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# Electron-transfer induced rearrangement of thiocyanate to isothiocyanate

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## Abstract

Benzyl thiocyanates with an electron-withdrawing group (**1a**, **1b**) and 9-fluorenyl thiocyanate (**1e**) rearrange to the corresponding isothiocyanate (**2**) under 9,10-diphenylanthracene (DPA) sensitization. The rearrangement would proceed via carbon–sulfur bond cleavage in an anion radical of **1** produced by photoinduced electron transfer, followed by back electron transfer to DPA$^{\cdot+}$ and recombination of the resulting radical or ion pair. © 2000 Elsevier Science Ltd. All rights reserved.

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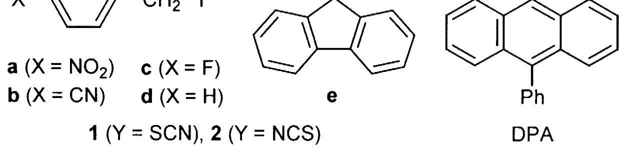
Organic thiocyanates and their isomeric compounds, i.e. isothiocyanates, are useful for syntheses of compounds containing both sulfur and nitrogen.[1] Although thermal or photochemical reactions of thiocyanates have been well investigated,[1–6] only a few studies of their ion radicals have been reported. Electrochemical studies of 4-nitrobenzyl thiocyanate (**1a**) have revealed that the benzylic carbon–sulfur bond of the anion radical of **1a** could be efficiently cleaved at the rate constant of about $2\times10^4$ s$^{-1}$, affording 4-nitrobenzyl radical and thiocyanate anion.[7] However, under these conditions the only products were 4,4′-dinitrobibenzyl and 4-nitrotoluene arising from the 4-nitrobenzyl radical; the rearrangement to the corresponding isothiocyanate (**2a**) did not occur. Photoinduced electron transfer (PET) has also been useful for a generation of ion radicals and it is expected that neutral radicals or ion pairs, resulting from back electron transfer, will play an important role. We report here the thiocyanate–isothiocyanate rearrangement via an anion radical under PET conditions.



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We used substituted benzyl thiocyanates (**1a**–**1d**) and 9-fluorenyl thiocyanate (**1e**) as the target thiocyanates, and 9,10-diphenylanthracene (DPA) as an electron-donative sensitizer. As listed in Table 1, the rate constant for fluorescence quenching of DPA by **1** ($k_q$) correlates with the free enthalpy changes ($\Delta G_{et}$) for the radical–ion pair formation in acetonitrile. Since the quenching rate in benzene is of the same order as in acetonitrile, we assume the formation of an exciplex (or a contact radical–ion pair) in benzene as well as the formation of a solvent-separated radical–ion pair in acetonitrile.† Unfortunately, the direct evidence of exciplex formation in benzene solution could not be obtained because of the lack of the exciplex emission, probably due to some chemical reactions (vide infra).

Table 1
The rate constants for DPA fluorescence quenching, the photoreaction results for **1** with DPA,[a] and the approximated free enthalpy changes for electron transfer [b]

| | $C_6H_6$ | | | $CH_3CN$ | | | $\Delta G_{et}$ |
|---|---|---|---|---|---|---|---|
| **1** | $10^{-9}k_q$ / $dm^3\ mol^{-1}\ s^{-1}$ | **1/2** ratio | yield / %[d] | $10^{-9}k_q$ / $dm^3\ mol^{-1}\ s^{-1}$ | **1/2** ratio | yield / %[d] | / $kJ\ mol^{-1}$ ($CH_3CN$) |
| **1a** | 25 | 63/37 | 65 | 15 | 99/1 | 100 | −100 |
| **1b** | 4.2 | 70/30 | 68 | 3.3 | 95/5 | 94 | −15 |
| **1c** | 0.6 | 99/1 | 100 | 0.5 | 99/1 | 100 | 29 |
| **1d** | 0.4 | 100/0 | 100 | 0.5 | 100/0 | 100 | >38 |
| **1e**[c] | 3.0 | 67/33 | 80 | 5.6 | 85/15 | 96 | 0.4 |

[a] Irradiation condition: 500-W Hg lamp, [**1**] = 0.01 mol $dm^{-3}$, [DPA] = 0.001 mol $dm^{-3}$, $\lambda > 350$ nm, 2 h.
[b] Calculated from the redox potentials of **1** (irreversible) and DPA and the excitation energy of DPA.
[c] $\lambda > 390$ nm.
[d] Total yield of **1** and **2**.

The results for photolyses of the solution containing both **1** (0.01 mol $dm^{-3}$) and DPA (0.001 mol $dm^{-3}$) under nitrogen atmosphere are shown in Table 1. It is found that only the stronger acceptors **1a**, **1b**, and **1e** afforded the isomeric mixture of **1** and **2** and they were more reactive in benzene than in acetonitrile.

Under the same conditions we also investigated the reverse reaction, i.e. the rearrangement from the isothiocyanate **2b**, but found that **2b** was almost completely recovered after irradiation for 2 hours both in benzene and in acetonitrile.‡ This would be due to the difference in strength between the carbon–sulfur bond in $\mathbf{1b}^{\cdot -}$ and the carbon–nitrogen bond in $\mathbf{2b}^{\cdot -}$.

Thermolysis and direct photolysis of benzyl thiocyanates (**1a**–**1d**) also afforded the corresponding isothiocyanates (**2a**–**2d**), whereas in the case of 9-fluorenyl thiocyanate (**1e**) either thermolysis in DMF or direct photolysis resulted in yielding a complex mixture, and the only isolated product in thermolysis was 9,9′-bifluorenylidene (3%).[10]

In order to gain insight into the reaction, we performed laser flash photolysis (LFP) experiments. When a deaerated acetonitrile solution containing both **1e** (0.01 mol $dm^{-3}$) and DPA (0.3 mmol $dm^{-3}$) was irradiated by a 355-nm nanosecond laser pulse (Nd-YAG), a sharp absorption band at around 500 nm was observed concomitant with absorption due to $DPA^{\cdot +}$ (Fig. 1c).[11] With reference to previous reports[12–15] and because of the nature of rapid quenching by molecular oxygen, the sharp 500-nm absorption can be

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† In the present case, free enthalpy changes for the radical–ion pair formation in benzene may be comparable to those in acetonitrile, because the decrease of the solvation energies will be cancelled by the increase of the Coulombic interaction between the more contacted radical–ions. See Refs. 8 and 9.

‡ Prolonged irradiation (30 h) of the benzene solution containing DPA and **1b** and/or **2b** afforded a complex mixture due to some secondary reactions, so that we could not find the stationary state.

assigned to a fluorenyl radical (FL·). If **1e**$^{\cdot -}$ survived, we expected to observe the absorption of **1e**$^{\cdot -}$ at the same region (550–750 nm) as the fluorene anion radical.[§] The spectrum shape in this region at 1 μs after laser pulse, however, is identical to the spectrum of DPA$^{\cdot +}$ without **1e**, which would be generated via photoionization as already mentioned by Wayner et al.,[11] so that within at least 1 μs **1e**$^{\cdot -}$ should be cleaved to FL· and SCN$^-$. The above observations indicate that the cleavage of the carbon–sulfur bond definitely occurs even in acetonitrile solutions in which the recovery of **1** is relatively high.

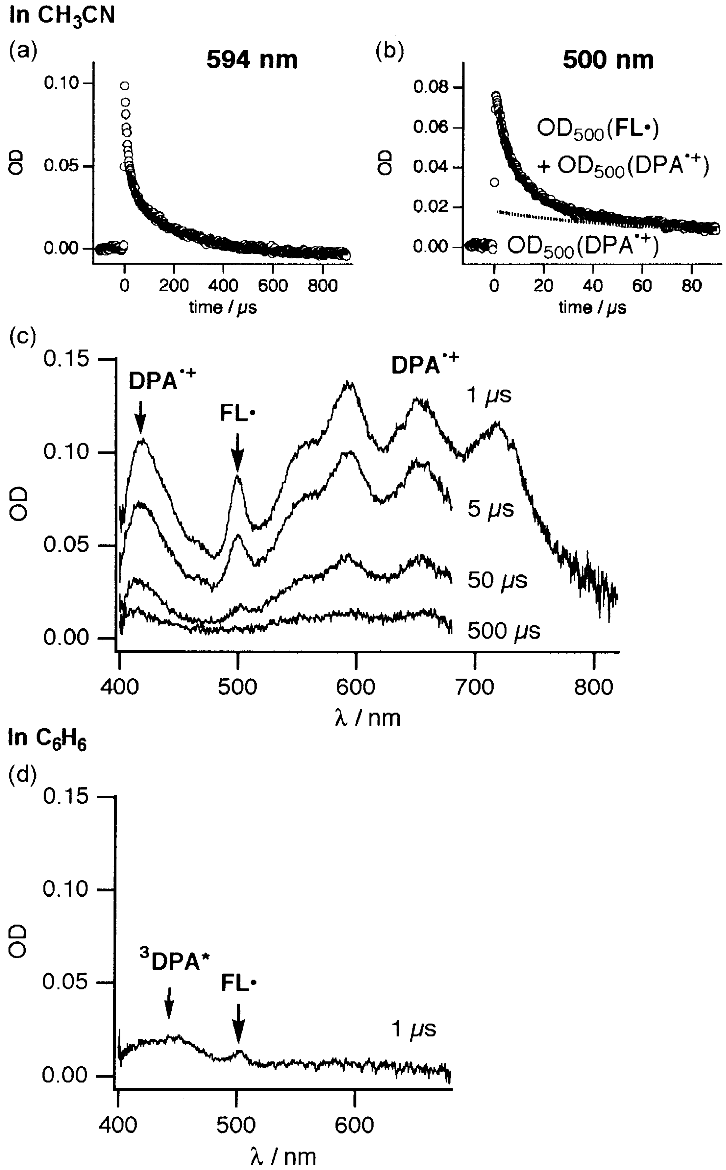

Fig. 1. Transient decay traces (a, b) and absorption spectra (c, d) after 355-nm laser excitation in deaerated solutions containing **1e** and DPA ([**1e**]=0.01 mol dm$^{-3}$, [DPA]=0.3 mmol dm$^{-3}$).

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[§] It is reported that the fluorene anion radical absorbs light at 650 and 707 nm in MTHF matrix. See Ref. 16.

The decay of DPA$^{\cdot+}$ was over 20 times slower in the presence of **1e** ($k_{\mathrm{d}}^{\mathrm{DPA}\cdot+}=1.6\times10^{9}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$, Fig. 1a) than that of DPA$^{\cdot+}$ without **1e** ($3.9\times10^{10}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$).[¶] In this case, DPA$^{\cdot+}$ would be quenched by hole transfer to FL$\cdot$ and the fairly long lifetime of DPA$^{\cdot+}$ might be due to the lower oxidizability of FL$\cdot$ than the electron-attached acetonitrile.[‖,**]

We tried to determine the second-order rate constant of FL$\cdot$ decay. The decay rate constant of FL$\cdot$ at 500 nm can be calculated by fitting the residual trace obtained by subtraction of the DPA$^{\cdot+}$ component at 500 nm, which can also be calculated by using the $k_{\mathrm{d}}^{\mathrm{DPA}\cdot+}$ value and the OD ratio (Fig. 1b). Then the derived rate constant ($k_{\mathrm{obs}} = k_{\mathrm{d}}^{\mathrm{FL}\cdot}/d\varepsilon_{500}^{\mathrm{FL}\cdot}=3.01\times10^{6}$ s$^{-1}$ ($d$=1 cm)) and the reported molar extinction coefficient ($\varepsilon_{500}^{\mathrm{FL}\cdot}$) in methanol (3600 dm$^{3}$ mol$^{-1}$ cm$^{-1}$)[15] allow us to determine the second-order rate constant, $k_{\mathrm{d}}^{\mathrm{FL}\cdot}=1.1\times10^{10}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$, assuming $\varepsilon_{500}^{\mathrm{FL}\cdot}$ is solvent-independent. FL$\cdot$ would react not only with DPA$^{\cdot+}$ but also with SCN$^{-}$. Since the rate constant of the former reaction has already been determined as $1.6\times10^{9}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$ ($k_{\mathrm{d}}^{\mathrm{DPA}\cdot+}$) from the decay profile of DPA$^{\cdot+}$ (Fig. 1a), we can obtain the rate constant of the latter as $9.4\times10^{9}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$. This undoubtedly shows the reaction between FL$\cdot$ and SCN$^{-}$ can compete with the hole transfer from DPA$^{\cdot+}$ to FL$\cdot$.

The most reasonable pathway for the reaction between the benzyl-type radical, including FL$\cdot$, and SCN$^{-}$ would be S$_{\mathrm{RN}}$1-like nucleophilic attack of SCN$^{-}$ to the radical. Since SCN$^{-}$ has an ambident character, both the sulfur side and the nitrogen side of the anion can react as a nucleophilic center. As is well-documented, the affinity between the two chemical groups can be interpreted by the hard–soft-acid-base (HSAB) theory.[19,20] According to the HSAB theory, the softer sulfur atom of SCN$^{-}$ can react with a soft electrophile, whereas the harder nitrogen atom prefers the harder center. Actually, the variation of the thiocyanate/isothiocyanate ratio in the nucleophilic reaction of SCN$^{-}$ toward several carbocations has been well explained by using the HSAB theory, and in the case of 1-phenylethyl cation, which can be regarded as a harder carbocation, the ratio has been reported to be only 0.01.[3] The benzyl-type radical in the current case should be much softer than the corresponding benzyl-type cation. Therefore, the extent of the nucleophilic attack of the sulfur side of SCN$^{-}$ to the radical, leading to regeneration of the thiocyanate anion radical, would be higher than that in the case of the attack to the cation.

In a similar experiment in benzene the absorption of DPA$^{\cdot+}$ was not observed and only weak absorption (ca 0.005 at 1 μs) due to FL$\cdot$ was detected accompanied by the absorption of DPA triplet [21] at around 450 nm (Fig. 1d). The weaker absorption of FL$\cdot$ would reflect a fast back electron transfer within the solvent-cage [FL$\cdot$ SCN$^{-}$ DPA$^{\cdot+}$].

The mechanism of the rearrangement from **1** to **2** under DPA sensitization would be explained by Scheme 1. Both in acetonitrile and in benzene the stronger electron accepter (**1a**, **1b**, **1e**) effectively quenches the DPA excited singlet, affording the **1**$^{\cdot-}$–DPA$^{\cdot+}$ pair. The resulting **1**$^{\cdot-}$ would be dissociated to the benzyl-type radical and SCN$^{-}$ within 1 μs. In acetonitrile, as revealed by LFP experiments, the nucleophilic attack of SCN$^{-}$ to the radical center can compete with the hole transfer from DPA$^{\cdot+}$ to the radical, and the lower yield of **2** can be explained by assuming the sulfur side of SCN$^{-}$ does the nucleophilic attack more preferentially. On the other hand, in benzene, since the radical and the ions are kept in the same solvent cage, the rate for the electron transfer from the radical or SCN$^{-}$ to DPA$^{\cdot+}$ may increase as well as that for the nucleophilic attack of SCN$^{-}$ to the radical. However, the contribution of

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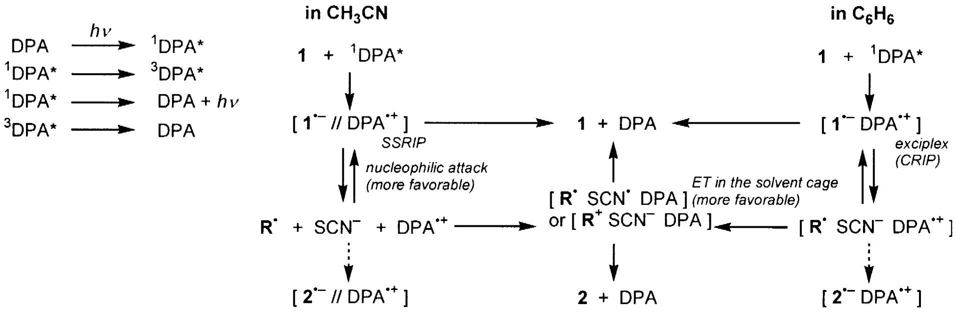
[¶] The decay of DPA$^{\cdot+}$ without **1e** seems to be slightly faster than the diffusion-controlled process, and this will probably be due to the contribution of the decay of DPA$^{\cdot+}$ pairing with the electron-attached acetonitrile molecule.

[‖] The lifetime of DPA$^{\cdot+}$ is affected by the presence of oxygen (longer than under a nitrogen atmosphere) and it is reasonably explained that the counter of DPA$^{\cdot+}$ (oxidation potential of DPA: +1.19 V versus SCE) is changed from FL$\cdot$ (oxidation potential: +0.76 V[17]) to the less reductive FL–O$_{2}\cdot$.

[**] FL$^{+}$ generated by the hole transfer could not be observed, which absorption should appear at around 515 nm as a broader band than that of FL$\cdot$.[18] This would be due to the rapid reaction of FL$^{+}$ with SCN$^{-}$.

the former process would be more significant than that in acetonitrile, so that the recombination of the benzyl-type radical (cation) and SCN radical (anion) resulting from the electron transfer within the cage would lead to higher yield of **2** analogously to the usual thermal or photochemical rearrangement.



Scheme 1.

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