# A Novel Photocatalysis of Phosphorous Porphyrins for Hydration of Benzonitrile

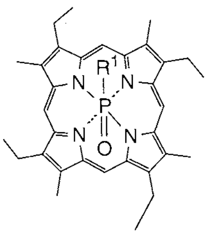
Takeshi Igarashi, Katsuaki Konishi, and Takuzo Aida*
*Department of Chemistry and Biotechnology, Graduate School of Engineering,*
*The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656*

(Received July 6, 1998; CL-980509)

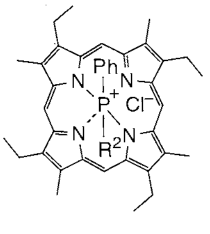
Under irradiation with visible light, oxophosphorous porphyrins [(EtioP)PR(=O), **1** (R = Ph) and **2** (R = Et); EtioP = etioporphyrinato I] and phenyl(methoxy)phosphorous porphyrin chloride [[(EtioP)PPh(OMe)]Cl, **3**] catalyzed hydration of benzonitrile to benzamide in alkaline methanol.

Phosphorous porphyrins have recently attracted attention from their unique photochemical properties, and are expected to serve as photocatalysts because of their long lifetimes of the excited states.[1] However, only limited studies have been reported for their reactivities and catalyses upon photoexcitation.[2] In the present communication, we report that phosphorous porphyrins serve as novel photocatalysts for hydration of nitrile.

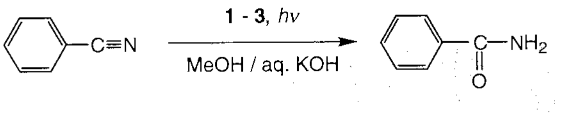
A typical example is shown below by the hydration of benzonitrile catalyzed by **1** (Scheme 1): To a 10-mL flask containing a MeOH solution (3.6 mL) of **1** (7.7 mg, 12.8 $\mu$mol)[3] were successively added 10 equivalents of benzonitrile (13 $\mu$L, 128 $\mu$mol), an aqueous solution (0.4 mL) of KOH (400 $\mu$mol), and 3,4-dimethoxytoluene (HPLC internal standard, 40 $\mu$L), and the mixture was irradiated under aerobic conditions with a xenon arc light ($\lambda$ > 420 nm) at 25 °C. Aliquots were periodically withdrawn from the reaction mixture and subjected to HPLC analysis[4] to determine the yield of benzamide. As shown in Figure 1 (◇), the reaction proceeded under irradiation with visible light for 25 h to afford benzamide in 95% yield, which corresponds to a turnover number ([benzamide]/$[\mathbf{1}]_0$) of 9.5. When the reaction was carried out with an excess amount of benzonitrile relative to KOH under otherwise identical conditions ($[\mathbf{1}]_0$/[benzonitrile]$_0$/[KOH]$_0$ = 3.2/320/100 mM), the yield of benzamide reached a plateau in 25 h at 30% (96 mM) (Figure 1 (□)), which corresponds to 96% based on the initial amount of KOH. Interestingly, the reaction mixture at this stage was completely neutralized (pH ~7), indicating that $OH^-$ ions participate in this reaction. In fact, in the absence of KOH under similar conditions, the reaction did not occur at all.



**1** $R^1$ = Ph
**2** $R^1$ = Et



**3** $R^2$ = OMe



**Scheme 1.**

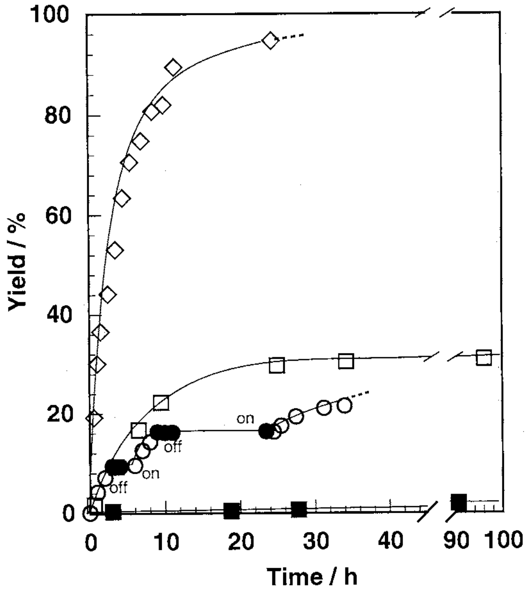
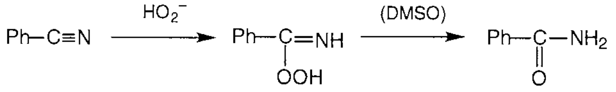


**Figure 1**. Photoinduced hydration of benzonitrile catalyzed by phosphorpus porphyrin (**1**) in MeOH (3.6 mL)/aq. KOH (0.4 mL) ($[\mathbf{1}]_0$/[KOH]$_0$ = 3.2/100 mM) under aerobic conditions at 20 °C. Time courses of the reactions under irradiation (◇) at [nitrile]$_0$ = 32 mM, and under irradiation (□), in the dark (■), and under light on/off conditions (O, ●) at [nitrile]$_0$ = 320 mM.

Even more interestingly, the reaction hardly took place in the dark (Figure 1 (■)), indicating that photoexcitation of **1** is essential for this reaction. The essential effect of visible light was clearly demonstrated by a light on (O)/off (●) experiment (Figure 1), in which the hydration proceeded only when the reaction mixture was exposed to visible light, whereas the reaction totally stopped when the light was switched off. Similarly to **1**, an ethyl(oxo)phosphorous complex (**2**) and a cationic phosphorous complex (**3**) catalyzed the hydration of benzonitrile under irradiation with visible light ([**2** or **3**]$_0$/[benzonitrile]$_0$/[KOH]$_0$ = 3.2/320/100 $\mu$M), where the yields based on the initial amount of KOH after 25-h photoirradiation were 80 and 89%, respectively.

As described above, $OH^-$ participates in the photohydration of nitrile. We assume that the phosphorous porphyrins may photosensitize electron transfer from $OH^-$ to $O_2$.[5] Hydration of nitriles is known to occur in alkaline $H_2O_2$ or $KO_2$, where a peroxycarboxyimidic acid (**4**), an equimolar adduct between a nitrile and $HO_2^-$, has been considered a likely intermediate (Scheme 2).[6] This idea has been supported by an acceleration effect of DMSO, which possibly serves as oxygen acceptor for the intermediate (**4**) to be broken into the corresponding amide. In our case was also observed a dramatic acceleration effect of



4

**Scheme 2.**

DMSO: Upon addition of DMSO (32 mM) to an alkaline MeOH solution of benzonitrile in the presence of **1** ($[\mathbf{1}]_0$/$[\text{benzonitrile}]_0$/$[\text{KOH}]_0$ = 3.2/32/100 mM), the reaction on irradiation with visible light was completed within only 3 h (25 h without DMSO) to give benzamide in a quantitative yield with a simultaneous formation of dimethylsulfone. Therefore, it is most likely that **1** upon photoexcitation in the presence of $OH^-$ is reduced to the corresponding anion radical,[8] which then undergoes electron transfer to existing $O_2$ to generate $O_2^-$ (or $HO_2^-$ in the presence of water). Thus, **1** appears to serve as a photosensitizer, which induces a flow of electron from $OH^-$ to $O_2$. In accordance with this mechanism, the photoinduced hydration by **1** did not occur at all under Ar in the absence of $O_2$.

Along the line of this idea, we also found that a zinc porphyrin ZnTCPP (zinc tetrakis(4-carboxyphenyl)porphyrin), a representative photosensitizer, catalyzes photohydration of benzonitrile, however the efficiency is much lower than those of phosphorous porphyrins. For example, at $[\text{ZnTCPP}]_0$/$[\text{benzonitrile}]_0$/$[\text{KOH}]_0$ = 3.2/32/100 mM, the reaction subsided in 25-h irradiation to give benzamide in only 39% yield (*cf.* 95% with **1**). In relation to this observation, it is also worth noting that the phosphorous porphyrins are highly robust toward photochemical decompositions: Throughout the reaction in Figure 1 (□), characteristic absorption bands of **1** were not at all decreased in intensity. Accordingly, upon addition of a fresh feed of KOH (0.4 mmol) to the final reaction mixture, the hydration restarted upon irradiation to afford an additional turnover number of 30 for 47 h. In sharp contrast, ZnTCPP was completely bleached under the above reaction conditions. Thus, phosphorous porphyrins are unique and robust photocatalysts.

In conclusion, we have demonstrated a novel photocatalysis of phosphorous porphyrins, which allow hydration of nitriles by $OH^-/O_2$ under mild conditions without using peroxy compounds. Although the mechanism seems to be different,[7] the catalysis of phosphorous porphyrins is similar to that of photoresponsive nitrilehydratase, an enzyme that catalyzes hydration of nitrile to amide in response to visible light. Mechanistic studies and application of *in situ* generated $O_2^-$ ($HO_2^-$) to oxidation of other substrates are the subjects worthy of further investigation.

## References and Notes

1 a) A. J. Harriman, *J. Photochem.*, **23**, 37 (1983). b) H. Segawa, K. Kunimoto, K. Susumu, M. Taniguchi, and T. Shimizu, *J. Am. Chem. Soc.*, **116**, 11193 (1994). c) Y. H. Liu, M.-F. Benassy, S. Chojnacki, F. D'Souza, T. Barbour, W. J. Becher, P. J. Brothers, and K. M. Kadish, *Inorg. Chem.*, **33**, 4480 (1994). d) T. A. Rao and B. G. Maiya, *Inorg. Chem.*, **35**, 4829 (1996) and references cited therein.

2 a) H. Inoue, T. Okamoto, M. Komiyama, and M. Hida, *J. Photochem. Photobiol., A.: Chem.*, **65**, 221 (1992). b) H. Segawa, A. Nakamoto, and T. Shimizu, *J. Chem. Soc., Chem. Commun.*, **1992**, 1066.

3 K. Konishi, M. Suezaki, and T. Aida, submitted.

4 HPLC analyses were carried out on a Senshupak PEGASIL ODS column at 1.0 mL/min by using methanol/water (50/50 v/v) as eluent. Retention times of benzamide and benzonitrile were 5.0 and 10.0 min, respectively, which were identified by comparison with those of the authentic samples. Formation of possible by-products such as benzoic acid (retention time: 4.3 min) was not observed.

5 Formation of an anion radical of an antimony porphyrin by electron transfer from $OH^-$ ion to the excited triplet state has been reported, see: S. Takagi, T. Okamoto, T. Shiragami, and H. Inoue, *Chem. Lett.*, **1993**, 793. One electron reduction potentials and excitation energies of phosphorous porphyrins have been reported to be -0.3 - -0.6 V vs SCE and 2.00 - 2.02 eV, respectively (ref 1d and references cited therein).

6 Y. Sawaki and Y. Ogata, *Bull. Chem. Soc. Jpn.*, **54**, 793 (1981) and references cited therein.

7 M. Odaka, K. Fujii, M. Hoshino, T. Noguchi, M. Tsujimura, S. Nagashima, M. Yohda, T. Nagamune, Y. Inoue, and I. Endo, *J. Am. Chem. Soc.*, **119**, 3785 (1997).