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A Mechanistic Study of Photocyanation of Pyrene in Oil-in-Water Emulsion Systems

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A highly efficient one-step photocyanation reaction of pyrene was shown to proceed in oil-in-water emulsion systems. As a typical example, photoirradiation of pyrene in the presence of 1,4-dicyanobenzene and NaCN in a benzonitrile/water mixture (1/100, vol %) under vigorous stirring gave 1-cyanopyrene in a conversion yield of 83%, while an analogous reaction in an acetonitrile/water mixture (9/1, vol %) yielded this product in 61% yield. We evaluated the quantum yield of photocyanation in the oil-in-water emulsion system to be 0.17. Under optimum conditions, the quantum yield was improved to 0.68. Characteristics and possible mechanisms of the photocyanation reaction are discussed in detail.

Introduction

Chemical reactions between hydrophobic and hydrophilic solutes proceed efficiently at an oil/water interface, and thus, oil/water emulsions have been employed widely in both basic science (liquid/liquid extraction, phase transfer catalysis, etc.) and industries (photographs, foods, etc.). Nonetheless, the chemistry in heterogeneous systems represented by emulsions is still controversial, since various factors govern overall reaction kinetics: distribution rate of a solute between two phases, interfacial reaction rate, and so forth. To obtain an inside look at emulsion chemistry, we have explored laser trapping-microanalytical studies on single oil droplets in water and reported several characteristics of microdroplet chemistry.[1] As an example, we showed that ferrocenium cations ($FeCp^+$) produced electrochemically in single oil droplets distributed very efficiently and quickly to the surrounding water phase, and subsequent reduction of the cations in water caused redistribution of FeCp to the oil droplets.[2] Furthermore, the surface area/volume ratio of a droplet increases with a decrease in the droplet diameter, and distribution of FeCp or $FeCp^+$ between the two phases becomes more efficient for smaller droplets. Besides this, we reported previously that the electron-transfer rate across a droplet/water interface[3] or the dimer formation efficiency of a dye[4] in a droplet was dependent on the droplet diameter through the change in the surface area/volume ratio of a droplet. On the basis of our previous studies, we consider that chemical reactions between hydrophobic and hydrophilic solutes could proceed very efficiently in oil/water emulsions, in particular, in those composed of minute droplets. To study such a possibility and to demonstrate a droplet-size dependence of a reaction efficiency, we explored a photocyanation reaction of an aromatic hydrocarbon in oil-in-water emulsion systems.

Photocyanation of an aromatic compound was first observed for *p*-nitroanisol and was extended to unsubstituted arenes by Havinga et al.[5] They employed aqueous *tert*-butyl alcohol as a solvent and KCN as a cyanation source. In 1975, Mizuno et al. reported for the first time cyanation of aromatic hydrocarbons (ArH = phenanthrene and naphthalene derivatives) via a photoinduced electron transfer (PET) mechanism in a $CH_3CN{:}H_2O$ mixture (9:1, vol %).[6] Later, Yasuda et al.[7] and Bunce et al.[8] proposed that the cation radicals of ArH were produced as a primary step for photocyanation in the presence of an electron acceptor (*p*-dicyanobenzene; DCB) and were subject to nucleophilic attack by a cyanide anion. After these reports, various attempts have been conducted to improve the reaction yield. As an example, Beugelmans et al. reported that the product yield could be improved by using aprotic solvent−crown ether combinations to dissolve alkali cyanide[9] as well as by employing a phase-transfer catalyst.[10] The efficiency of photocyanation reaction is also dependent on the number of the aromatic rings ArH. Photoirradiation of benzene in a polar medium in the presence of KCN produces only a trace amount of benzonitrile,[11] while that of phenan-

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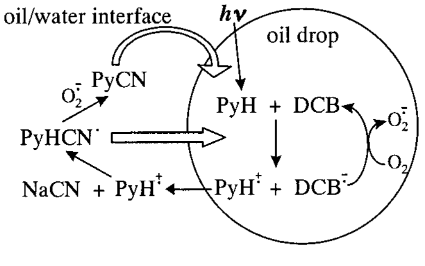
Scheme 1. Photocyanation Reaction of PyH in an Oil-in-Water Emulsion System



threne under the conditions mentioned above gives 9-cyanophenanthrene in a 78% yield.[7] On the other hand, although a photoreaction of pyrene (PyH) in aqueous *tert*-butyl alcohol in the presence of CN^- produces 1-cyanopyrene in a 68% yield,[12] that of PyH or other fused ArH via a PET mechanism has not been reported. Moreover, the number of studies on the photoreaction of PyH is still limited,[13] despite the importance of its derivatives as fluorescent probes in biological and other macromolecular systems.[14] Since the photophysical and spectroscopic properties of PyH and its derivatives are well-known,[15] PyH is very suitable for a mechanistic study of a photocyanation reaction via PET in oil-in-water emulsion systems. Therefore, we studied the photocyanation of PyH in an oil-in-water emulsion system in detail.

Our ideas on a photocyanation reaction in an emulsion system are as follows (see Scheme 1). When PET between PyH and DCB takes place in oil droplets dispersed in water, the cation radical of PyH would distribute efficiently to the water phase, as expected from our previously studies.[2] Under aerated conditions, the anion radical of DCB produced will be oxidized by O_2, regenerating DCB. These processes would enhance the charge separation efficiency of the ion radicals.[16] In the presence of NaCN in water, the PyH cation radical will be subjected to nucleophilic attack by a cyanide ion at the oil-droplet/water interface or in the water phase.[17] If oxidative dehydrogenation of the cyano-substituted pyrenyl radical (PyHCN•) with $O_2^{\bullet -}$ (or O_2) proceeds,[18] the cyanated product (PyCN) would be obtained. Furthermore, since PyCN is poorly soluble in water, it will be extracted to the oil droplets. Therefore, we anticipated that an efficient cyanation reaction via PET could be achieved in an oil-in-water emulsion system and the cyanated product could be obtained easily by separating the oil phase from the mixture. In this paper, we show that such an idea works very well and PyH is photocyanated in good yields.[18]

Experimental Section

Chemicals and Sample Preparations. All the reagents used in the present study were of a guaranteed reagent grade. Pyrene (PyH), anthracene (An), *N*-ethylcarbazole (ECZ), and 1,4-dicyanobenzene (DCB) were recrystallized from ethanol. For spectroscopic measurements, PyH was purified by column chromatography on silica gel with chloroform as an eluent before recrystallization. Benzonitrile (BN) was purified by vacuum distillation in the presence of P_2O_5 after washing with an aqueous HCl solution and drying over K_2CO_3. Water was purified by distillation and deionization prior to use (Advantech, GSR-200). Other solvents with the highest grade were used as received except for phenylacetonitrile and octanenitrile, which were purified by vacuum distillation over P_2O_5. Sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium chloride (DTAC) were recrystallized from methanol.

Photoreaction: Large-Scale Experiments. For the purpose of product analysis, a photoreaction was conducted by using an internal irradiation apparatus. Typically, a BN solution (25 mL) of PyH (80 mM; M = mol/dm^3) and DCB (80 mM) was mixed vigorously with an aqueous solution of NaCN (1 M, 250 mL) to obtain an oil-in-water emulsion (oil:water = 1:10 vol %). The oxygenated mixture was irradiated with a 300-W high-pressure mercury lamp through a $CuSO_4$ solution filter (ca. >330 nm) for 3 h under vigorous stirring. After the photoreaction, the products extracted from the mixture with chloroform were chromatographed on a silica gel column (*n*-hexane:chloroform = 1:2). 1-Cyanopyrene (PyCN) was isolated in 78% yield, as confirmed by ^1H NMR (300 MHz), IR, elemental analysis, melting point, and GC−MS: NMR (DMSO-*d*$_6$) δ 8.25 (1H, t), 8.35 (2H, d), 8.45 (2H, d), 8.51(3H, m), 8.56 (1H, d); IR (KBr, cm^{-1}) 2214 (ν_{CN}), 839, 823, 758, 711 cm^{-1} (lit.[19] IR 838, 823, 755, 709 cm^{-1}); mp 151−153 °C (lit. [20] mp 153 °C); MS showed a parent-mass peak number of 227. Anal. 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.

Photoreaction: Small-Scale Experiments. For kinetic analysis, quantum yield determination, and additive effects, photoreactions were conducted using a small reaction cell. A sample solution in a 3-cm i.d. Pyrex cell was irradiated externally with the 366 nm line from the high-pressure mercury lamp, which was isolated by using a band-pass filter (BP365 FS10-25, Andover). The sample cell was set approximately 5.5 cm from the lamp. The standard reaction conditions are as follows. A water-saturated oil solution (100 μL) of PyH (20 mM) and DCB (40 mM) was mixed with an oil-saturated aqueous solution of NaCN (1 M, 10 mL), and the aerated mixture was irradiated under stirring at a desired rate (500−24000 rpm) by using a homogenizer. After the photoreaction, the oil phase was extracted from the mixture with chloroform containing ECZ as an internal standard for GC. Analysis of the oil phase was performed by GC−MS.

Determination of Quantum Yield. Generally, determination of the incident light intensity [I_0 (photon number)] absorbed by a solute in an emulsion is very difficult, owing to light scattering. Therefore, special care is absolutely necessary to evaluate a quantum yield in an emulsion system. To evaluate I_0 accurately, we employed the photodimerization reaction of anthracene (An) with following procedures and steps. For determination of the light intensity and the quantum yield, the conversion of An was set below 31% in all the experiments. First, we studied photodimerization of An (5.0 mM) in deaerated benzene by using the sample cell for the small-scale experiments (see above). The photodimerization

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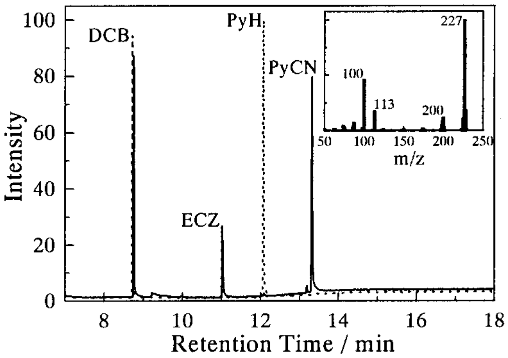

Figure 1. Gas chromatograms of the reaction mixtures (oil phase) before (dotted line) and after photoirradiation (solid line; 5 min). For the reaction conditions, see "Small-Scale Experiments" in the Experimental Section. The stirring rate was set 1500 rpm. Inset represents the mass spectrum of PyCN (t_R = 13.3 min).

reaction of An was followed by monitoring the absorbance of An at 379 nm. Knowing the quantum yield of An photodimerization (Φ_{An}) in deaerated benzene ([An] = 5.0 mM) to be 0.070,[21] we determined I_0 as $2.5 \pm 0.13 \times 10^{16}$ quanta/s. Under analogous experimental conditions, we conducted the photodimerization of An in a homogeneous water-saturated BN solution (deaerated) and determined Φ_{An} as 0.077 ± 0.0056 ([An] = 5.0 mM). It is worth noting that Φ_{An} determined for the water-saturated BN solution agrees well with that in the water-unsaturated BN solution. Therefore, we concluded that photodimerization of An was very suitable as a standard reaction for determining I_0 in an emulsion system. In the next step, we studied An photodimerization ([An] = 5.0 mM) in a BN:H_2O emulsion (1:100 vol %, total volume = 10 mL) at 1500 rpm and determined I_0 to be $7.2 \pm 0.60 \times 10^{15}$ quanta/s under the assumption of Φ_{An} in the system being equal to that in a water-saturated BN solution (0.077). In the third step, we conducted the photocyanation reaction of PyH in a BN:H_2O emulsion (1:100 vol %, total volume = 10 mL) under stirring at 1500 rpm. In the experiments, the concentration of PyH was adjusted to 25 mM to equalize the absorbance of PyH (molar absorptivity at 366 nm = ϵ_{366} (380 M^{-1} cm^{-1}) × [PyH] = 9.5 cm^{-1}) to that of An (ϵ_{366} (1900 M^{-1} cm^{-1}) × [An] = 9.5 cm^{-1}). The concentrations of DCB (in BN) and NaCN (in water) were set at 40 mM and a variable (0.3−2.0 M; described later), respectively. On the basis of GC−MS analysis of the reaction mixture and the known photon number (7.2×10^{15} quanta/s), we evaluated the quantum yield of the PyCN formation, Φ_{CN}.

Spectroscopic and Electrochemical Measurements. A Hitachi UV-3300 spectrophotometer and a Hitachi F-4500 spectrofluorometer were used for absorption and fluorescence spectroscopies, respectively. Fluorescence decay of PyH was measured by using the third harmonic from a pulsed Nd^{3+}:YAG laser (355 nm, Surelite, Continuum) as an excitation light source and a streak scope (C4334, Hamamatsu) as a detector. The redox potentials of PyH and DCB in BN were measured by cyclic voltammetry (vs FeCp/$FeCp^+$) with tetra-*n*-butylammonium hexafluorophosphate (0.05 M) being used as a supporting electrolyte. A Gemini 2000 300-MHz ^1H NMR spectrometer (Varian) and a FTIR-8300 infrared spectrometer (Hitachi) were used for structure identifications.

Results and Discussion

General Features of the Photoreaction. Figure 1 shows gas chromatograms of the oil phases of the reaction mixtures before and after 5 min photoirradiation. The volume ratio of the emulsion was set to BN:H_2O = 1:100 and the photoreaction was conducted by using the small-scale chamber (10 mL) at a stirring rate (*v*) of 1500 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 (Figure 1). The retention time and the mass number agreed very well with those of 1-cyanopyrene (PyCN). On the basis of the calibration curve made by separate experiments, the absolute yield of PyCN was determined to be 77% (conversion 83%), which was in good agreement with the isolated yield (78%). Knowing the incident photon number absorbed by PyH in the BN:H_2O emulsion, we calculated the quantum yield of the PyCN formation (Φ_{CN}) to be 0.17 ± 0.018.

The *m*/*z* value of a small peak observed at t_R = 13.1 min was 227, indicating that 2- or 4-cyanopyrene was also produced in low yield (~2.0%), though the product was not isolated. Besides cyanopyrenes, no product was detected in the oil phase as long as analysis was made by GC−MS. Thus, the present reaction is concluded to be very clean and highly selective. The chromatograms also demonstrated that consumption of DCB (t_R = 8.4 min) during the photoreaction was very low (~10%), indicating very good turn over as an electron acceptor. Since the photoreaction is conducted under aerated conditions, the DCB anion radical could be oxidized by O_2, as shown in Scheme 1, leading to a high turn over number of DCB (>5). It is worth noting, furthermore, that the use of a CH_3CN:H_2O mixture (9:1, vol %) as a medium gives PyCN in a 61% yield, despite using analogous reaction conditions to those mentioned above. In the absence of NaCN, we could not confirm cyanation of PyH, so that the CN source of the reaction is neither BN nor DCB. The present photoreaction in the emulsion system thus has a high potential for efficient one-pot cyanation of pyrene. Besides PyH, we confirmed photocyanation of other aromatic hydrocarbons in analogous emulsion systems: naphthalene, phenanthrene, and perylene.[22]

Other factors governing the photoreaction were also studied: effects of DCB and O_2 on the PyCN yield and Φ_{CN} (Table 1). Under aerated conditions (entries 1 and 2), the conversion yield of PyCN in the absence of DCB was slightly lower (67.3%) than that in the presence of DCB (83.2%), while Φ_{CN} was ~4 times larger in the presence of DCB. The photoreaction without DCB indicates that O_2 acts as an electron acceptor for the excited singlet state of PyH ($^1PyH^*$). In practice, the Gibbs free energy change for PET (ΔG)[23] between PyH and O_2 is calculated to be −120 kJ/mol,[24] which is exothermic enough for PET. Furthermore, we confirmed formation of a PyH radical cation in an aerated BN solution on the basis of laser-photolysis experiments. In the presence of DCB, on the other hand, the conversion yield of PyCN was almost independent of the presence or absence of O_2 (entries 1 and 3), while Φ_{CN} was 10-times lower in the absence of O_2 compared to that with O_2. Without O_2,

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(24) Calculated by the Rehm−Weller equation[23] on the basis of the following values. The oxidation and reduction potentials of PyH and DCB were +0.90 and −2.10 V (vs FeCp/$FeCp^+$), respectively. The electrostatic work necessary for separating product ions was estimated from $w_p = ((z_{D+}z_{A-})e^2/l\epsilon)$, where z_{D+} and z_{A-} were the electric charges of PyH and DCB, respectively, and *e*, *l*, and ϵ were the elementary charge, the separation distance of the two ions (0.7 nm), and the dielectric constant of a medium, respectively. In Table 2, w_p was calculated under the assumption of l = 0.7 nm, irrespective of a solvent.

Table 1. Photocyanation of PyH in BN:H_2O Emulsion System[a]

entry	[DCB] (mM)	additive	atmosphere	irradiation time (min)	consumed PyH (%)	absolute yield (%)	conversion yield[b] (%)	recovery of DCB (%)	Φ_{CN}
1	40		air	5	93.0	77.4	83.2	89.4	0.17
2	0		air	10	62.6	42.1	67.3		0.048
3	40		argon	30	66.5	48.2	72.5	91.9	0.016
4	0		argon	30	44.4	19.4	43.7		0.005
5	40	DTAC	air	1	81.7	64.1	78.5	89.7	0.68
6	40	SDS	air	30	97.6	63.9	65.5	85.2	0.024

[a] The reaction conditions are as follows. A BN solution (100 μL) of PyH (20 mM) was mixed with an aqueous solution of NaCN (1 M, 10 mL), and the mixture was irradiated (366 nm) under stirring at 1500 rpm. The concentration of DTAC or SDS was 0.5 mM. [b] The conversion yield based on PyH consumed.

Table 2. Solvent Dependence of Photocyanation of PyH in Emulsion Systems[a]

solvent	ϵ[b]	irradiation time (min)	consumed PyH (%)	absolute yield (%)	conversion yield[c] (%)	recovery of DCB (%)	Φ_{CN}	ΔG (kJ/mol)	k_q[d] $\times 10^9$ (M^{-1} s^{-1})
toluene	2.38	60	4.1	0	0	96.9	0	49.3	*e*
diethyl ether	4.34	60	10.5	0	0	89.1	0	12.6	*e*
ethyl acetate	6.02	30	23.2	14.4	62.1	92.8	0.004	0.18	*e*
DCE[f]	10.4	30	36.1	26.2	72.6	92.8	0.007	**−13.1**	9.3
ON[g]	13.9	30	64.3	52.8	82.1	67.5	0.016	**−19.6**	5.2
PAN[h]	18.7	5	93.8	83.7	89.2	96.7	0.19	**−20.7**	4.1
BN	25.2	5[m]	93.0[m]	77.4[m]	83.2[m]	89.4[m]	0.17[m]	**−23.4**	7.2
CH_3CN:H_2O[i,j]	37.5[k]	60	97.9	60.2	61.5	90.9		**−25.1**	14
PC[l]	64.9	4	100	75.2	75.2	96.0	0.24	**−31.7**	1.9

[a] The volume ratio of oil to water was set 1/100. Other reaction conditions are the same as those in Table 1. The incident photon number absorbed by PyH in each system was assumed to be equal to that in the BN:H_2O emulsion. [b] The dielectric constant of an oil.[27] [c] The conversion yield based on PyH consumed. [d] The fluorescence quenching rate constant of PyH by DCB in a neat oil. [e] Too small to determine accurately.[28] [f] 1,2-Dichloroethane. [g] Octanenitrile. [h] Phenylacetonitrile. [i] The solution was a water-in-oil emulsion in the presence of NaCN (1 M), and the I_0 value could not be determined. [j] The concentration of PyH was set 20 mM. [k] The value in neat CH_3CN. [l] Propylenecarbonate. [m] The data are the same with those in Table 1 (entry 1).

charge recombination between a PyH cation radical and a DCB anion radical would proceed very efficiently, so that this reduces Φ_{CN}. Furthermore, it has been reported that the presence of an oxidizing agent is essential for formation of PyCN from a cyanated pyrenyl radical (PyHCN$^\bullet$, see also Scheme 1).[25] Therefore, O_2 and/or a superoxide anion ($O_2^{\bullet -}$) produced by ET with a DCB anion radical play an important role for the photocyanation reaction of PyH (discussed later again). In the absence of both DCB and O_2, although the photoreaction proceeds as seen in entry 4, the Φ_{CN} value is ~34 times lower (0.005) than that in the presence of DCB and O_2 (0.17). Under such conditions, BN would act as an electron acceptor for ^{1}PyH* (fluorescence quenching rate constant, $k_q = 4 \times 10^6$ M^{-1} cm^{-1}).[26] Otherwise, there is a possibility for a photoreaction via the excited triplet state of PyH ($\phi_T = 0.38$)[26] or PyH excimer as reported by Bunce et al.[8] The present results demonstrate that the presence of both DCB and O_2 (air) is essential for efficient photocyanation of PyH to proceed. The results suggest the reaction mechanisms in the Scheme 1.

Solvent Effects. To obtain further insight about the reaction mechanisms, we studied the solvent (i.e., nature of the oil) dependence of the cyanation yield in the emulsion systems. Table 2 summarizes the results, including the dielectric constant of the oil (ϵ) and the fluorescence quenching data of PyH by DCB. As seen from the table, the PyCN yield was strongly dependent on the nature of the solvent and increased with increasing the solvent polarity. In nonpolar solvents, such as toluene and diethyl ether, the photocyanation reaction did not proceed at all. The results are readily understood by the endothermic nature ($\Delta G > 0$) of PET in some solvents.[28] In a moderately polar solvent such as ethyl acetate, 1,2-dichloroethane (DCE), or octanenitrile (ON), the conversion yield of PyCN was 62−82%. Nonetheless, Φ_{CN} was as low as 0.004−0.016. In the water-in-oil emulsion consisting of a high-polarity oil, on the other hand, PyCN was obtained in a 61~89% yield with Φ_{CN} being 0.17~0.24. The increasing order of Φ_{CN} almost agrees with that of the polarity of the oil in the emulsion and, photoinduced electron transfer between PyH and DCB becomes more facile in this order as revealed by the ΔG and k_q values. It has been reported, furthermore, that the yield of a PyH radical ion produced by PET increases with an increase in the dielectric constant of a medium, as demonstrated by laser flash photolysis and transient photocurrent measurements.[29] Therefore, we conclude that the reported PET mechanisms for photocyanation of phenanthrene and other aromatic hydrocarbons by Yasuda et al.[7] are responsible for the present reaction as well (see Scheme 1).

A close inspection of the data in Table 2 indicates, however, that the PyCN yield and Φ_{CN} are somewhat scattered among those for PAN (phenylacetonitrile), BN, AN (acetonitrile), and PC (propylene carbonate). We suppose that this could be due to the stability of the emulsion, depending on the solubility of an oil in water or that of water in an oil (discussed later again). Among the systems, BN produces a very stable oil-in-water emulsion (solubility in water = 0.2 wt %).[27] Therefore,

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[27] Riddick, J. A.; Bunger, W. B. *Techniques of Chemistry: Organic Solvents*; Wiley-Interscience: New York, 1970; Vol. II.

[28] The fluorescence quenching rate constant in nonpolar solvents (toluene, diethyl ether, and ethyl acetate) cannot be determined accurately, because the rate constant was too small. Also, the emission from the ground-state complex between PyH and DCB disturbed observation of fluorescence quenching of PyH.

[29] Taniguchi, Y.; Nishina, Y.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 764.

we chose BN as a model solvent for following mechanistic studies.

Kinetic Analysis. The above discussions demonstrate that the present photocyanation reaction proceeds via the PET mechanism in the Scheme 1 and, its elementary processes are given by the following equations.[8]

$$ {}^1\text{PyH*} \xrightarrow{k_1} \text{PyH} \tag{1} $$

$$ {}^1\text{PyH*} + \text{DCB} \xrightarrow{k_2} \text{PyH}^{\bullet+} + \text{DCB}^{\bullet-} \tag{2} $$

$$ \text{PyH}^{\bullet+} \xrightarrow{k_3} \text{deactivation and/or side reactions} \tag{3} $$

$$ \text{PyH}^{\bullet+} + \text{CN}^- \xrightarrow{k_4} \text{PyHCN}^{\bullet} \tag{4} $$

$$ \text{PyHCN}^{\bullet} \xrightarrow{k_5} \text{deactivation and/or side reactions} \tag{5} $$

$$ \text{PyHCN}^{\bullet} \xrightarrow{k_6} \text{PyCN} \tag{6} $$

The rate constants k_1 and k_2 represent those of the excited singlet state decay and the PET reaction, respectively. The cation radical of PyH produced by PET undergoes either deactivation/side reaction (k_3) or cyanation with CN^- (k_4), giving a cyanated pyrenyl radical ($\text{PyHCN}^{\bullet}$). The pyrenyl radical then deactivates (k_5) or reacts with an oxidative reagent (k_6, possibly be $\text{O}_2^{\bullet-}$). Under the steady-state approximation of all the intermediates, the Stern–Volmer equation for the photocyanation reaction can be derived as in eq 7.

$$ \frac{1}{\Phi_{\text{CN}}} = \left(1 + \frac{k_5}{k_6}\right)\left(1 + \frac{k_3}{k_4[\text{CN}^-]}\right)\left(1 + \frac{k_1}{k_2[\text{DCB}]}\right) \tag{7} $$

Equation 7 indicates that, at a fixed DCB concentration ([DCB]), the $\Phi_{\text{CN}}{}^{-1}$ value should increase linearly with the inverse of the NaCN concentration ($[\text{CN}^-]$). As shown in Figure 2, we obtained good linear relationships between $\Phi_{\text{CN}}{}^{-1}$ and $[\text{CN}^-]^{-1}$ for both a BN:H_2O emulsion (1:100 vol %) and a CH_3CN:H_2O mixture (9:1 vol %),[30] supporting the present PET mechanisms in Scheme 1 or eqs 1–6. It is worth pointing out that the $[\text{CN}^-]$ range studied for the CH_3CN:H_2O mixture is much lower than that in the emulsion, owing to the low solubility of NaCN in the former system. In particular, a CH_3CN:H_2O mixture is strongly turbid at $[\text{CN}^-] > 20$ mM and emulsion-like, so that a direct comparison of the two data sets in Figure 2 is not necessarily warranted. Nonetheless, the limiting Φ_{CN} value extrapolated to an infinite NaCN concentration was calculated to be 0.25 ($\Phi_{\text{CN}}{}^{-1} = 4.0$) or 0.10 (10.0) for the emulsion or CH_3CN:H_2O system, respectively, demonstrating that the photocyanation quantum yield in the emulsion system was superior to that in the CH_3CN:H_2O system. The possible reasons for this are discussed in a separate section.

Surfactant Effects. If the present photocyanation reaction involves distribution of PyH cation radicals across the droplet/water interface or the reaction of the cation radical with CN^- proceeds at the oil-droplet/water interface, the reaction efficiency would depend on the structures and/or properties of the interface. Therefore, we studied ionic surfactant effects of dodecyltrimethylammonium chloride (DTAC) or sodium dodecyl sulfate (SDS) on the photoreaction. The data are included in Table 1. Although addition of the surfactant to the water phase (5.0×10^{-4} M) influenced slightly the conversion yield (entries 5 and 6; 65–78%) as compared with that without the surfactant (entry 1, 83%), it brought about a dramatic change in Φ_{CN}. Namely, Φ_{CN} in the presence of DTAC was 0.68, which was 4 times larger than the value without DTAC, 0.17. On the other hand, addition of SDS inhibited the photoreaction and Φ_{CN} became as low as 0.024. These results demonstrate clearly that the electric charge of the surfactant is a very important factor governing Φ_{CN}. It is worth noting, furthermore, that a surfactant effect on Φ_{CN} has not been observed in the CH_3CN:H_2O mixture, so that the surfactant effects are unique to the oil-in-water emulsion system.

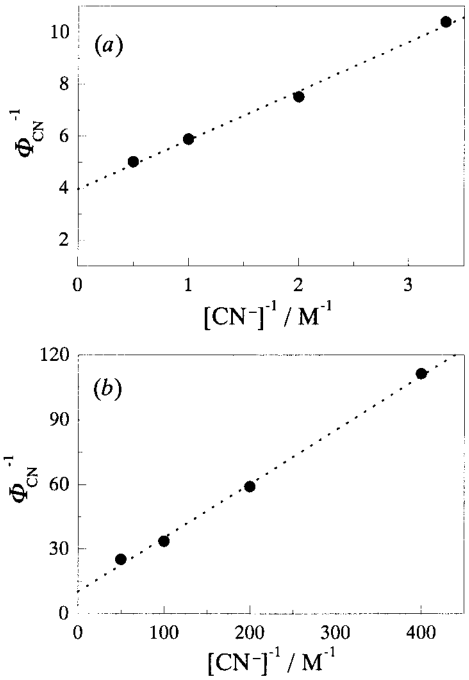

Figure 2. Stern–Volmer plots for PyCN formation in the BN:H_2O emulsion (*a*, 1:100 vol %) and the CH_3CN:H_2O solution (*b*, 9:1 vol %). [PyH] = 20 mM and [DCB] = 40 mM.

In the present experiments, the concentrations of the surfactants in water were below their critical micellar concentrations (DTAC, 20 mM; SDS, 8.2 mM),[31] so PyH and DCB in the BN droplets will not distribute appreciably to the water phase. It is predicted very easily that the added surfactant adsorbs strongly on the droplet surface. Therefore, the surfactant effects on Φ_{CN} could be explained by the electrical double layer produced at the oil droplet/water interface. Namely, addition of SDS decreases the CN^- concentration at or in the vicinity of the droplet/water interface, so that the smaller Φ_{CN} value compared to that without SDS would be a reasonable consequence. In the case of DTAC, on the other hand, CN^- anions are likely to be concentrated in the electrical double layer, and this causes acceleration of the cyanation reaction (eq 4) and, thus, the increase in Φ_{CN}. However, the observed Φ_{CN} value of 0.68 is very high

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(30) For determination of Φ_{CN} in CH_3CN:H_2O solutions, the incident photon number (2.5×10^{16} quanta/s) was determined on the basis of the photodimerization of An in a deaerated benzene solution ($\Phi_{\text{An}} = 0.070$).

(31) Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley-Interscience: New York, 1978.

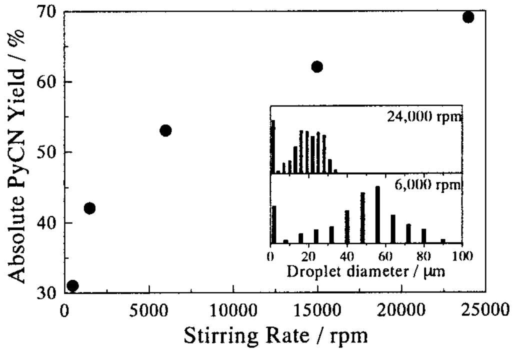

Figure 3. A *v* dependence of the absolute PyCN yield. The reaction conditions were the same with those in Figure 1, except for irradiation time (3 min). Insets represent the droplet size distributions in the BN:H_2O emulsions prepared at $v = 24\,000$ and 6000 rpm.

compared to the limiting Φ_{CN} value at $[NaCN] = \infty$ (0.25, Figure 2), so the results cannot be explained by the concentration effect of CN^- alone. Besides the electrical double layer effects, we suppose that DTAC acts as a phase-transfer catalyst. Indeed, Beugelmans et al. reported that the photocyanation yield of nitroaromatics in methylene chloride/water (KCN as a reagent) could be improved by adding tetra-*n*-butylammonium cyanide.[10] If ion pair formation between a dodecyltrimethylammonium cation and a cyanide anion proceeds in the present system and the ion pairs distribute to the oil droplets to some extent, the cyanation reaction in eq 4 would take place partly in the droplet interior, causing the increase in the reaction efficiency. Thus, we consider that the DTAC effects on Φ_{CN} originate cooperatively from both formation of the electrical double layer at the interface and ion pair extraction of cyanide ions to the oil droplets. Furthermore, the addition of a surfactant causes a decrease in the droplet size in the emulsion. This will be an another possible reason for the DTAC effects on Φ_{CN} through a droplet-size dependence on Φ_{CN}, as described in the following section.

Droplet-Size Dependence. The large surfactant effects on Φ_{CN} indicate that the overall reactions involve an interfacial process(es) at and/or across the droplet/water boundary. If this is the case, the reaction yield should depend on the droplet diameter (*d*) through a variation of the surface area/volume (*A*/*V*) ratio of a droplet. To study the droplet-size dependence of the reaction efficiency, single droplet experiments based on a laser-trapping microspectroscopy technique reported earlier by us are desired.[1,3] However, PyH is not suitable for spectroscopy under an ordinary optical microscope, since transmittance of the microscope optics decreased considerably in the wavelength region shorter than 400 nm. Therefore, we studied the stirring rate (*v*) dependence of the cyanation yield. The results are summarized in Figure 3 (reaction time = 3 min). The *d* distribution of the oil droplets in the BN:H_2O emulsion (1:100 vol %) was 1−30 or 1−80 μm at $v = 24\,000$ or 6000 rpm, respectively, as estimated by observation under an optical microscope. The data in Figure 3 demonstrated clearly that the absolute PyCN yield increased from 31 to 69% with an increase in *v* from 500 to 24000 rpm, while the conversion yield of PyCN was almost constant at ~80% irrespective of *v* (data are not shown).

For the reaction with CN^-, a PyH radical cation must diffuse to the droplet/water interface or the water phase within its lifetime (τ). For a BN droplet with the diameter of 10 μm, as an example, it takes ~25 ms for the cation radical to diffuse from the center of the droplet to the surface, as calculated from the equation: $\theta = \sqrt{2Dt}$, where θ and *D* are the diffusion length (*d*/2) and the diffusion coefficient of the cation radical (assumed to be equal to that of PyH and determined by cyclic voltammetry to be $\sim 5 \times 10^{-6}$ $cm^2\ s^{-1}$), respectively. The τ value of an ion radical produced by PET would be on the order of microseconds. The θ and τ values indicate that only the cation radical produced in the surface layer of the droplet can react with a cyanide ion. On the other hand, the cation radical produced in the droplet interior would deactivate through the charge recombination reaction with the anion radical of DCB or O_2 before diffusing to the droplet surface. With decreasing droplet diameter, the mole number of the cation radical that can react with a cyanide ion increases through the increase in the *A*/*V* ratio of the droplet, leading to the droplet-size or *v* dependence of the absolute PyCN yield. The conversion yield is determined by the diffusion length of the cation radical within its lifetime, which is much shorter than *d*/2. Therefore, the conversion yield is essentially independent of *v*, while only the absolute yield is under the influence of the droplet diameter.

It is worth noting that the incident photon number absorbed by PyH in 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* in Figure 3 is not necessarily straightforward. Since determinations of the incident photon numbers absorbed by the emulsions at various *v* are very laborious, we cannot discuss the results on the basis of Φ_{CN}. 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*, suggesting that the photon number absorbed by PyH in the emulsion is lower at a higher *v*. Indeed, the incident light intensity absorbed by the emulsion system (7.2×10^{15} quanta/s at $v = 1500$ rpm) was much lower than that by a homogeneous CH_3CN:H_2O solution (2.5×10^{16} quanta/s). Therefore, the observation of the *v* or *d* dependence of the yield indicated that the quantum yield of photocyanation increased with decreasing the droplet size.

Mechanistic Origins for High Reaction Efficiency in the Emulsion System. In the preceding sections, we showed characteristic aspects of the photocyanation reaction in the emulsion system, and the reaction yield of PyCN was shown to be superior to that in a homogeneous CH_3CN:H_2O solution. On the basis of the present observations, it is worth discussing mechanistic origins for the high reaction efficiency in the emulsion system.

Some additional information about the mechanisms is provided by the Stern−Volmer plots in Figure 2 and eq 7. Namely, since we can evaluate the k_1 and k_2 values on the basis of fluorescence decay and quenching experiments, respectively, the parameters $k_3/(k_3 + k_4)$ and $k_5/(k_5 + k_6)$ can be calculated from the slope and the intercept of the Stern−Volmer plot. The k_1 value in BN or CH_3CN:H_2O (9:1, vol %) was determined to be 2.2×10^7 or 5.6×10^7 s^{-1}, respectively, and k_2 was assumed to be equal to the k_q value in Table 2. The $k_3/(k_3 + k_4)$ and $k_5/(k_5 + k_6)$ values thus determined at [DCB] = 40 mM are summarized in Table 3.

Table 3. Kinetic Data for Photocyanation of PyH in BN:H_2O Emulsion and a CH_3CN:H_2O Mixture[a]

solvent	slope	intercept	k_1[b]	k_2[c]	$k_3/(k_3 + k_4)$	$k_5/(k_5 + k_6)$
BN:H_2O	1.9	4.0	2.2×10^7	7.2×10^9	0.32	0.73
CH_3CN:H_2O	0.25	10	5.6×10^7	14×10^{10}	0.024	0.90

[a] See Figure 2. [b] Reciprocal of the fluorescence lifetime of PyH in an aerated BN or CH_3CN:H_2O (9:1) solution. [c] Fluorescence quenching rate constant (k_q in Table 2).

The $k_3/(k_3 + k_4)$ ratio in the oil-in-water emulsion (0.32) was larger than that in the CH_3CN:H_2O solution (0.024), indicating that the reaction efficiency of the PyH radical cation with CN^- in the emulsion was lower than that in the homogeneous solution. This is readily understood by analogy with the discussion of the droplet-size effects shown in Figure 3. As discussed in the preceding section, the PyH cation radical in the droplet interior is likely to deactivate before the reaction with CN^-, which is disadvantageous for photocyanation in the droplets as compared to in the homogeneous solution. Nevertheless, the overall reaction yield in the emulsion is higher than that in the homogeneous solution. This is due to the smaller $k_5/(k_5 + k_6)$ ratio in the emulsion (0.73) as compared to that in the CH_3CN:H_2O mixture (0.90) and, thus, to larger k_6 in the former system. It has been reported that O_2 or $O_2^{\bullet-}$ acts as a reagent for oxidative dehydrogenation of a cyanated aryl radical. Zuihof et al. have reported that the energy barrier for abstracting the hydrogen atom from 1-cyano-1-hydronaphthyl radical by O_2 or $O_2^{\bullet-}$ is 28 or <2 kcal/mol, respectively. Assuming equal concentrations of O_2 and $O_2^{\bullet-}$ at room temperature, these values indicate that the hydrogen atom abstraction rate by $O_2^{\bullet-}$ is 10^{17} times faster than that by O_2. Therefore, we suppose that oxidative dehydrogenation of the cyanated pyrenyl radical is primary ascribed to $O_2^{\bullet-}$ formed by the reaction between O_2 and $DCB^{\bullet-}$, as shown in the Scheme 1. Although the cyanation reaction in eq 4 proceeds *at* or *in the vicinity of* the droplet/water interface, oxidative dehydrogenation of the $PyHCN^{\bullet}$ radical by $O_2^{\bullet-}$ would take place in the droplet interior, owing to nonionic nature of the radical. The oxidation reaction in the oil droplet is favorable, since the solubility of O_2 in an oil (1.9 mM)[32a] is higher than that in water (0.3 mM). On the other hand, the concentration of O_2 in CH_3CN (1.4 mM)[32b] is lower than that in BN. Furthermore, $O_2^{\bullet-}$ produced by ET from DCB to O_2 in the BN droplet will be more stable than that in the CH_3CN:H_2O solution, since $O_2^{\bullet-}$ is likely to react with water (H^+) to produce an HO_2 radical in the latter system. Therefore, the smaller $k_5/(k_5 + k_6)$ ratio in the emulsion compared to that in the homogeneous CH_3CN:H_2O solution would be a reasonable consequence.

According to the Stern–Volmer plots, the limiting quantum yield is 2.5-fold higher for the emulsion as compared with that in the homogeneous solution, while the $k_3/(k_3 + k_4)$ and $k_5/(k_5 + k_6)$ ratios observed in the emulsion were ~130 times larger and 1.2-fold smaller than those in the homogeneous solution, respectively. Therefore, one of the primary reasons for the high photocyanation efficiency in the emulsion is concluded to be the rate constant (k_6) and the subsequent rate of oxidative dehydrogenation of the $PyHCN^{\bullet}$ radical.

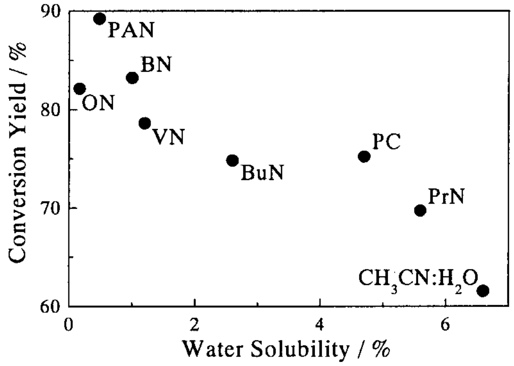

Figure 4. A water solubility dependence of the conversion yield of PyCN. The reaction conditions were the same with those in Figure 1. The water solubility in an oil was estimated on the basis of the absorbance at ~5260 cm^{-1} (combination tone of OH stretch).[33] VN, BuN, and PrN represents valeronitrile, butyronitrile, and propionitirile, respectively, and other abbreviations are the same with those in Table 2.

Bunce and co-workers reported that the photocyanation yield of naphthalene or biphenyl in a CH_3CN:H_2O mixture in the presence of DCB decreased from ~30 to ~20% as the water content increased from 0 to 50%.[8] We think that the solubility of water in the oil phase is another important factor determining the yield. Therefore, we studied the water solubility dependence of the photocyanation yield by varying the nature of the oil. Besides the water solubility, the variation of the oil changes solution properties such as dielectric constant and O_2 solubility. Therefore, Φ_{CN} also varied with the system, and the results on the water solubility dependence on the photoreaction were not straightforward. Nonetheless, the data in Figure 4 demonstrate that the conversion yield increases from 62 to 89% with a decrease in the water solubility in an oil phase from 6.6 to 0.48%. These results indicate that a side reaction becomes more efficient in an oil droplet having a higher water solubility, as reported by Bunce et al.[8] The possible side reaction is considered to be photoamidation and/or thermal amidation of PyCN with O_2 ($O_2^{\bullet-}$) and H_2O acting as oxidation/amidation reagents. Furthermore, the increase in the water solubility in an oil causes protonation of $O_2^{\bullet-}$, which is disadvantageous for the overall reaction efficiency, as discussed above. In our investigations, BN and PAN (phenylacetonitrile) are the best oil media for the present high quantum yield and high conversion photocyanation reaction. Further detailed photocyanation mechanisms in the emulsion system would be revealed by single droplet experiments and transient absorption spectroscopy, which are now in progress in this laboratory and will be reported in separate publications.

Conclusion

We demonstrated the solvent, surfactant, droplet-size, and water-solubility effects on the photocyanation yield of pyrene in oil-in-water emulsion systems. It is worth

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(32) (a) Konishi, T.; Fujitsuka, M.; Ito, O. *Chem. Lett.* **2000**, *3*, 202. (b) Coetzee, J.; Kolthoff, I. M. *J. Am. Chem. Soc.* **1957**, *79*, 6110.

(33) Kolthoff, I. M.; Elving, Ph. J. *Treatise on Analytical Chemistry*; Interscience Publishers: New York, 1961; Part II, Vol. 1.

emphasizing that the quantum yield of PyCN formation as high as 0.68 has been achieved in the presence of a cationic surfactant, DTAC. Furthermore, we showed for the first time the droplet-size dependence of the reaction yield in the emulsion system. This demonstrates that the reaction yield can be controlled through the droplet size, which is a very unique characteristics of the present emulsion system. The emulsion method could be used as a new synthetic approach to various cyanoaromatics.

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