reduction proceeds by a one-step hydride transfer (two-electron equivalent) from 1,4-dihydronicotinamides or by multistep mechanisms involving the initial one-electron transfer or the formation of the charge-transfer complexes.[2] The same mechanistic dichotomy remains unresolved in the photochemical reductions of substrates by 1,4-dihydronicotinamides. Photochemical activation of 1,4-dihydronicotinamides makes it possible to increase the number of substrates which is quite limited in the thermal reactions. Only a few works have, however, been reported on photochemical reactions of NADH models.[3,4] We report here the photoreduction of alkyl halides by 1-benzyl-1,4-dihydronicotinamide (BzlNH) in the presence of pyridine in MeCN to give an evidence for initial one-electron transfer from the excited state of BzlNH to alkyl halides in the primary process of the photoreduction.

The electronic absorption spectrum of BzlNH in MeCN shows the lowest energy band at 349 nm ($\varepsilon = 6.00 \times 10^4$ $mol^{-1}dm^2$).[5] Only this band was excited by the use of a Ushio Model Ul-501C Xenon lamp with a filter transmitting the light λ > 360 nm (a Toshiba glass filter L-39). Irradiation of a degassed MeCN solution (1 cm^3) containing BzlNH (4.67×10^{-2} mmol) and benzyl bromide (8.41×10^{-1} mmol) together with pyridine (1.24×10^{-1} mmol) for 2.6 h resulted in the consumption of 79 % BzlNH to give toluene (73 % based on the initial amount of BzlNH) as a main product

(Eq. 1) and a small amount of 1,2-diphenylethane (2.7 %) as determined by GLC.



(1)

Methyl iodide also was reduced by BzlNH to yield methane as a main product under irradiation of the light λ > 360 nm. Yields of the products under various experimental conditions are listed in Table 1.

Two opposing mechanisms (Schemes 1 and 2) are considered for the photoreduction of alkyl halides by BzlNH; one is the photoreduction initiated by one-electron

Scheme 1.

$$\mathrm{BzlNH^{*}} + \mathrm{RX} \xrightarrow{\text{electron transfer}} \mathrm{BzlNH^{+\cdot}} + \mathrm{RX^{-\cdot}} \quad (2)$$

$$\mathrm{RX^{-\cdot}} \xrightarrow{\text{fast}} \mathrm{R\cdot} + \mathrm{X^{-}} \quad (3) \qquad \mathrm{R\cdot} \longrightarrow \text{Products} \quad (4)$$

transfer from BzlNH* (the excited state of BzlNH) to alkyl halides (RX).[6] One-electron transfer to RX (Eq. 2) is known to result in the fission of the R-X bond, yielding alkyl radical (Eq. 3).[7] Abstraction of a hydrogen from BzlNH (or a solvent) by benzyl radical or methyl radical then yields toluene or methane as the final product. Diametrically opposed to Scheme 1 is the suggestion that the photoreduction proceeds *via* a direct hydride transfer (a transfer of two-electron

Table 1. Yields of the products in the photoreduction of benzyl bromide and methyl iodide by BzlNH under irradiation of the light λ > 360 nm.

BzlNH mmol	Reactant	Pyridine	Condition	Time h	Conv. of BzlNH/%	Yields of products/%	
						$PhCH_3$	PhC_2H_4Ph
4.67×10^{-2}	BzBr[a]	1.24×10^{-1}	degassed	2.6	79	73	2.7
1.64×10^{-2}	BzBr[a]	7.42×10^{-2}	degassed	2.6	87	80	3.9
4.67×10^{-2}	BzBr[a]	4.70×10^{-2}	degassed	2.5	80	52	3.4
5.60×10^{-1}	BzBr[b]	0	degassed	6.0	91	1.7	2.1
						CH_4	C_2H_6
4.67×10^{-3}	MeI[c]	2.47×10^{-2}	N_2[d]	5.0	51	51	trace
4.67×10^{-3}	MeI[c]	1.24×10^{-2}	N_2[d]	2.8	57	43	trace

[a] 0.841 mmol Benzyl bromide in 1 cm^3 MeCN. [b] 5.04 mmol Benzyl bromide in 6 cm^3 MeCN. [c] 0.805 mmol Methyl iodide in 1 cm^3 MeCN. [d] Under a nitrogen atmospheric pressure.

equivalent) from $BzlNH^*$ to RX as shown in Scheme 2. In this case, expulsion of

Scheme 2.

$$BzlNH^* + RX \xrightarrow{\text{hydride transfer}} BzlN^+ + RXH^- \quad (4)$$

$$RXH^- \xrightarrow{\text{fast}} RH + X^- \quad (5)$$

the halide ion from RXH^- gives the product RH only (Eq. 5). The formation of the coupling product of benzyl radicals (1,2-diphenylethane in Table 1) thus favors Scheme 1.

In the absence of pyridine, the yield of toluene in the photoreduction of benzyl bromide by BzlNH is significantly lower than that in the presence of pyridine with approximately the same conversion of BzlNH (Table 1). Such a decrease of the yield of toluene in the absence of pyridine is consistent with the formation of $BzlNH^{+\cdot}$ (Eq. 2 in Scheme 1) since $BzlNH^{+\cdot}$ is known to undergo disproportionation (Eq. 6), which is a common reaction of free radical species, and the resulting

$$2BzlNH^{+\cdot} \longrightarrow BzlN^+ + H(BzlNH)^+ \quad (6)$$

protonated species $H(BzlNH)^+$ causes the catalytic decomposition of BzlNH.[8] A similar decrease of yields of the product in the absence of pyridine has been reported for the photoreduction of diethylfumarate by BzlNH, where the role of pyridine is suggested to increase the reaction rate by solvation to $BzlNH^*$.[3] However, the rate constants of electron transfer reactions between $BzlNH^*$ and electron acceptors, determined from the quenching of the $BzlNH^*$ fluorescence (λ_{max} = 443 nm), are approximately the same irrespective of the presence of pyridine, as shown in Table 2. Thus, the role of pyridine in the photoreduction of benzyl bromide by BzlNH is suggested to prevent the acid catalyzed decomposition of BzlNH, resulting in the increase of the selectivity to the formation of toluene (Table 1).

Table 2. Quenching rate constants (k_q) of the $BzlNH^*$ fluorescence with electron acceptors in the absence and the presence of pyridine

Electron acceptor	Solvent	k_q/mol^{-1}dm^{3}s^{-1}	Solvent	k_q/mol^{-1}dm^{3}s^{-1}
Diethylfumarate	MeCN	1.6×10^9 [a]	C_5H_5N	1.3×10^9
Dimethylterephthalate	MeCN	1.7×10^9 [a]	C_5H_5N	1.6×10^9
Methyl iodide	MeCN	1.4×10^9	MeCN + C_5H_5N [b]	1.3×10^9
Ethyl iodide	MeCN	1.5×10^9	MeCN + C_5H_5N [b]	1.5×10^9

[a] Taken from ref. 5). [b] Containing 1.23×10^{-2} mol dm^{-3} pyridine.

Unambiguous evidence for the formation of benzyl radicals (Eq. 3 in Scheme 1) has been obtained by the analysis of products in the photochemical reaction under oxygen atmosphere. The GLC analysis of products after the photochemical reaction of benzyl bromide (8.41×10^{-1} mmol) with BzlNH (4.67×10^{-2} mmol) in 1 cm^3 MeCN containing pyridine (1.24×10^{-1} mmol) under irradiation (λ > 360 nm) for 3.6 h showed the formation of equimolar amounts of benzyl alcohol and benzaldehyde (22 % based on the initial amount of BzlNH). This result confirms the formation of benzyl radicals which are trapped with oxygen to form benzylperoxyl radicals (Eq. 7), followed by the known termination reaction of the peroxyl radicals to yield equimolar amounts of benzyl alcohol and benzaldehyde (Eq. 8).[9] Irradiation

$$PhCH_2\cdot + O_2 \longrightarrow PhCH_2O_2\cdot \quad (7) \qquad 2PhCH_2O_2\cdot \longrightarrow PhCH_2OH + PhCHO + O_2 \quad (8)$$

of an oxygen saturated MeCN solution (1 cm^3) of BzlNH (4.67×10^{-3} mmol) and methyl iodide (8.05×10^{-1} mmol) containing pyridine (2.47×10^{-2} mmol) by the light λ > 360 nm for 6.5 h gave methanol in a 58 % yield, which also suggests the formation of methyl radicals in the one-electron process (Scheme 1).

In conclusion, firm evidence for one-electron primary process (Scheme 1) has been obtained for the photoreduction of alkyl halides by an NADH model. A further detailed study on the mechanisms of photochemical reactions of NADH models is now under progress.

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(Received August 2, 1982)