

Photochromic Processes in Solutions of Di(mercaptoquinolinato)nickel(II) and Perfluoro-2,2'-dinaphthyl Disulfide

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Received April 21, 2011; in final form, December 30, 2011

Abstract—Reactions of transient species for a new photochromic system composed of perfluoro-2,2'-dinaphthyl disulfide ((SC₁₀F₇)₂ = (SNF)₂) and the planar complex di(mercaptoquinolinato)nickel(II) (Ni(SC₉H₆)₂ = Ni(SR)₂) in benzene solutions have been studied. Under UV irradiation, the disulfide dissociates yielding two sulfur-centered radicals (@SC₁₀F₇ @ @SNF), which rapidly enter into the coordination sphere of the Ni(II) ion to give the radical complex (@SNF)Ni(SR)₂. This species disappears in a second-order reaction yielding the dimer (RS)₂Ni(RSSR)Ni(SR)₂. The photochromic system returns to the initial state via dissociation of the dimer to the parent disulfide and two Ni(SR)₂ molecules.

DOI: 10.1134/S0018143912030034

Photochromic systems attract considerable attention due to their potential use in various engineering applications [1, 2]. Thus, discovery and investigation of new photochromic systems is not only of theoretical but also significant practical interest. Recently, we proposed novel photochromic systems that operate on the principle of reversible coordination of sulfur-centered radicals (S-radicals) to planar dithiolate complexes of divalent nickel [3–7]. The ability of planar Ni(II) complexes to reversibly coordinated extra ligands of the pyridine type [8–10] forms the basis for the designing of such systems. In order to convert N(II) complexes into photochromic systems, it is necessary that extra ligands be produced by the action of light. Disulfides are good objects for this purpose, since they dissociate to S-radicals under UV irradiation [11–13].

It was shown [3–7] that S-radicals coordinate to planar Ni(II) dithiolate complexes with a high rate constant. The coordination is reversible, resulting in recombination of S-radicals to the parent disulfide and, thus, imparting photochromic properties to such systems. The lifetime of radical complexes depends on the nature of both the radical and the Ni(II) complex and varies from microseconds to milliseconds. Repeated coordination can increase the effective lifetime of the radical complexes to periods on the order of seconds.

In this study, we examined the nature, spectroscopy, and reaction kinetics of transient species in a novel photochromic system containing perfluoro-

2,2'-dinaphthyl disulfide (SNF)₂ and the planar nickel(II) dimercaptoquinolate complex (Ni(SR)₂).

EXPERIMENTAL

Experiments were performed on a laser flash photolysis facility with a XeCl excimer laser (308 nm, 15 ns, 10 mJ) or a YAG : Nd laser (355 nm, 7 ns, 10 mJ) [14]. Millisecond-scale processes were studied in a microcell (*l* = 2–10 mm, *S* = 2 × 5 mm²) in which the volume of a solution is fully illuminated with a laser pulse. Thus arrangement precludes distortion of the transformation kinetics of transient species by convective flow in the cell.

Optical absorption spectra were recorded with an HP 8453 spectrophotometer. Spectrally pure solvents available from Merck were used to prepare solutions. The differential equations used in numerical calculation of the kinetics of transient optical absorption were solved with the software program developed for this purpose on the basis of the fourth-order Runge–Kutta method.

RESULTS AND DISCUSSION

The Ni–S and Ni–N distances in the planar Ni(SR)₂ complex are 2.40 and 2.06 Å, respectively [15]. The optical absorption spectrum of Ni(SR)₂ in benzene exhibits charge-transfer bands with maximums at 555, 396, 336, and 308 nm and absorption coefficients of 5900, 7240, 12270, and 11970 L mol⁻¹cm⁻¹, respectively [16]. Perfluoro-2,2'-dinaphthyl disulfide is characterized by an absorption

band peaked at 350 nm ($\epsilon = 10\,500\text{ L mol}^{-1}\text{ cm}^{-1}$). Continuous photolysis of a disulfide solution does not alter its optical spectrum. Nor $\text{Ni}(\text{SR})_2$ in benzene displays a photochemical activity.

The continuous photolysis of a $\text{Ni}(\text{SR})_2$ and $(\text{SNF})_2$ solution in benzene leads to disappearance of the absorption band of the complex at 555 nm and to the formation of a new spectrum (Fig. 1a). The isosbestic points at 406, 500, and 602 nm are retained during the course of photolysis. After cessation of irradiation, the optical spectrum returns to the initial pattern with the same isosbestic points (Fig. 1b). Thus, the solution of the complex $\text{Ni}(\text{SR})_2$ and the disulfide $(\text{SNF})_2$ is a photochromic system.

Absorbing UV photons, disulfides dissociate to give two sulfur-centered radicals [11–13]. Flash photolysis of $(\text{SNF})_2$ in benzene enabled us to record the absorption spectrum of the $\cdot\text{SNF}$ radical, which turned out to agree well with the spectrum of this radical in acetonitrile [12]. The decay of the absorption follows the second-order rate law and corresponds to recombination of $\cdot\text{SNF}$ into the parent disulfide:



The observed radical decay rate constant k_{obs} is linearly related to the initial absorbance of the radical (ΔD_0) after a laser pulse ($k_{obs} = 2k_1 \Delta D_0 / \epsilon_R l$), where $2k_1/\epsilon_R = (6.94 \pm 0.13) \times 10^5\text{ cm s}^{-1}$. To determine the absorption coefficient ϵ_R , we used the reaction of the S-radical with a stable nitroxyl radical [12]. The values of ϵ_R (395 nm) and $2k_1$ for the $\cdot\text{SNF}$ radical are given in the table.

During the flash photolysis of $(\text{SNF})_2$ in the presence of $\text{Ni}(\text{SR})_2$, absorption due to the S-radical appears after a laser pulse; this absorption within a few microsecond transforms with isosbestic points at 361, 407, 500, and 682 nm into a new spectrum (Fig. 2a) belonging to the radical complex $(\cdot\text{SNF})\text{Ni}(\text{SR})_2$:



The kinetics of reaction (2) is shown in the inset (Fig. 2b). Clearing induced at 555 nm is associated with the disappearance of absorption due to the initial complex $\text{Ni}(\text{SR})_2$.

Spectral and kinetic parameters of transient species induced by flash photolysis of a benzene solution of the disulfide $(\text{SNF})_2$ and the $\text{Ni}(\text{SR})_2$ complex

Species	λ , nm	$\epsilon \times 10^{-3}$	$2k_1 \times 10^{-9}$	$k_2 \times 10^{-9}$	$k_3 \times 10^{-9}$	$2k_4 \times 10^{-7}$	$k_5 \times 10^3, \text{ s}^{-1}$
		$\text{L mol}^{-1}\text{ cm}^{-1}$			$\text{L mol}^{-1}\text{ s}^{-1}$		
$\cdot\text{SNF}$	395	4.3 ± 0.1	2.7 ± 0.2	5.0 ± 0.2	1.8 ± 0.2		
$(\cdot\text{SNF})\text{Ni}(\text{SR})_2$	430	18.7 ± 1.0				3.5 ± 0.2	
$[(\text{SNF})\text{Ni}(\text{SR})_2]_2$	430	8.52					3.3 ± 0.2

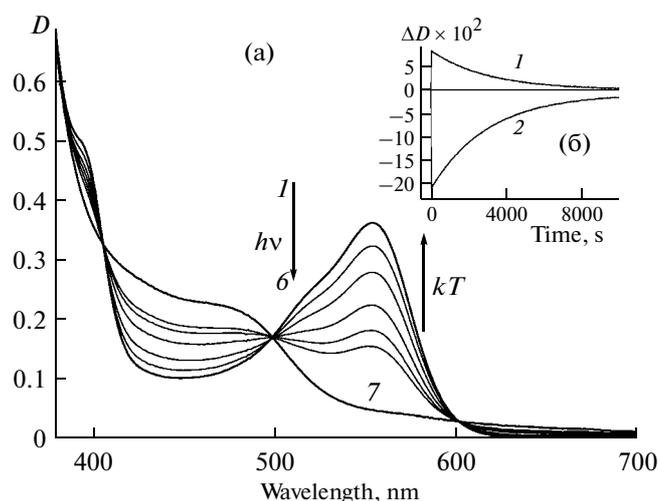


Fig. 1. (a) Change in optical absorption spectrum of a benzene solution of the disulfide $(\text{SNF})_2$ ($4 \times 10^{-5}\text{ mol L}^{-1}$) and the complex $\text{Ni}(\text{SR})_2$ ($1.1 \times 10^{-5}\text{ mol L}^{-1}$) during steady-state photolysis and the reverse dark reaction at 298 K with ($I-6$) 0, 50, 150, 500, 1000, and 1500 laser pulses (308 nm, 10 Hz), respectively, and (7) calculated spectrum of the photolysis product. (b) Kinetics of change in absorption at (1) 460 and (2) 555 nm during the reverse dark reaction (exponential curves with a time constant of 3000 s).

The time dependences for the concentrations of the S-radical $R(t)$ and the radical complex $A(t)$ in the case of radical recombination are defined as follows:

$$\frac{R(t)}{R_0} = \frac{e^{-k_2 C_0 t}}{1 + \frac{2k_1 R_0}{k_2 C_0} (1 - e^{-k_2 C_0 t})}, \quad (3)$$

$$\frac{A(t)}{R_0} = \frac{k_2 C_0}{2k_1 R_0} \ln \left[1 + \frac{2k_1 R_0}{k_2 C_0} (1 - e^{-k_2 C_0 t}) \right],$$

where C_0 and R_0 are the initial concentrations of the complex $\text{Ni}(\text{SR})_2$ and the S-radical, respectively. A change in absorbance (optical density) in flash photolysis experiments is defined by the expression:

$$\Delta D(t) = \epsilon_R R(t)l + (\epsilon_A - \epsilon_C) A(t)l, \quad (4)$$

where ϵ_R , ϵ_A , and ϵ_C are the absorption coefficients of the S-radical, the radical complex, and the initial complex, respectively. The absorbance ratio at the

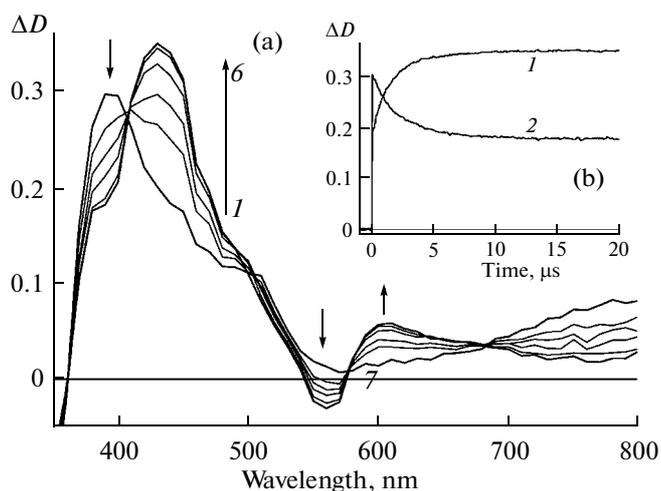


Fig. 2. (a) Transient spectra arising during laser flash photolysis (308 nm) of a benzene solution of $(\text{SNF})_2$ ($6.25 \times 10^{-4} \text{ mol L}^{-1}$) and $\text{Ni}(\text{SR})_2$ ($1.28 \times 10^{-4} \text{ mol L}^{-1}$) at $T = 298 \text{ K}$: (1–6) spectra at 0, 0.1, 0.3, 0.7, 1.3, and 5 ms, respectively. (b) Kinetics of change in absorbance at (1) 430 and (2) 560 nm.

maximum of the $(\text{SNF})\text{Ni}(\text{SR})_2$ absorption band (ΔD_∞ at 430 nm) at times when the formation of this complex is completed ($50 \mu\text{s}$) and at the maximum of the S-radical absorption band (ΔD_0 at 390 nm) after a laser pulse is as follows:

$$\frac{\Delta D_\infty}{\Delta D_0} = \frac{\varepsilon_A - \varepsilon_C}{\varepsilon_R} \frac{k_2 C_0}{2k_1 R_0} \ln \times \left(1 + \frac{2k_1 R_0}{k_2 C_0} \right) \xrightarrow{R_0 \rightarrow 0} \frac{\varepsilon_A - \varepsilon_C}{\varepsilon_R} \quad (5)$$

When the intensity of the laser pulse decreases, this ratio becomes $\Delta D_\infty / \Delta D_0 \xrightarrow{R_0 \rightarrow 0} 4.37 \pm 0.20$ and $\varepsilon_A = \varepsilon_C + 4.37\varepsilon_R = 18700 \pm 1000 \text{ L mol}^{-1} \text{ cm}^{-1}$. This value of ε_A made it possible to calculate the rate constant k_2 for the coordination of the SNF radical to the complex $\text{Ni}(\text{SR})_2$ (table).

Numerical solution of the differential equations with the known values of ε_C , ε_R , ε_A , $2k_1$, and k_2 allows us to calculate the buildup kinetics of the radical complex $(\text{SNF})\text{Ni}(\text{SR})_2$. At low initial concentrations of radicals R_0 , the calculated rate curves fit well with the experimental curves. However, when the laser pulse intensity (and, hence, R_0) is significantly higher, the calculated rate curves describe well only the initial, fast kinetic regions and substantially deviate from the experimental curves in the onset flattening region (completion of the formation of the radical complex). Curves 1'–4' in Fig. 3 refer to calculation by Eq. (4), which predicts considerably higher values of absorbance compared with the experimental data (curves 1–4).

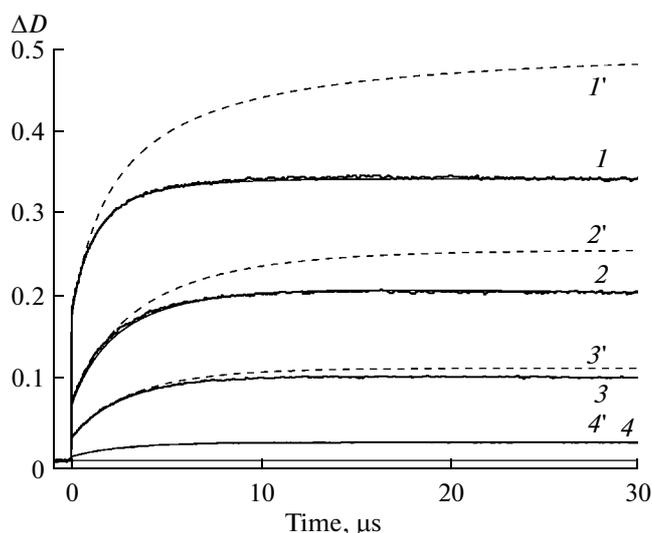
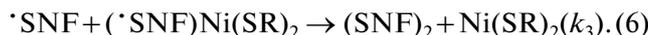


Fig. 3. Kinetics of appearance of absorption due to the complex $(\text{SNF})\text{Ni}(\text{SR})_2$ at 430 nm with different initial concentrations of the SNF radical. A benzene solution of $(\text{SNF})_2$ ($6.25 \times 10^{-4} \text{ mol L}^{-1}$) and $\text{Ni}(\text{SR})_2$ ($1.28 \times 10^{-4} \text{ mol L}^{-1}$) at $T = 298 \text{ K}$. Curves 1–4 refer to the experimental kinetic data, and dashed curves 1', 2', 3', and 4' represent the results of calculation of the kinetics by Eq. (5) with initial SNF radical concentrations of $R_0 \times 10^5 = 13.1, 3.04, 0.97, \text{ and } 0.30 \text{ mol L}^{-1}$, respectively. Smooth curves 1–4 represent the results of calculation of the kinetics by solving differential equations with allowance for reaction (7) and the same values of R_0 .

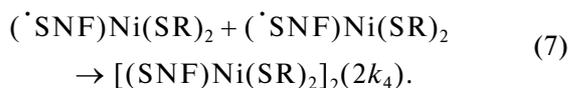
Thus, at high laser pulse intensities, the relative concentration of the radical complex decreases owing to a reaction with one of the species present in the solution. This reaction is not supposed to lead to the appearance of a new transient species, since the spectra formed by the 50th μs does not depend of the laser pulse intensity. The only reaction that meets these conditions is the reaction of the SNF radical with the radical complex $(\text{SNF})\text{Ni}(\text{SR})_2$:



Note that a similar reaction was detected for the dithiophosphinate disulfide–Ni(II) dithiophosphinate complex [6] and 8,8'-diquinolinyl disulfide–di(mercaptoquinolinato)Ni(II) systems [7]. The introduction of reaction (6) leads to the complete fitting of the calculated with the experimental rate curves at any initial concentration of the S-radical (Fig. 3, curves 1–4). The rate constant k_3 calculated in terms of this approach is given in the table.

The absorption due to the radical complex $(\text{SNF})\text{Ni}(\text{SR})_2$ begins to disappear on the millisecond time scale (Fig. 4). Remaining by the time of 100–200 ms is the absorption whose spectrum corresponds to the difference of the spectra recorded in the case of continuous photolysis. In Fig. 4a, this difference (difference of the spectra before and after irradiation, Fig. 2a) is depicted by the solid line

(spectrum 2). The kinetics of change in absorbance (430 nm, Fig. 4b) follows the second-order rate law, which can be explained by the dimerization reaction of the radical complex:



The solid curve in Fig. 4b refers to calculation in terms of the second-order rate law. The observed rate constant k_{obs} in this case will be defined by the expression

$k_{obs} = \frac{2k_4}{(\epsilon_A - \epsilon_D/2)} \times \left(1 - \frac{\epsilon_C}{\epsilon_A - \epsilon_D/2}\right) \times \frac{\Delta D}{l}$, where ΔD is the initial amplitude of absorption at 430 nm due to the radical complex, l is the optical path length of the cell, and ϵ_D is the absorption coefficient of the dimer $[(\text{SNF})\text{Ni}(\text{SR})_2]_2$. Figure 4c shows a linear relation between k_{obs} and ΔD , which confirms that the radical complex disappears in a second-order reaction. The isosbestic points of the spectrum in the case of continuous photolysis (Fig. 1a) makes it possible to determine the value of ϵ_D (430 nm) = 8520 L mol⁻¹ cm⁻¹, and the dimerization rate constant of the radical constant can be calculated from the slope in Fig. 4 as $2k_4 = (3.5 \pm 0.2) \times 10^7$ L mol⁻¹ s⁻¹.

The dimer $[(\text{SNF})\text{Ni}(\text{SR})_2]_2$ is a long-lived species; its decay kinetics along with the absorption buildup kinetics of the parent complex are shown in Fig. 1b. The curves are described well by the first-order rate law with the same rate constant. Thus, the return of the system to the initial state is determined by the unimolecular dissociation of the dimer



to the disulfide and the reactant complexes with a rate constant of $k_5 = (3.3 \pm 0.3) \times 10^{-3}$ s⁻¹.

Planar Ni(II) complexes can add nitrogen-containing extra ligands to form an Ni–N bond with an energy of 30–40 kJ/mol [8–10]. In photochromic systems composed of planar Ni(II) complexes and disulfides [3–7], the extra ligands are S-radicals. The N–S bond energy for the dithiocarbamate radical is ~30 kJ/mol [3], which is close to the bonding energy of nitrogen-containing extra ligands. In the complex of the dithiophosphinate radical with the Ni(II) dithiophosphinate complex, the bond energy is about 15 kJ/mol [8].

In the case of $(\cdot\text{SNF})\text{Ni}(\text{SR})_2$, which disappears via the dimerization reaction, the rate constant of unimolecular dissociation is low ($k < 10$ c⁻¹ as estimated from the intercept in Fig. 4c). Using the expression for the unimolecular dissociation rate constant

$(k_{diss} = k_0 e^{-\frac{E_{act}}{kT}} \approx 10^{13} e^{-\frac{E_{act}}{kT}} \approx 10$ c⁻¹), we can estimate the activation energy of this reaction at $E_{act} \geq 65$

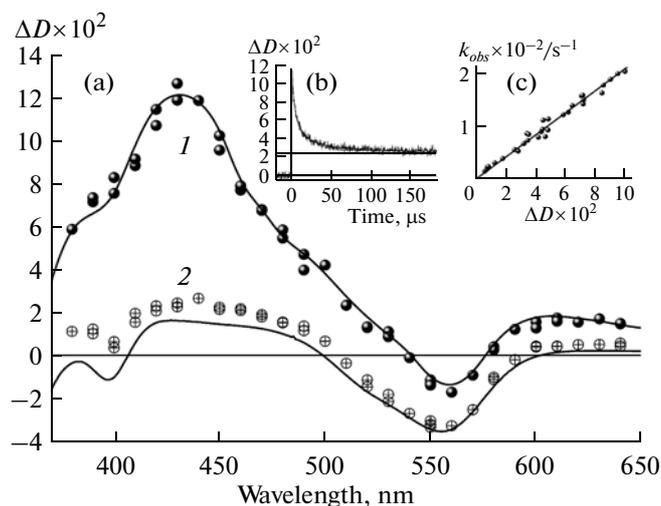


Fig. 4. (a) Change in the spectrum of the complex $(\cdot\text{SNF})\text{Ni}(\text{SR})_2$ during flash photolysis of a solution of $(\text{SNF})_2$ (1.24×10^{-4} mol L⁻¹) and $\text{Ni}(\text{SR})_2$ (1.78×10^{-5} mol L⁻¹) in a cell with an optical path length of 1 cm: (1) the initial spectrum of the radical complex and (2) the spectrum of the dimer $[(\text{SNF})\text{Ni}(\text{SR})_2]_2$ after 100 ms. (b) Decay kinetics of $(\cdot\text{SNF})\text{Ni}(\text{SR})_2$ absorption at 430 nm. (c) Dependence of k_{obs} for the decay of the radical complex upon the amplitude of its initial absorption ΔD at 430 nm.

kJ/mol. Since the formation of the radical complex proceeds with the rate constant close to the diffusion-controlled limit (table), the activation energy of diffusion $E_{diff} \approx 10$ kJ/mol can be taken as that of the complexation. In this case, the value of $E_{\text{Ni}-\cdot\text{SNF}} \approx E_{act} - E_{diff} \geq 55$ kJ/mol can be an estimate of the Ni– $\cdot\text{SNF}$ bond energy [4–7]. The –S–S– bond energy in disulfides is considerably greater (~230 kJ/mol [25]); therefore, the attack by the second $\cdot\text{SNF}$ radical involves switching from the Ni–S to the S–S bond (reaction (6)).

Radical complexes of many S-radicals with the Ni(II) ion decay through the dissociation reaction [3–7]; however, this system is characterized by the presence of another, faster degradation pathway, the formation of the dimer $[(\text{SNF})\text{Ni}(\text{SR})_2]_2$ in which the disulfide ties up two $\text{Ni}(\text{SR})_2$ molecules. Figure 5 shows the full scheme of reactions to correspond to kinetic transformations in this photochromic system.

8-Mercaptoquinolate complexes of metal ions with the occupied d shell (Zn^{2+} , Cd^{2+}) exhibit an absorption band at 420 nm, which corresponds to intraligand transitions [18]. Coordination to transition metal ions (Ni^{2+} , Cu^{2+}) complicates the spectrum, resulting in the appearance of intense charge-transfer bands in the spectral region at longer wavelengths [19, 20]. In the case of planar nickel complexes, the $4p_z$ orbital of the ion and four π orbitals of the ligands form a π bonding molecular orbital, which takes part in many transitions [21]. When a nitrogen-containing

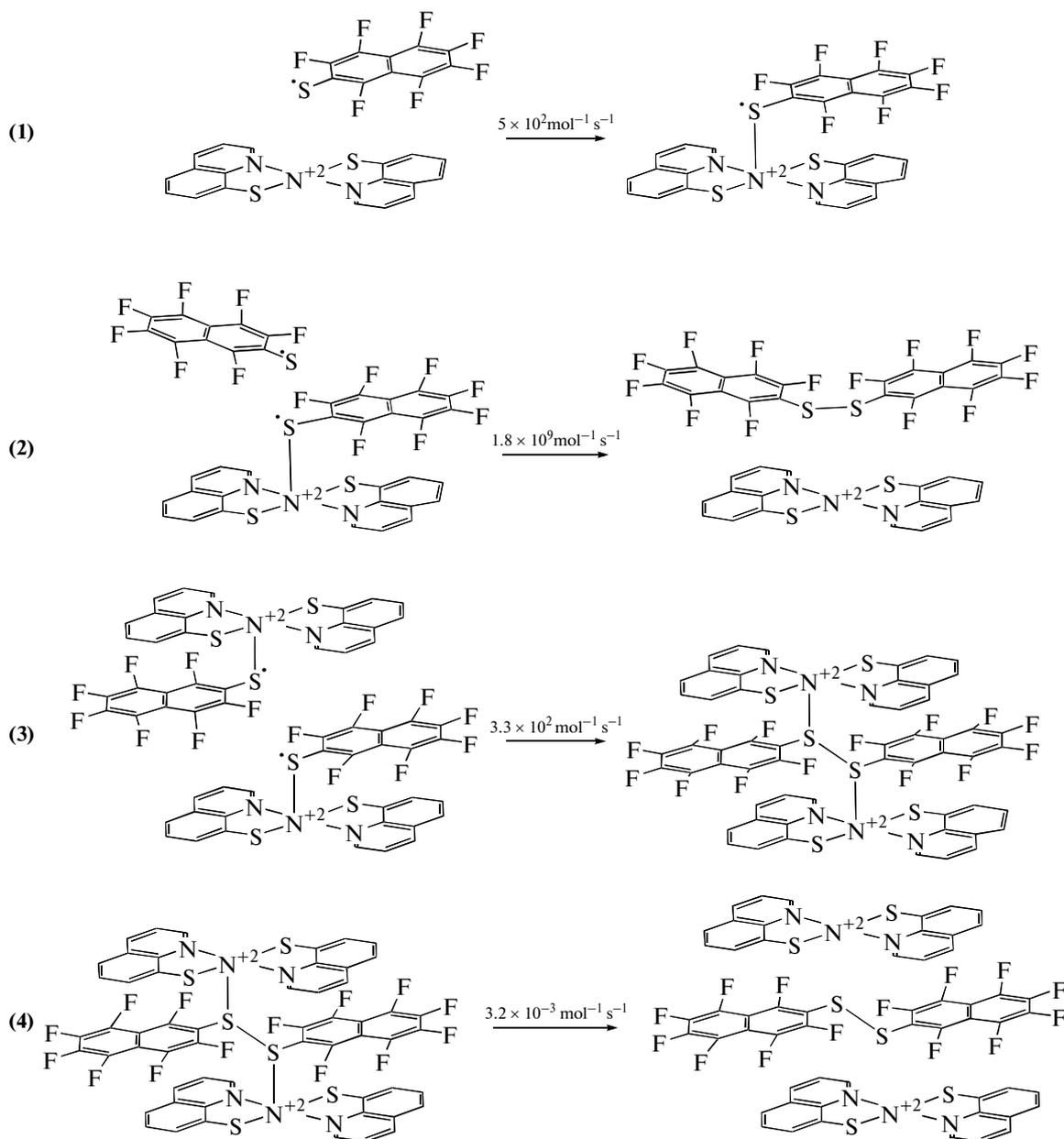


Fig. 5. Scheme of photochemical transformations of the disulfide $(\text{SNF})_2$ and the $\text{Ni}(\text{SR})_2$ complex in benzene: (1) the coordination reaction of the $\cdot\text{SNF}$ radical with the $\text{Ni}(\text{SR})_2$ complex; (2) the reaction of the $\cdot\text{SNF}$ radical with the radical complex $(\cdot\text{SNF})\text{Ni}(\text{SR})_2$; (3) the reaction of two radical complexes yielding the dimer $[(\text{SNF})\text{Ni}(\text{SR})_2]_2$; and (4) the final reaction of photochromic transformations, the dissociation of the dimer to give the disulfide and two parent complexes.

extra ligand is coordinated axially, the $4p_z$ orbital stops interacting with the π orbitals of the equatorial ligands and the charge-transfer bands disappear [16]. In the case of coordination of the $\cdot\text{SNF}$ radical, the long-wavelength band of the parent complexes also disappears (Fig. 2a). This finding suggests that the S-radical is axially coordinated as well.

Thus, the nature of photochromic processes has been determined for the system composed of perfluorodiphthalyl disulfide and the planar di(mercapto-

quinolinato)nickel(II) complex. It has been shown that after the photodissociation of the disulfide, the nascent S-radicals coordinate to the $\text{Ni}(\text{SR})_2$ complex at a high rate to yield radical complexes $(\cdot\text{SNF})\text{Ni}(\text{SR})_2$, which disappear on the millisecond timescale in the dimerization reaction. The dimer $[(\text{SNF})\text{Ni}(\text{SR})_2]_2$ in which two nickel ions are tied up by the disulfide molecule, degrades into the free disulfide and the two parent complexes over a few tens of

minutes, completing the photochromic transformation cycle.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project nos. 11-03-00268 and 09-03-00330; the Chemistry and Materials Science Division of the Russian Academy of Sciences, grant no. 5.1.6; and the Russian Academy of Sciences Siberian Branch Program of International Integration Projects, grant no. 70.

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