Temperature Dependence of Photosensitized Nucleophilic Addition to Alkenes

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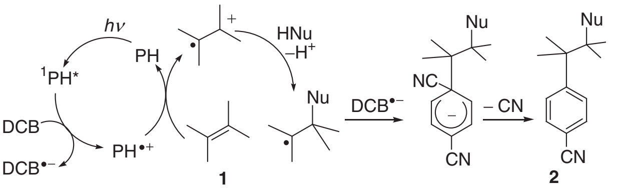
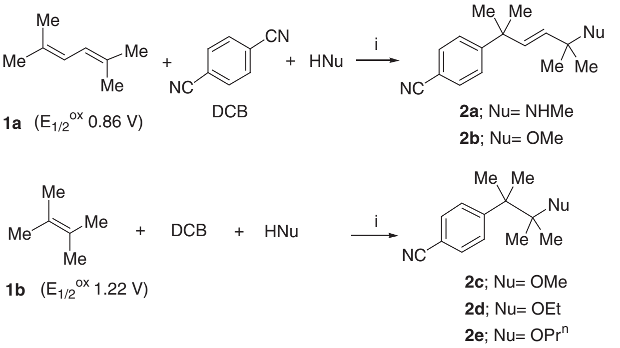
Photosensitized nucleophilic additions of 2,5-dimethyl-2,4-hexadiene and 2,3-dimethyl-2-butene were performed in a microchannel reactor using phenanthrene and *p*-dicyanobenzene as a redox pair. The quantum yields for the formation of photo-NOCAS products were remarkably enhanced at lower temperatures. The exciplex formation disturbed the reaction at higher temperatures.

A pair of aromatic hydrocarbon and aromatic nitrile is the most familiar donor and acceptor pair to enable the sensitizing of a variety of photoinduced electron-transfer reactions.[1] However, this pair tends to undergo a strong exciplex interaction, competing with the formation of free ion radicals even in polar solvents.[2] Therefore the generation of free ion radicals has been enhanced by applying polar solvent[3] and salt effects.[4] Also, temperature effects are a useful method to control the interaction between the donor and acceptor. In general the encounter rate becomes higher at high temperature.[5] Here, we report on a temperature dependence on redox-sensitization of the pair of phenanthrene (PH) and *p*-dicyanobenzene (DCB) toward nucleophilic addition reaction of simple alkenes **1**, which proceeds through the generation of cation radicals of **1** by the redox-photosensitization by the PH/DCB pair (Scheme 1).[1]

The PH/DCB-photosensitized nucleophilic addition (PNA) with nucleophiles (HNu) such as $MeNH_2$ and alcohols were applied to 2,5-dimethyl-2,4-hexadiene (**1a**) and 2,3-dimethyl-2-butene (**1b**) which had no absorption at >300 nm.[6] In order to prevent the further reaction of the products and control the reaction temperature precisely, the PNA was examined by the flow system using a microchannel reactor (MCR) which was kept at a given reaction temperature (T, 5–50 °C). The reactant solution flowed from an inlet into the microchannel using a microsyringe pump and was irradiated >290 nm with a high pressure Hg lamp. Irradiation time was equal to the retention time (Z) in the MCR which was adjusted to be 9.4, 32, 63, 94, and 118 s by changing the flow rate (F) in 10, 3.0, 1.5, 1.0, and 0.8 µL min^{-1}: $Z = 60 \times V/F$ where the channel volume (V) was 1.57 µL.



Scheme 1. Photosensitized nucleophilic addition reaction.



Scheme 2. The PH/DCB redox-photosensitized nucleophilic addition (PNA) of **1** in MCR: (i) *hν*, PH.

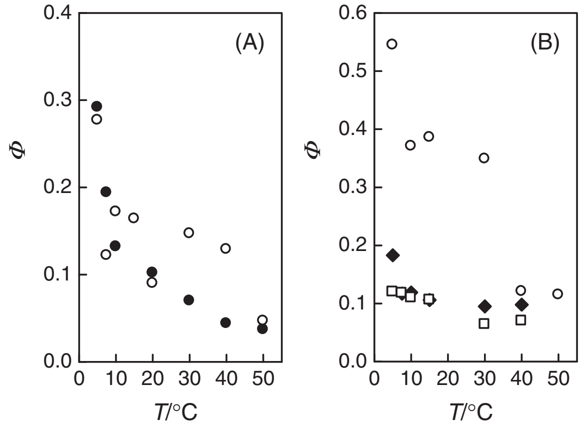


Figure 1. The temperature dependence of *Φ* for (A) the formation of **2a** (●) and **2b** (○) from the PNA reaction of **1a** and (B) the formation of **2c** (○), **2d** (◆), and **2e** (□) from the PNA reaction of **1b**.

The PNA of **1a** with $MeNH_2$ and MeOH in MCR gave **2a** and **2b**, respectively. Similarly the PNA of **1b** with ROH (R = Me, Et, and *n*-Pr) gave **2c**–**2e** (Scheme 2).[7] The quantum yields (*Φ*) for the formation of **2a**–**2e** were determined at various *T*. Figure 1 shows the *T*-dependence of *Φ*. As *T* became lower, the *Φ* became higher. The chemical and quantum yields of **2a**–**2e** in the PNA reaction under the optimized *T* and *Z* are summarized in Table 1.

As shown in Scheme 1, the PNA was initiated by the electron transfer from the excited singlet state of PH to DCB to give the cation radical of PH (PH$^{•+}$) and the anion radical of DCB (DCB$^{•-}$). This step was examined by the quenching of the fluorescence PH ($\lambda_{max} = 365$ nm) by DCB in MeCN–H_2O

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Table 1. Yields of **2a**–**2e** in PNA Reaction of **1** in MCR under the Optimized Conditions[a)]

1	PH /mM	HNu	Z/s[b)]	**2**[c)] (yield/%)	Conv. /%[d)]	Φ
1a	0.05	$MeNH_2$	63	**2a** (93)	94	0.29
1a	0.05	MeOH	63	**2b** (96)	96	0.28
1b[e)]	0.10	MeOH	94	**2c** (67)	100	0.54
1b[e)]	0.10	EtOH	118	**2d** (62)	100	0.18
1b[e)]	0.10	*n*-PrOH	118	**2e** (67)	100	0.12

a) Irradiation was performed for an MeCN–H_2O solution (19:1) containing **1** (0.2 M), DCB (0.1 M), PH (0.05 M), and $MeNH_2$ (0.2 M) and an MeCN–ROH solution (2:1) containing **1** (0.2 M), DCB (0.1 M), and PH (0.05 M) at 5 °C. b) Reaction time (Z) in MCR. c) Chemical yields based on DCB used. d) The conversion of DCB. e) In MeCN–ROH (3:1).

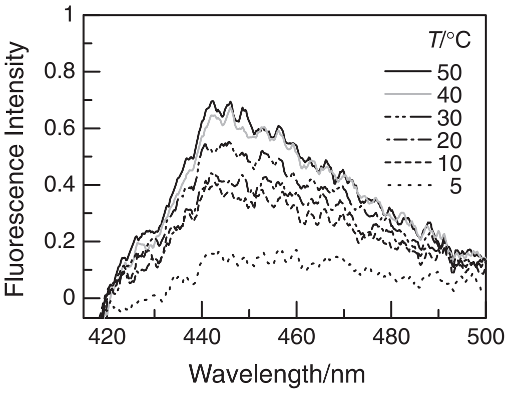


Figure 2. Temperature dependence of the exciplex emission between PH and DCB.

(19:1) at various T. The rate constant (k_Q) was determined from the Stern–Volmer constants and the fluorescence lifetime (τ) of PH (57.5 ns).[8] As the k_Q depended on T as has been reported in a variety of donor–acceptor systems,[5] the k_Q values gradually increased from $6.75 \times 10^9\,M^{-1}\,s^{-1}$ at 5 °C to $1.11 \times 10^{10}\,M^{-1}\,s^{-1}$ at 40 °C. Thus, the k_Q values were smaller at the lower T, although the Φ values were larger at the lower T. Arrhenius plots of $\ln k_Q$ vs. $1/(T + 273)$ led to the activation enthalpy ($E_a = 10.0\,kJ\,mol^{-1}$) and the frequency factor ($\log A = 11.8$).[5]

Moreover, a weak exciplex emission of $^1[PH\bullet DCB]^*$ was remarkably observed at 442 nm with an isoemissive point at 420 nm at higher T, as shown in Figure 2 which was the spectral subtraction between the fluorescences in the absence and the presence of DCB (5 mM). These suggested that the formation of the radical ion ($PH^{\bullet+}$ $DCB^{\bullet-}$) took place competitively with the exciplex formation at higher T.

In general, the exciplex formation occurred in less polar solvents whereas the radical ion pair formed predominantly in polar solvents.[9] The solvent parameter, $E_T{}^N$ values, of MeCN–H_2O (19:1) and MeCN–MeOH (3:1) were measured in various T and were plotted against T in Figure 3A. The $E_T{}^N$ values of these solvents were higher at lower T. Moreover, the plots of viscosity (η) against T are shown in Figure 3B. The η of the mixed solvents were higher at lower T. Therefore, it is expected that the exciplex formation is favorable at higher T, due to low polarity and low viscosity.

A hole transfer from $PH^{\bullet+}$ to **1** could occur exothermically to generate the cation radical of **1**, since the oxidation potential of PH (1.29 V vs. $Ag/AgNO_3$)[8] was higher than those of **1a** (0.86 V)[6] and **1b** (1.22 V).[6] The hole-transfer process proceeded at near diffusional controlled limits ($10^{10}\,M^{-1}\,s^{-1}$). On the other hand, the rate constant for the nucleophilic reaction of $MeNH_2$ to $PH^{\bullet+}$ was found to be $2 \times 10^8\,M^{-1}\,s^{-1}$.[10] This is a reason why hole transfer from $PH^{\bullet+}$ to **1** proceeded efficiently without the occurrence of the nucleophilic attack of $MeNH_2$ to $PH^{\bullet+}$. The cation radical of **1** allowed the nucleophilic addition of HNu to give adduct radicals which underwent to the *ipso*-substitution on $DCB^{\bullet-}$ to give the photo-NOCAS (photochemical nucleophile–olefin combination, aromatic substitution) products **2** combined between HNu, **1**, and DCB.

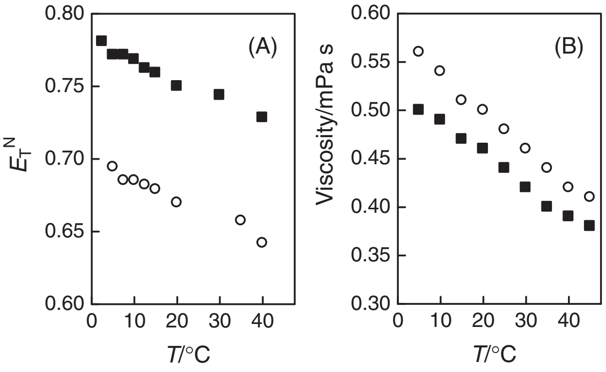


Figure 3. Temperature-dependence of (A) solvent parameter ($E_T{}^N$) and (B) viscosity (η) of MeCN–H_2O (19:1) (○) and MeCN–MeOH (3:1) (■).

$$PH^* + DCB \xrightarrow{k_{RI}} \underset{\text{Radical ions}}{PH^{\bullet+}\ DCB^{\bullet-}} \xrightarrow{\beta} \longrightarrow \mathbf{2}$$

$$PH^* + DCB \xrightarrow{k_{EX}} \underset{\text{Exciplex}}{^1[PH\bullet DCB]^*}$$

$$PH^* \xrightarrow{1/\tau} PH$$

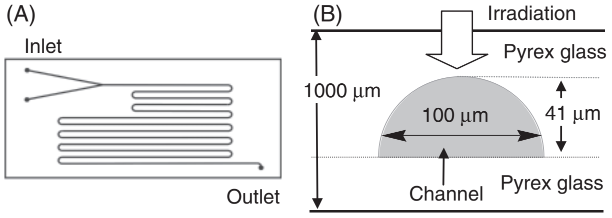
$$k_Q = k_{RI} + k_{EX} \qquad (1)$$

$$\Phi = \beta k_{RI}[DCB]/(1/\tau + k_{RI}[DCB] + k_{EX}[DCB]) \qquad (2)$$

Scheme 3.

Scheme 3 can be postulated as the quenching process of PH with DCB when k_{EX} and k_{RI} are defined to be the rate constants for the formation of the exciplex and the radical ions, respectively. The k_Q was equal to summation of k_{EX} and k_{RI} (eq 1). As mentioned above, $\log A$ was small. Therefore, the E_a can be assigned to be the activation energy for the formation of the exciplex from PH^* and DCB. Probably the k_{RI} was constant to T.

The Φ can be represented by eq 2 where β denotes the efficiency of the process from $\mathbf{1}^{\bullet+}$ to **2**. The Φ values were almost the same in the PNA of **1a** by $MeNH_2$ and MeOH with different nucleophilicities. Moreover, the nucleophilic addition to the localized positive charge of $\mathbf{1}^{\bullet+}$ is expected to be faster than the case of $PH^{\bullet+}$ where the positive charge delocalized over the π-conjugation. Therefore, the nucleophilic addition to $\mathbf{1}^{\bullet+}$ was thought to be near the diffusion-controlled limit ($10^{10}\,M^{-1}\,s^{-1}$). It was deduced that the quantum yield (β) for the process from $\mathbf{1}^{\bullet+}$ to **2** was high and independent of T.



Scheme 4. (A) Top view and (B) cross section of MCR: width = 100 μm; depth = 41 μm, length = 500 mm, volume (V) = 1.57 μL.

Therefore, the T-dependence on Φ can be attributed to the T-dependence on the interaction of $^1PH^*$ to DCB.

Thus, k_Q became higher but Φ for the PNA reaction were lower at higher T where the exciplex formation occurred considerably. Judging from these results, it was concluded that the exciplex formation retarded the PNA reaction of **1**. Thus, we found the PNA which is a convenient synthetic method to introduce functional groups to alkenes can be enhanced by lowering the reaction temperature.

Experimental

Instruments. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were taken on a Bruker AV 400M spectrometer for $CDCl_3$ solutions with tetramethylsilane used as an internal standard. The viscosity (η) of the mixed solvents was measured on a viscometer SV-10 (A&D Co., Limited). A Pyrex glass MCR (ICC-SY500) was purchased from Institute of Microchemical Technology (IMT, Kanagawa, Japan). The channel shape was as follows: channel width: 100 μm, channel depth: 41 μm, cross-section area: 3.14×10^{-5} cm^2, length: 50 cm, V: 1.57 μL (Scheme 4). The MCR was set in a water bath which was kept at a given T by the temperature-controlling circulator.

The PNA Reaction in MCR. An MeCN–H_2O solution (19:1) containing **1a** (0.2 M), DCB (0.1 M), and PH (0.05 M), and $MeNH_2$ (0.2 M) was introduced to the MCR under irradiation. The reaction solution (1 mL) was collected from the outlet of the MCR and subjected to separation by column chromatography to give **2a**. In the cases of PNA reaction of alcohols (ROH), MeCN–ROH (R = Me, Et, and *n*-Pr) solution (2:1 and 3:1) containing **1** (0.2 M), DCB (0.1 M), and PH (0.05 or 0.1 M) was irradiated in MCR to give **2b**–**2e**.

2-(4-Cyanophenyl)-2,5-dimethyl-5-methylamino-3-hexene (2a): ^{1}H NMR: δ 1.19 (s, 6H), 1.41 (s, 6H), 1.59 (s, 1H), 2.28 (s, 3H), 5.42 (d, $J = 16.0$ Hz, 1H), 5.62 (d, $J = 16.0$ Hz, 1H), 7.43 (d, $J = 8.4$ Hz, 2H), 7.58 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR: δ 26.95, 28.74, 29.43, 40.73, 53.80, 109.64, 119.08, 127.03, 132.00, 135.04, 136.67, 154.80.

2-(4-Cyanophenyl)-5-methoxy-2,5-dimethyl-3-hexene (2b): ^{1}H NMR: δ 1.28 (s, 6H), 1.42 (s, 6H), 3.16 (s, 3H), 5.48 (d, $J = 16.0$ Hz, 1H), 5.72 (d, $J = 16.0$ Hz, 1H), 7.43 (d, $J = 8.8$ Hz, 2H), 7.59 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR: δ 25.92, 28.61, 40.75, 50.29, 74.74, 109.78, 119.02, 127.00, 132.05, 133.04, 138.09, 154.49.

2-(4-Cyanophenyl)-3-methoxy-2,3-dimethylbutane (2c): ^{1}H NMR: δ 1.00 (s, 6H), 1.38 (s, 6H), 3.11 (s, 3H), 7.53 (d, $J =$ 8.8 Hz, 2H), 7.57 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR: δ 19.80, 24.31, 46.00, 49.42, 78.27, 109.24, 119.39, 129.44, 130.67, 153.30.

2-(4-Cyanophenyl)-3-ethoxy-2,3-dimethylbutane (2d): ^{1}H NMR: δ 0.99 (s, 6H), 1.10 (t, $J = 6.9$ Hz, 3H), 1.38 (s, 6H), 3.27 (quint, $J = 6.9$ Hz, 4H), 7.53 (d, $J = 8.8$ Hz, 2H), 7.59 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR: δ 15.96, 20.46, 24.24, 45.91, 56.52, 77.89, 109.13, 119.42, 129.52, 130.51, 153.44.

2-(4-Cyanophenyl)-2,3-dimethyl-3-propoxybutane (2e): ^{1}H NMR: δ 0.87 (t, $J = 7.4$ Hz, 3H), 0.99 (s, 6H), 1.38 (s, 6H), 1.45 (qt, $J = 7.4, 6.3$ Hz, 2H), 3.18 (t, $J = 6.3$ Hz, 2H), 7.52 (d, $J = 8.8$ Hz, 2H), 7.58 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR: δ 11.04, 20.34, 23.72, 24.24, 46.02, 62.71, 77.67, 109.11, 119.42, 129.57, 130.49, 153.44.

Determination of Quantum Yield. The conversion curve was obtained from the PNA reaction under varying irradiation times controlled by the flow rate at a given T. From the slope of the straight line of the conversion curve, the production amounts of **2** per second were obtained. Light intensity per second adsorbed by sensitizer (PH) was determined to be 7.28×10^{-6} einstein s^{-1} using the photoamination of PH (0.1 M) with $MeNH_2$ (0.5 M) in the presence of DCB (0.1 M) in the MCR as chemical actinometer where the quantum yield for the formation of 9-methylamino-9,10-dihydrophenanthrene has been found to be 0.141.[10] Here the concentration of PH of actinometer was set to be the same as that for the PNA reaction. Thus the Φ for the formation of **2** was calculated by the division of the production amounts of **2** per one second by light intensity per one second.

Measurements of Solvent Polarity (E_T^N). The solvent polarity of MeCN–H_2O (19:1) and MeCN–MeOH (3:1) at various T was evaluated by the solvent parameter, $E_T(30)$, which was the wavelength in kcal mol^{-1} at the absorption maxima of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Reichardt's dye)[11] in the sample solvent. The $E_T(30)$ was transformed to E_T^N by the equation: $E_T^N = (E_T(30) - 30.7)/32.4$.

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