Direct Observations of the Intermediate Species in the Photodissociation of Bis(*S*-benzyl-1,2-diphenyl-1,2-ethylenedithiolato)nickel by Time-Resolved EPR and UV–Vis Absorption Spectroscopy

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Bis(1,2-ethylenedithiolato or 1,2-benzenedithiolato)nickel complexes show unusual and useful physical and chemical properties originating from the unique electronic structure of the highly delocalized planar $NiS_4C_4R_4$ system.[1] The neutral complexes and their dianions, $(NiS_4C_4R_4)^{2-}$, undergo interesting reactions, mainly at the sulfur atoms.[2,3] Schrauzer et al. have prepared various S,S'-dialkyl and S,S'-diaralkyl derivatives[4–6] and showed that the latter undergo photolysis with C–S bond cleavage more rapidly aerobically than anaerobically, consistent with a homolytic process, ultimately affording the neutral nickel complexes and termination products derived from aralkyl radicals. The aim of the present study was to elucidate the mechanisum of photodissociation of bis(*S*-benzyl-1,2-diphenyl-1,2-ethylenedithiolato)nickel (**1**)[4,6,7] by means of EPR and UV–vis absorption spectrometry. We were interested primarily in the following questions: (1) Are intermediate radicals observed, and can they be assigned? (2) Does the dissociation of both C–S bonds in **1** occur in one step or in a stepwise fashion, with intermediate formation of the radical species $[Ni(S_2C_2Ph_2)\{S_2(CH_2Ph)C_2Ph_2\}]^{\bullet}$ (**2**)? (3) Which of the excited states (singlet or triplet) is responsible for the reaction? The possible existence of **2** was previously suggested by Schrauzer and Rabinowitz.[4]

To demonstrate the formation of **2** in the photolysis of **1**, a dilute benzene solution (ca. 1×10^{-3} M) of complex **1** was irradiated (>360 nm) by a 500-W Xe arc lamp with an appropriate filter. UV–vis absorption spectra were observed by using a Photal MCPD-1000 rapid-scan spectrometer. EPR spectra were observed with a JEOL RE 3X X-band EPR spectrometer. In a time-resolved EPR (TREPR) experiment, the deaerated solutions were allowed to flow into a quartz tube (i.d. = 4 mm) in a cavity at a rate of ca. 2 mL/min and were excited by a Lamda Physik LPX 100i excimer laser at 308 nm. The signals were observed with an NF BX-531 digital boxcar integrator. The details of the TREPR apparatus and experimental procedure have been reported elsewhere.[8]

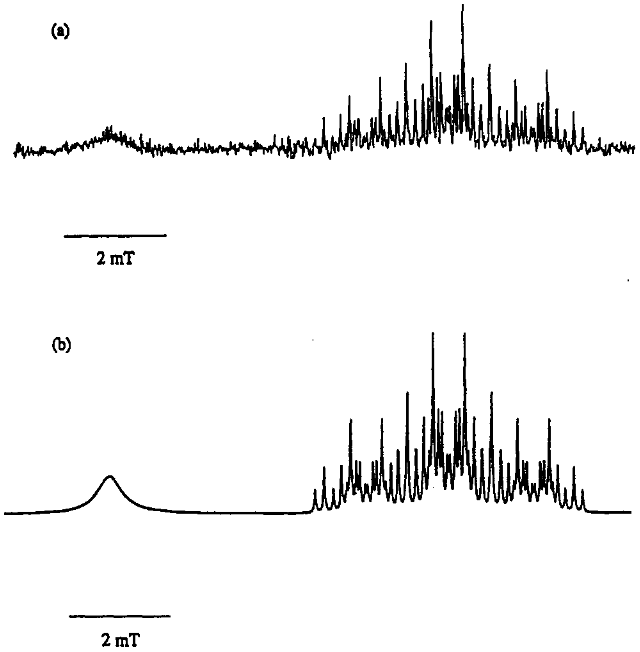

Figure 1. (a) Time-resolved EPR spectrum observed at 1 μs for the photodissociation of **1** in benzene at room temperature. (b) Simulated EPR spectrum of the benzyl radical.[9]

The TREPR spectrum was observed 1 μs after the laser pulse at room temperature, as shown in Figure 1a. EPR signals due to two kinds of radicals were observed. The one with $g = 2.0021$, which has rather complicated structure, is easily assigned to the benzyl radical by comparison with the simulated spectrum based on the reported hyperfine coupling constants[9] (Figure 1b). For another radical having $g = 2.042$, the assignment was made by comparing the spectrum with steady-state EPR spectra, which were observed with conventional EPR equipment. The steady-state EPR signal with $g = 2.042$ was observed at room temperature, as shown in Figure 2a, and is certainly assigned to the same radical as observed by TREPR (Figure 1a). The spectrum varied with temperature, reflecting an anisotropy of the *g* factor. The spectrum observed at 77 K is shown in Figure 2b, which is analyzed by an $S = {}^{1}/_{2}$ system with anisotropic *g* factors of $g_1 = 1.997$, $g_2 = 2.035$, and $g_3 = 2.088$ (Figure 2c). This radical is safely assigned to $[Ni(S_2C_2Ph_2)\{S_2(CH_2Ph)C_2Ph_2\}]^{\bullet}$ (**2**) by reference to the reported *g* factors of the radical, $[Ni(S_2C_2Ph_2)_2]^{\bullet-}$ having $g_1 = 2.000$, $g_2 = 2.043$, and $g_3 = 2.119$.[10] We now conclude that the benzyl radical and radical **2** were formed on a 10^{-7}-s time scale in the initial step of the reaction.

The other important result of the TREPR experiment is a polarity of the EPR signal. Both radicals gave absorptive TREPR signals with little distortions (Figure 1a,b). These polarizations are definitely due to a so-called triplet mechanism (TM). This

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(1) For reviews on this topic see: (a) Mueller-Westerhoff, U. T.; Vance, B. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 2, p 545. (b) Sugimori, A.; Kajitani, M. *Kagaku, Zokan (Kyoto)* **1988**, *115*, 113. (c) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49. (d) Schrauzer, G. N. *Transition Met. Chem.* (*N.Y.*) **1968**, *4*, 299–235.

(2) Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* **1965**, *87*, 1483.

(3) Kajitani, M.; Kohara, M.; Kitayama, T.; Akiyama, T.; Sugimori, A. *J. Phys. Org. Chem.* **1989**, *2*, 31.

(4) Schrauzer, G. N.; Rabinowitz, H. N. *J. Am. Chem. Soc.* **1968**, *90*, 4297.

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(6) Zhang, C.; Reddy, H. K.; Schlemper, E. O.; Schrauzer, G. N. *Inorg. Chem.* **1990**, *29*, 4100.

(7) On the basis of variable-temperature ^1H NMR measurements, Schrauzer et al. have indicated that two benzyl groups of this complex are bound to the S atoms in the different dithiolene rings, leading to three forms in equilibrium.[6] We use **1** as a representative of the three isomers.

(8) (a) Yamauchi, S.; Hirota, N. *J. Phys. Chem.* **1984**, *88*, 4631. (b) Tominaga, K.; Yamauchi, S.; Hirota, N. *J. Chem. Phys.* **1989**, *88*, 533.

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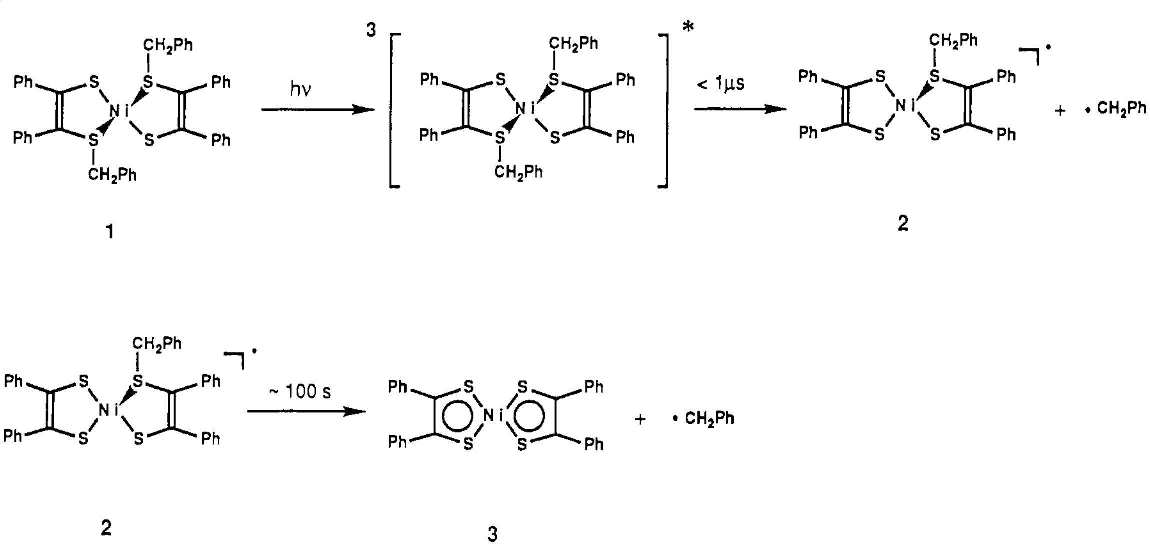
Scheme I



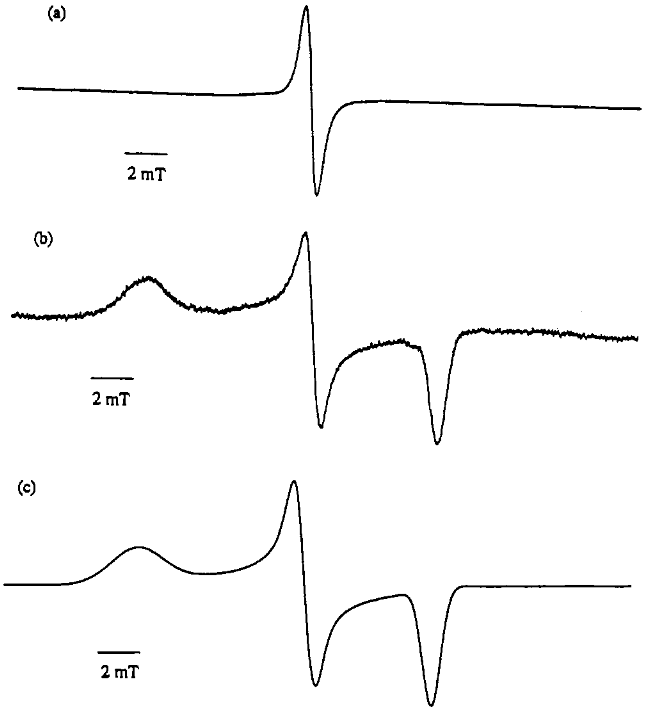


Figure 2. Steady-state EPR spectra observed for the photodissociation of **1** at (a) room temperature and (b) 77 K in benzene. Curve c is the simulated EPR spectrum of an $S = {}^1/_2$ system with $g_1 = 1.997$, $g_2 = 2.035$, and $g_3 = 2.088$.

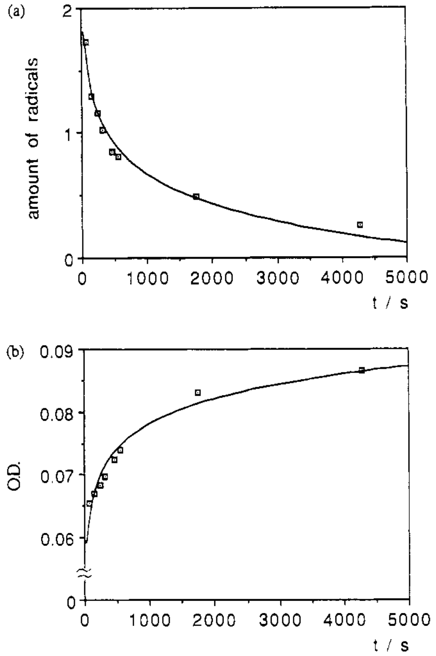


Figure 3. (a) Decay curve of the steady-state EPR signal (Figure 2a) and (b) rise of the absorption intensity observed at 857 nm in benzene at room temperature. These decay and rise curves were observed simultaneously.

indicates that the reaction occurs from the excited triplet state of dithiolato complex **1**. The moderate intensities of the TM signals observed further support that the first dissociation process occurs within an order of 1 μs.[11] In contrast, the second dissociation turned out to be very slow from the following experiment.

We have observed the decay of the steady-state EPR signal (Figure 2a) of intermediate **2** at room temperature. The radical decays very slowly with an order of 100 s, as shown in Figure 3a. Under the same experimental conditions, we observed time-resolved UV–vis absorption spectra. Each spectrum varied with time, having two isosbestic points around 350 and 700 nm. The ultimate spectrum, which has a finger print peak at 857 nm, is easily assigned as that of the free (dithiolato)nickel complex[4] $Ni(S_2C_2Ph_2)_2$ (**3**). The rise curve at 857 nm (Figure 3b) has the same time constant as that of the EPR decay (Figure 3a) of intermediate **2**. These results clearly indicate that intermediate radical **2** decomposes, forming product **3** on a 10^2-s time scale.[12]

On the basis of these results, we could determine the mechanism (Scheme I) involving the excited triplet state of **1** and two-step elimination of two benzyl radicals for the photodissociation of bis(*S*-benzyl-1,2-diphenyl-1,2-ethylenedithiolato)nickel.

Studies are continuing for complexes of different metals and benzyl derivatives, including detailed kinetic analyses.

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(12) The observation that both the rise and decay (Figure 3a,b) curves are not analyzed by a single-exponential function may by due to other reactions such as a disproportionation and/or a radical-coupling reaction.