Photocyanation of Pyrene in an Oil-in-Water Emulsion System

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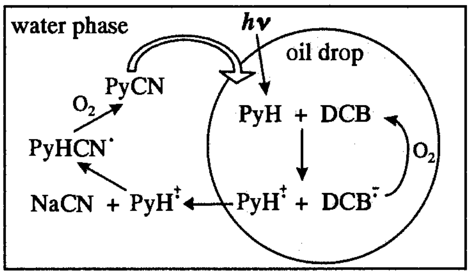
Photoirradiation of pyrene in the presence of 1,4-dicyanobenzene and NaCN in a benzonitrile/water mixture (1/100, vol/vol%) under vigorous stirring gave 1-cyanopyrene (PyCN) in an 83% yield, while an analogous reaction in acetonitrile/water (9/1, vol/vol%) yielded PyCN in a 61% yield.

So far, we have explored laser trapping–microanalytical studies on single oil-droplets in water, and reported several characteristics of the microdroplet chemistry.[1–4] As an example, we showed that ferrocenium cations ($FeCp^+$) produced electrochemically in single oil droplets distributed very efficiently to the surrounding water phase and subsequent reduction of the cations in water rendered redistribution of FeCp to the oil droplets. Thus, FeCp shuttles between the two phases upon a redox reaction in an emulsion system. Furthermore, since the surface area/volume (A/V) ratio of a droplet increases with a decrease in the droplet diameter (*d*), distribution of FeCp or $FeCp^+$ between the two phases becomes more efficient for smaller droplets.[1] Such characteristics of a redox reaction in an emulsion might be used as a new synthetic system and, if this is the case, a reaction yield could be controlled by the size of a droplet: *d*. In order to test such a possibility, we explored photocyanation of pyrene in an emulsion system.

A photoreaction studied was analogous to that reported by Mizuno et al.[5] They reported that phenanthrene and naphthalene derivatives were cyanated in CH_3CN–H_2O (9:1, vol/vol%) via a photoinduced electron transfer (PET) mechanism, with NaCN being used as a cyanation reagent.[5,6] Such a photoredox reaction could be applied to that in an emulsion system. As shown in Scheme 1, namely, when PET between pyrene (PyH) and 1,4-dicyanobenzene (DCB) takes place in oil droplets dispersed in water, the ion radicals of PyH would distribute to water as expected from our previous studies. In the presence of NaCN in water, furthermore, the PyH cation radical is expected to proceed a cyanation reaction with CN^- and the cyanated product will be redistributed or extracted to the oil droplets. As one of the advantages of such a system, a photoproduct(s) would be isolated very easily by separating the oil phase from the mixture. We anticipated that a cyanation reaction of PyH via PET could be achieved in an oil-in-water emulsion system. In this letter, we show that such an idea works very well and PyH can be photocyanated in a good yield.



Scheme 1. Photocyanation reaction of PyH in an oil-in-water emulsion system.

Benzonitrile (BN, Tokyo Kasei Kogyo Co. Ltd., EP grade) and NaCN (Wako Pure Chemical Industries Ltd., S grade) were used as supplied. PyH and DCB, both purchased from Wako Pure Chemical Industries Ltd., were purified by successive recrystallizations from ethanol. A benzonitrile solution (25 mL) of PyH (2 mmol) and DCB (2 mmol) was mixed vigorously with an aqueous solution of NaCN (1 M (= mol/dm^3), 250 mL) to obtain an oil-in-water emulsion (oil:water = 1:10 vol/vol%). The oxygenated mixture was irradiated with a 300 W high-pressure mercury lamp through a $CuSO_4$ solution filter ($\lambda > \sim 330$ nm) for 3 h under vigorous stirring by using a homogenizer. After the photoreaction, the oil phase was separated, washed with water, and evaporated to dryness. The residue was chromatographed on silica gel (*n*-hexane: chloroform = 1:2). 1-Cyanopyrene (PyCN) was obtained in an absolute yield of 78% as confirmed by ^{1}H NMR (300 MHz; Varian, Gemini 2000), elemental analysis,[7] and GCMS (Shimadzu, GCMS-QP5000). The absorption and fluorescence spectra also showed those characteristic to a pyrene derivative. It is worth noting that no other product is isolated. In the absence of NaCN, we could not confirm formation of PyCN, so that the CN source of the reaction was neither BN nor DCB.

Figure 1 shows gas chromatograms of the oil phases of the reaction mixtures before and after 30 min photoirradiation. The

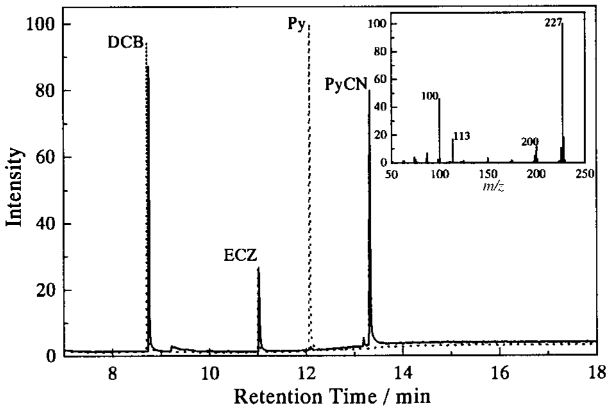


Figure 1. Gas chromatograms of the oil phase before (dotted line) and after photoirradiation (solid line; 30 min).
The reaction conditions are as follows. A BN solution (100 μL) of PyH (40 mM) and DCB (80 mM) was mixed with an aqueous solution of NaCN (1 M, 10 mL) and, the mixture was irradiated (>330 nm) under stirring at 24000 rpm.
N-Ethylcarbazole (ECZ) was used as an internal standard for quantitative analysis of the products in the GC experiments.
Inset represents the mass spectrum of PyCN (t_R = 13.3 min).

volume ratio of the emulsion was BN:H_2O = 1:100 (vol/vol%) and the reaction was conducted at a stirring rate (v) of 24000 rpm. The results demonstrated that PyH (retention time (t_R) = 12.1 min) disappeared almost completely after photoirradiation, and a new peak appeared at t_R = 13.3 min, whose mass number was 227 as is shown in the inset of Figure 1: PyCN. The absolute PyCN yield was determined to be 83%. Besides PyCN, no major product was detected in the oil phase as long as analysis was made by GCMS. The chromatograms also demonstrated that consumption of DCB (t_R = 8.4 min) during the photoreaction was very low (~ 10%), demonstrating efficient turnover of DCB as an electron acceptor. Since the photoreaction was conducted under an oxygen atmosphere, the DCB anion radical could be oxidized by O_2 (probably in the droplets). Furthermore, the use of CH_3CN–H_2O (9:1, vol/vol%) as a medium gives PyCN in a 61% yield, despite analogous reaction conditions to those mentioned above. The present emulsion system is thus concluded to be more favorable than the CH_3CN–H_2O system for cyanation of pyrene.

If the overall reactions proceed across the oil-droplet/water interface as shown in Scheme 1, the reaction yield should depend on d through a variation of the A/V ratio of a droplet. At the present stage, we have not succeeded in single droplet experiments because of the difficulty in determining the reaction yield on the basis of spectroscopic measurements. Therefore, we studied a v dependence of the absolute cyanation yield as the results were summarized in Figure 2 (reaction time = 15 min). The d distribution of the BN droplets in the emulsion was 1–30 or 1–80 μm at v = 24000 or 6000 rpm, respectively, as estimated by observation under an optical microscope. The data in Figure 2 demonstrate clearly that the yield increases from 22 to 67% with an increase in v from 500 to 24000 rpm. Since the conversion percentage of PyH to PyCN was almost constant irrespective of v, the results indicated that distribution of the PyH cation radical to the water phase became more efficient at a higher v through the increase in the A/V ratio of the droplet. It is worth noting that the incident photon number absorbed by the emulsion depends on v owing to turbidity of the mixture being varied with v, so that a comparison of the datum at each v is not necessarily straightforward. Nonetheless, it is true that the emulsion is more turbid and scattering of incident light by the emulsion is more serious at a higher v. Therefore, an observation of the v (or d) dependence of the yield indicated that the quantum yield of photocyanation increased with decreasing the droplet size.

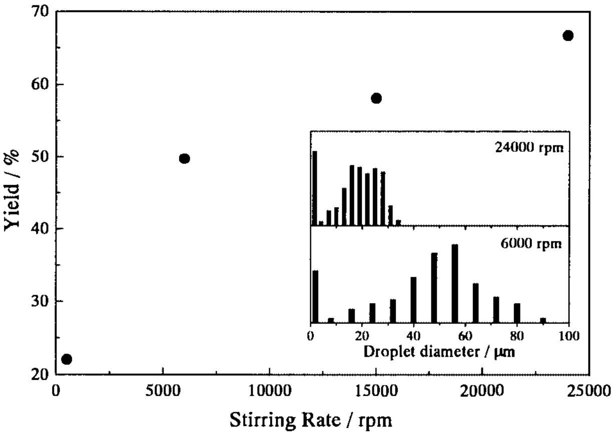


Figure 2. A v dependence of the PyCN yield. The reaction conditions were the same with those in Figure 1 except for an irradiation time (15 min). Insets represent the droplet size distributions in the BN/H_2O emulsions prepared at v = 24000 and 6000 rpm.

The use of BN as an oil is the one of the key conditions for the present photoreaction. BN produces a very stable oil-in-water emulsion and is polar enough for PET (solubility in water = 0.2 wt% and dielectric constant (ε = 25.2).[8] In BN, the fluorescence of PyH was quenched in the presence DCB: free energy change for PET = –23.0 kJ/mol and k_q (quenching rate constant) = 7.2×10^9 M^{-1} s^{-1}.[9] These results indicate that the reported PET mechanism by Yasuda et al.[6] is responsible for the present reaction as well (see Scheme 1). We expect that various aromatic hydrocarbons other than PyH could be efficiently photocyanated in emulsion systems and the reaction yield would be also controlled by the droplet size.

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References and Notes.

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7 Elemental analysis, Calcd for $C_{17}H_9N$: C, 89.85; H, 4.23; N, 6.25%. Found: C, 89.86; H, 3.97; N, 6.16%.
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9 The following values were used for the calculations. The redox potentials of PyH and DCB in BN were 0.90 and –2.10 V (vs FeCp/FeCp$^+$), respectively, and the excited state energy of PyH was 320.5 kJ/mol. The electrostatic work necessary for separating the product ions was –7.9 kJ/mol for the separation distance of 0.7 nm. The k_q value in deaerated BN was determined by a Stern–Volmer plot for the fluorescence intensity of PyH (10 μM). The fluorescence lifetime of PyH in deaerated BN was 160 ns.