A Novel Type of Hydride-transfer Photocatalysis by Ru^{II}–Pyridine Complexes: Regiocontrolled Reduction of an NAD(P) Model Compound by Triethylamine

Osamu Ishitani,* Nobuyo Inoue, Kazuhide Koike and Takashi Ibusuki

Photoenergy Application Laboratory, National Institute for Resources and Environment, 16-3 Onogawa, Tsukuba Science City 305, Japan

$[Ru(trpy)(bpy)(py)]^{2+}$ (trpy = 2,2′ : 6′,2″-terpyridine, bpy = 2,2′-bipyridine, py = pyridine) and $[Ru(LL)_2(py)_2]^{2+}$ (LL = a bidentate ligand) photocatalysed the regiocontrolled reduction of 1-benzyl-4-carbamoyle-pyridinium cation to the dihydro form with no formation of the half-reduced dimers, the photocatalysis proceeds through the photosubstitution of a py ligand of the Ru complexes and the subsequent photoformation of $[Ru(trpy)(bpy)H]^+$ or $[Ru(LL)_2(py)H]^+$

Photocatalytic reduction of the pyridine nucleotide coenzyme NAD(P) and related models to dihydronicotinamides is of significance to artificial photosynthesis.[1] However, the usual electron-transfer photocatalysis affords undesired half-reduced dimers, unless the conditions are specifically designed to avoid one-electron transfer processes. Although several attempts have been made on the non-enzymatic photoreduction of NAD(P) and models,[2–7] the following problems remain unsolved: (1) Uncontrolled hydride-transfer reduction gives mixtures of 1,4- and 1,6-dihydronicotinamides in unpredictable ratios. How can the regioselectivity of the reduction be controlled? (2) In the usual homogeneous photocatalytic systems, accumulation of the photoformed dihydronicotinamides is very frequently inhibited by reoxidation of the products, since they are good electron donors. How can the dihydronicotinamides be blocked against this photochemical reoxidation? Herein we report that some Ru^{II}–pyridine complexes do photocatalyse the regiocontrolled reduction of the 1-benzyl-3-carbamoyl-pyridinium cation (BNA^+), a typical NAD(P) model, to the dihydro form (BNAH) with no formation of the half-reduced dimers (BNA_2s).

In a typical run, irradiation (>500 nm) of a 5 cm^3 DMF solution of $[Ru(trpy)(bpy)(py)](PF_6)_2$ **1** (2 μmol), $BNA^+PF_6^-$ (10 μmol) and triethylamine (Et_3N) (0.5 mol dm^{-3}) under Ar for 50 h gave regioselectively 1,4-BNAH in a 59% yield along with an equimolecular amount of diethylamine [eqn (1)].† On the other hand, with $[Ru(LL)_2(py)_2]^{2+}$ as the photocatalyst **2a–d**, mixtures of 1,4- and 1,6-BNAH were formed in ratios dependent on LL, as shown in Table 1. It appears that increasing the electron-accepting power of LL favours a higher selectivity of 1,4-BNAH formation. In all cases, no half-reduced dimers were detected by HPLC. Moreover, it should be noted that BNAH accumulates without parallel photoconsumption during the photoreaction, even after prolonged irradiation.

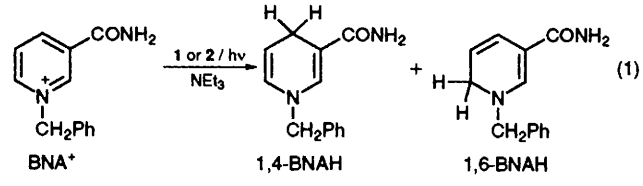


Table 1 Photocatalysed reduction of BNA^+ with triethylamine

Photocatalyst	Selectivity[a] (%)	Yield[b]/μmol 1,4-BNAH	1,6-BNAH	TN
1	100	5.86	*ca.* 0	2.9
5	100	8.85	*ca.* 0	4.4
$[Ru(LL)_2(py)_2]^{2+}$				
2a LL = phen[c]	97	3.94	0.04	2.0
2b LL = bpy	93	5.84	0.16	3.0
2c LL = Me_2bpy[c]	79	4.54	0.68	2.6
2d LL = $(MeO)_2$bpy[c]	38	2.12	2.18	2.2

[a] 100 × [1,4-BNAH]/([1,4-BNAH] + [1,6-BNAH]), after 2 h irradiation. [b] Irradiation for 50 h. [c] phen = 1,10-phenanthroline; Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine; $(MeO)_2$bpy = 4,4′-dimethoxy-2-2′-bipyridine.

By contrast, photocatalysis using $[Ru(bpy)_3]^{2+}$ gave neither 1,4-BNAH nor 1,6-BNAH, but BNA_2s in 34% yield, after 2 h irradiation, as the consequence of single-electron-transfer photocatalysis. It is, therefore, very unlikely that the photocatalytic hydride-transfer reaction is initiated by simple intermolecular electron transfer of the excited-state ruthenium complexes with either Et_3N or BNA^+. A photobleaching of **1** and **2** occurrs early in the reaction, with or without BNA^+, being attributable to the substitution of a py ligand with Et_3N and/or DMF to give **3** or **4** [eqn. (2)].[9] Since the photocatalytic reduction of BNA^+ did not occur in the absence of Et_3N even though **1** and **2** were invariably photobleached, the photocatalysis clearly requires formation of **3**. Accordingly, **1** did not photocatalyse the reduction of BNA^+ using tri(iso-butyl)amine in place of Et_3N, probably owing to the steric bulkiness of the iso-butyl groups which will hinder the coordination of the amine of the Ru^{II} centre.

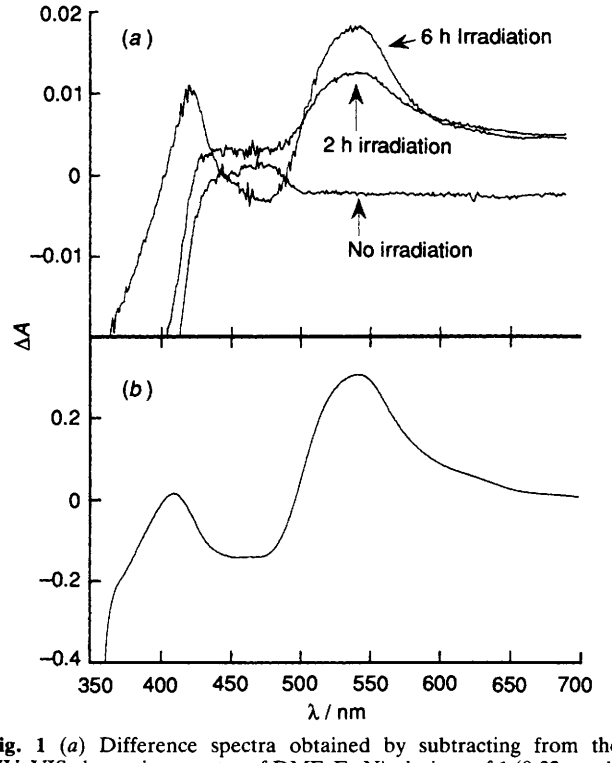
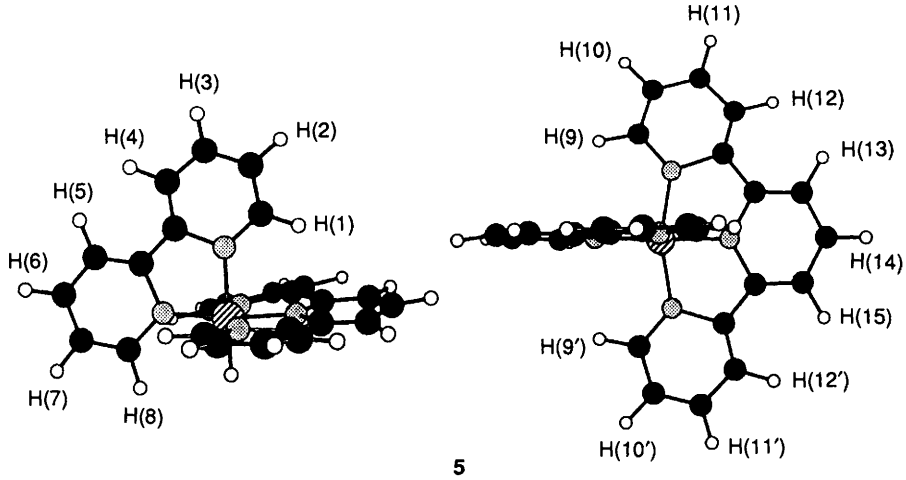


Fig. 1 (*a*) Difference spectra obtained by subtracting from the UV–VIS absorption spectra of DMF–Et_3N solutions of **1** (0.32 μmol) that had been irradiated for 0, 2 and 6 h, the absorption spectra after BNA^+ (0.8 μmol) had been added to the same preirradiated solutions then allowed to stir in the dark for 1 min. (*b*) A difference spectrum obtained by subtracting from the absorption spectrum of a DMF–Et_3N solution of **5** (0.24 μmol), the absorbance of the same solution after BNA^+ (0.8 μmol) had been added then allowed to stir in the dark for 1 min.



5

Moreover, it is of mechanistic significance that the reduction of BNA^+ occurred rapidly in the dark upon addition of BNA^+ to a preirradiated DMF solution of **1** and Et_3N; yields of 1,4-BNAH after 2 h and 6 h preirradiation were 1.9 and 3.5% based on the amount of **1** used respectively.

$$[Ru(trpy)_n(LL)_{2-n}(py)_{2-n}]^{2+} + L' \xrightarrow{h\nu}$$
1 ($n = 1$); **2a–d** ($n = 0$)
$$[Ru(trpy)_n(L\text{-}L)_{2-n}(py)_{1-n}(L')]^{2+} + py \quad (2)$$
3 ($L' = Et_3N$); **4** ($L' = DMF$)

It is highly probable that the hydride-transfer photocatalysis proceeds through the photoformation of a reductant from **3**. It was confirmed that $[Ru(trpy)(bpy)(H)](PF_6)\cdot 1/2H_2O$ **5** can selectively reduce BNA^+ to 1,4-BNAH in the dark in a quantitative yield based on **5** and can also photocatalyse the selective hydride transfer (Table 1). The changes in the UV–VIS absorption spectra, after addition of BNA^+ to a preirradiated DMF solution of **1** and Et_3N, are very similar to those after the addition of BNA^+ to a DMF solution of **5** (Fig. 1). In the absence of Et_3N, the addition of BNA^+ did not cause such changes in the spectrum of a 6 h preirradiated solution of **1**. These data clearly show that **5** is produced by the photoreaction of **3**. The yields of **5** can be calculated from the ΔA of the difference spectra. They were 1.9 and 3.4% based on **1** used after two and six h of preirradiation, respectively; they are very similar to those of BNAH formed in the dark after preirradiation, described above.

These observations suggest that the photocatalysis proceeds through the prior photosubstitution of a py ligand of **1** and **2** with Et_3N, the subsequent photoformation of a hydride complex **5**‡ or $[Ru(LL)_2(py)(H)]^+$ accompanied by elimination of $Et_2N^+ = CHMe$[10] and regeneration of **3** (and **4**) coupled with hydride transfer from the hydride complexes to BNA^+. BNAH is not consumed even after prolonged irradiation, perhaps owing to the inability of BNAH to coordinate to reactive species. The formation ratio of 1,4- and 1,6-BNAH would be kinetically controlled by the hydride-transfer capabilities of the photoformed reductants.

The authors thank Dr Chyongjin Pac (Kawamura Institute of Chemical Research), and Dr Frank P. A. Johnson (University of Nottingham) for helpful discussions. This work was partially supported by the Accelerated Basic Research fund from the Science and Technology Agency.

Received, 6th July 1993; Com. 3/03927G

Footnotes

† Although BNA^+ reacted with triethylamine in the dark, the yield of BNAH was less than 2% after 50 h.[8]

‡ Analytical and spectral data for $[Ru(trpy)(bpy)(py)](PF_6)_2\cdot 1/2H_2O$ **5**. UV–VIS Absorption (DMF) λ_{max} (ε/dm^3 mol^{-1} cm^{-1}): 535 nm (12200), 385 nm (10100) ^{1}H NMR (DMF-d_7) δ 9.75 [d, 1H, J 5.2 Hz, H (1)], 8.56 [d, 1H, J 8.1 Hz, H (4)], 8.36 [d, 2H, J 8.3 Hz, H (13), (14)], 8.35 [d, 2H, J 8.0 Hz, H (5)], 8.30 [d, 2H, J 8.0 Hz, H(12), (12′)], 8.09 [d, 1H, J 8.1 Hz, H(3)], 7.87 [d, 1H, J 8.3 Hz, H (14)], 7.84 [d, 2H, J 5.5 Hz, H (9,9′)], 7.79 (t, 2H, J 8.0 Hz, H(11), (11′)], 7.73 (t, 1H, J 8.0, 4.7 Hz, H(7)], 2.19 (brs, 1H, 1/2H_2O), −14.70 [(s, 1H, Ru(H)].

References

1 U. Eisner and J. Kuthan, *Chem. Rev.*, 1972, 72, 1; S. Fukuzumi and T. Tanaka, in *Photoinduced Electron Transfer*, ed. M. A. Fox and M. Chanon, Elsevier, NY, 1988, vol. C, p. 578; C. Pac and O. Ishitani, *Photochem. Photobiol.*, 1988, **48**, 767.
2 Y. Ogata, K. Takagi and Y. Tanabe, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1069.
3 R. Wienkamp and E. Steckhan, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 497; M. Franke and E. Steckhan, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 265.
4 I. Tabushi, S. Kugimiya and T. Mizutani, *J. Am. Chem. Soc.*, 1983, **105**, 1658.
5 Y. Aoyama, K. Midorikawa, H. Toi and H. Ogoshi, *Chem. Lett.*, 1987, 1651.
6 K. Kalyanasundaram, T. Colassis, R. Humphry-Backer, P. Savarino, E. Barni, E. Pelizzetti and M. Grätzel, *J. Am. Chem. Soc.*, 1989, **111**, 3300.
7 I. Willner, R. Maidan and M. Shapira, *J. Chem. Soc., Perkin Trans. 2*, 1990, 559.
8 Y. Ohnishi, *Tetrahedron Lett.*, 1977, 2109.
9 B. Durham, J. L. Walsh, C. L. Carter and T. J. Meyer, *Inorg. Chem.*, 1980, **19**, 860; D. V. Pinnick and B. Durham, *Inorg. Chem.*, 1984, **23**, 1440; S. J. Valenty and P. E. Behnken, *Anal. Chem.*, 1987, **50**, 834.
10 P. J. DeLaive, T. K. Foreman, C. Giannotti and D. G. Whitten, *J. Am. Chem. Soc.*, 1980, **102**, 5627.