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PAPER

Photochromic processes in di(mercaptoquinolinato)Ni(II) complex and perfluordiphenyl disulfide solutions

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Laser flash photolysis was used to study the nature and reactions of intermediates for a novel photochromic system consisting of perfluorodiphenyl disulfide ($F_5C_6SSC_6F_5 = (SBF)_2$) and a flat di(mercaptoquinolinato)Ni(II) ($Ni(SC_6H_3NC_3H_3)_2 = Ni(SR)_2$) complex in benzene solutions. Under UV-radiation disulfide dissociates into two sulfur-containing radicals ($F_5C_6S^{\bullet} = {}^{\bullet}SBF$) that vanish in recombination. In the presence of the $Ni(SR)_2$ complex recombination competes with radical coordination yielding the radical $(SBF^{\bullet})Ni(SR)_2$ complex. This complex has an absorption band in the visible region and disappears in the second-order reaction when radical-complex recombines into dimer ($(RS)_2Ni(SBF)_2Ni(SR)_2$). Subsequent dimer dissociation into initial disulfide and two $Ni(SR)_2$ complexes completes the photochromic cycle.

Introduction

Photochromic systems receive widespread attention because of their possible technological applications.[1–3] Hence, the study of a novel photochromic systems is of both fundamental and practical interest. Recently we found a new family of photochromic systems where photochromic behavior is driven by reversible coordination of sulfur-containing radicals (S-radicals) with flat dithiolate complexes of bivalent nickel (NiL_2).[4–8] The development of these systems resulted from the ability of some flat Ni(II) complexes to coordinate reversibly with extraligands of the pyridine type.[9–11] The solutions of Ni(II) complexes transform into photochromic systems only after the formation of new extraligands under light. Disulfides are best suited for that. Under UV-radiation they dissociate into chemically passive S-radicals that usually recombine back into the initial disulfide.[12–16] Because of their low reactivity there are practically no side reactions, which increases the number of the photochromic cycles without significant degradation of the system.

Using laser flash photolysis we demonstrated[4–8] that the S-radicals efficiently coordinate with flat dithiolate Ni(II) complexes. The transient radical $(RS^{\bullet})NiL_2$ complexes display strong absorption bands in both UV and visible regions. Coordination is reversible which results in subsequent recombination of the S-radicals into the initial disulfide which explains photochromic properties of such systems. The lifetime of radical complexes depends on the nature of both the radical and the Ni(II) complex and varies from several microseconds to tens of milliseconds. The repeated coordination can increase the observed lifetime of radical complexes into seconds. Cooling down the solutions makes it possible to increase this time even further, to accumulate sufficient concentration of radical complexes and to record the EPR spectrum of these particles.[5] In the dithiophosphinate disulfide and dithiophosphinate Ni(II) complex solutions we observed the coordination of the second S-radical and the formation of biradical $(RS^{\bullet})_2NiL_2$ complex.[7] Coordination of both S-radicals is reversible and the systems reverts to the initial state due to radical recombination.

In this work we have studied the nature, spectroscopy, and kinetics of the reaction intermediates in a photochromic system, containing perfluordiphenyl disulfide and a flat dimercaptoquinolinate complex of bivalent nickel ($Ni(SR)_2$). Strong absorption band in the visible spectrum region allowed us to follow the transformations of the complex in the laser flash photolysis experiments. Perfluordiphenyl disulfide $(SBF)_2$ was used as a source of S-radicals.

Experimental

Laser flash photolysis was carried out using a setup with either an excimer XeCl (308 nm, 15 ns, 30 mJ, beam area on a sample –10 mm^2) or a YAG:Nd (the 3rd harmonic, 355 nm, 7 ns, 30 mJ) laser.[17] The excitation and probe light beams entered solution in a 1 cm cuvette at a small angle (~2°). The slow processes in millisecond and second time domains were studied using special microcuvettes of volume 40 mm^3 ($l = 2$ mm, $S = 2 \times 10$ mm^2). In this case all volume of examined solution was exposed to the laser pulse to exclude distortions of the kinetics due to the convection in the cuvette. At long measurement times the photochemical effect of

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the probing light on the studied solutions was reduced by using a halogen incandescent lamp (less intensive than the xenon one) whose radiation was passed through the narrow-band interference filters. Some experiments were performed on a slightly different laser flash photolysis setup[18] with perpendicular excitation and probe light beams. The signal from the photomultiplier was recorded by Tektronix 7912AD oscilloscope connected to a computer.

Optical absorption spectra were recorded using HP 8453 and Shimadzu UV-2501 spectrophotometers. Solutions were prepared in spectrally pure solvents manufactured by Merck. In numeric kinetic simulations differential equations were solved using proprietary software based on the fourth-order Runge–Kutta method. The $Ni(SR)_2$ complex was synthesized according to the previously described protocol.[19] Perfluordiphenyl disulfide $(SBF)_2$ was produced as described elsewhere.[20]

Results and discussion

Stationary photolysis of the $Ni(SR)_2$ complex and $F_5C_6S\text{-}SC_6F_5$ disulfide solutions

In the flat $Ni(SR)_2$ complex the distances between Ni–S and Ni–N are 2.40 Å and 2.06 Å, respectively.[21] The optical absorption spectrum of the $Ni(SR)_2$ complex in benzene contains the bands of charge transfer (Fig. 1) with maxima at 555, 396, 336, and 308 nm with absorption coefficients of 5900, 7240, 12 270, and 11 970 M^{-1} cm^{-1}, respectively.[22] For perfluordiphenyl disulfide ($F_5C_6SSC_6F_5 = (SBF)_2$) the region recorded includes only the edge of the absorption band (Fig. 1). The absorption coefficients at the wavelengths of laser radiation are 2200 M^{-1} cm^{-1} (308 nm) and 214 M^{-1} cm^{-1} (355 nm).

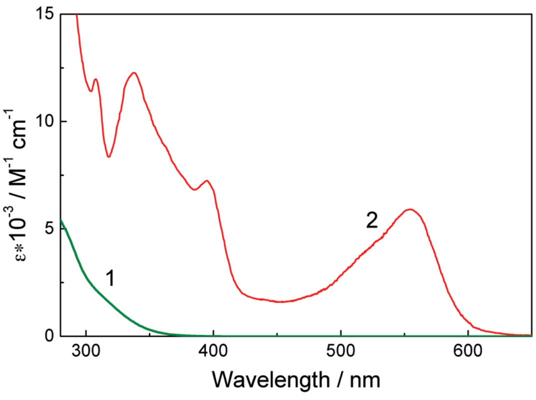

Fig. 1 Optical absorption spectra of disulfide perfluordiphenyl ($F_5C_6SSC_6F_5$ = $(SBF)_2$) (1) and the di(mercaptoquinolinato)Ni(II) ($Ni(SR)_2$) complex (2) in benzene.

The stationary photolysis of the disulfide solution (without $Ni(SR)_2$ complex) causes no changes in optical spectrum. The sulfur-containing radicals, arising from $(SBF)_2$ photodissociation, disappear in the reaction of recombination.[14] The photolysis of the $Ni(SR)_2$ solutions in benzene also produces no changes in its optical spectrum due to the quick relaxation of the excited state into the ground electron state.

The stationary photolysis of the $Ni(SR)_2$ and $(SBF)_2$ solutions in benzene by either 308 nm (XeCl laser) or 355 nm (YAG:Nd laser) pulses leads to both the disappearance of the absorption band of the complex with a maximum at 555 nm and the formation of a new spectrum which contains a band with a maximum near 470 nm with a tail into longer wavelength region (Fig. 2a). Three isosbestic points at 402, 504, and 596 nm are observed during phototransformations. After irradiation the optical spectrum reverts to its initial state. It takes several tens of minutes and the same isosbestic points are preserved in the process. The kinetic curves are shown in Fig. 2b. Thus, the $Ni(SR)_2$ and $(SBF)_2$ solution is a good photochromic system.

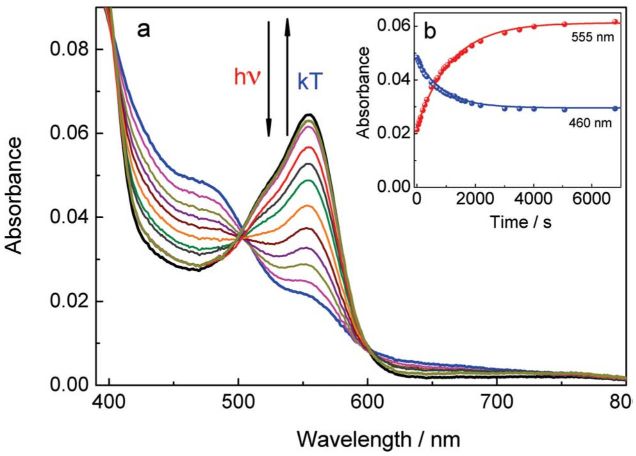

Fig. 2 A change in the optical spectrum (a) of disulfide $(SBF)_2$ (4×10^{-5} M) and the $Ni(SR)_2$ (1.1×10^{-5} M) complex in benzene upon stationary photolysis (XeCl laser pulses, 308 nm) and the reverse reaction. The kinetic curves of the absorbance at 460 and 555 nm (b) in the reverse reaction. Solid lines: single exponential model with time constant of 1000 s.

Spectroscopy and kinetics of S-radicals reactions upon laser flash photolysis of disulfide solution

The energy of the –S–S– bond in disulfides is about 230 kJ mol^{-1}. Upon absorption of the UV light quanta with energy of 340–400 kJ mol^{-1} these molecules dissociate with a high quantum yield into two sulfur-containing radicals.[12–16] Fig. 3a shows the absorption spectrum of the perfluorthiophenyl radical ($^{\bullet}SBF$) recorded during laser flash photolysis (50 ns after laser pulse) of the $(SBF)_2$ solutions in benzene (the bands with maxima at 475 and 430 nm). The spectrum obtained is in fair agreement with that of the $^{\bullet}SBF$ radical in acetonitrile[14] and the literature data for the non-fluorized $^{\bullet}SBH$ radical.[23–27] The absorption disappearance adheres to the second-order kinetic law and corresponds to the $^{\bullet}SBF$ radical recombination into the initial disulfide $(SBF)_2$:

$$^{\bullet}SBF + {}^{\bullet}SBF \rightarrow (SBF)_2,\ (2k_1) \tag{1}$$

The observed rate constant k_{obs} of radical disappearance is linearly dependent on the initial absorbance ΔD_0 (Fig. 3b) after laser pulse ($k_{obs} = 2k_1\Delta D_0/\varepsilon l$), which confirms radical disappearance in the second-order recombination. The slope of the straight line in Fig. 3b determines the value $2k_1/\varepsilon = (1.70 \pm 0.02) \times 10^6$ cm s^{-1}, where ε is the radical absorption coefficient.

The absorption coefficients and the recombination rate constant $2k_1$ were estimated from the fast reaction between the S-radical and the stable nitroxyl radical ($RNO^{\bullet}$):[14]

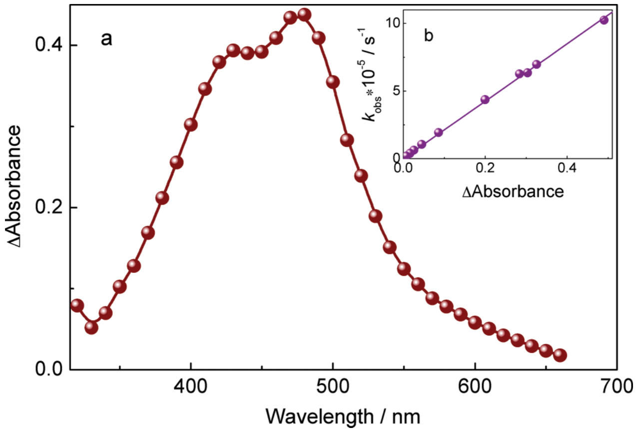

Fig. 3 The $^{\bullet}$SBF radical spectrum in laser flash photolysis (308 nm) of the $(SBF)_2$ (1.0×10^{-3} M) solution in benzene 50 ns after laser pulse (a). Dependence of the observed rate constant k_{obs} of radical disappearance on its initial absorption at 470 nm (b).

$$^{\bullet}\mathrm{SBF} + \mathrm{RNO}^{\bullet} \rightarrow \text{products}, (k_{^{\bullet}\mathrm{SBF+RNO}^{\bullet}}) \qquad (2)$$

that exhibits strong absorption bands in the UV and visible spectrum regions. The reaction products do not absorb in the visible spectrum region and as such do not interfere with determination of the absorption coefficients of the S-radical. The ε value (475 nm) of the $^{\bullet}$SBF radical is given in Table 1. This absorption coefficient was used to determine the rate constants of S-radical recombination and its reaction with the RNO$^{\bullet}$ radical, listed in Table 1. A decrease in the rate constant as compared with diffusion parameters (k_{diff}) is due to the steric (sulfur atoms recombine) and spin (recombination is observed only for pairs in the singlet state) factors.

In acetonitrile, the spectroscopic parameters and recombination rate constants of thiyl radical ($^{\bullet}$SBH = PhS$^{\bullet}$) and its fluorized analog ($^{\bullet}$SBF) are actually the same.[14] In the literature, the absorption coefficient of the $^{\bullet}$SBH radical band at 460 nm varies from 2000 to 2700 M^{-1} cm^{-1}.[23–27]

The optical spectra of intermediates formed in the solutions containing disulfide $(SBF)_2$ and $Ni(SR)_2$ complex

In the laser flash photolysis studies of disulfide solution in the presence of the $Ni(SR)_2$ complex we observed the spectrum of S-radical formed immediately after the laser pulse which during several microseconds transformed, with isosbestic points at 484 and 600 nm, into a new spectrum (Fig. 4a) belonging to the radical $(SBF^{\bullet})Ni(SR)_2$ complex:

$$^{\bullet}\mathrm{SBF} + \mathrm{Ni(SR)_2} \rightarrow (\mathrm{SBF}^{\bullet})\mathrm{Ni(SR)_2}, (k_2) \qquad (3)$$

The radical complex displays the band with a maximum at 430 nm. The kinetics of reaction (3) is shown in the insert (Fig. 4b). It is worth noting that the reaction of coordination of many sulfur-containing radicals with the flat dithiolate complexes of bivalent nickel was observed before.[4–8] The absorption depletion near 555 nm is caused by the disappearance of the initial $Ni(SR)_2$ complex whose absorption band is located in this region (Fig. 1).

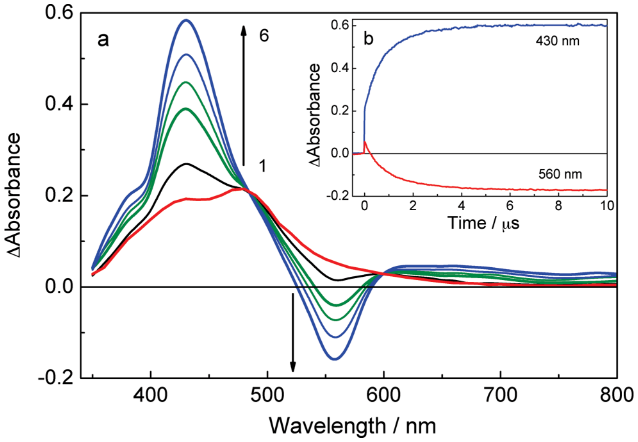

Fig. 4 Intermediate spectra (a), arising from laser flash photolysis of the $(SBF)_2$ (6.25×10^{-4} M) and $Ni(SR)_2$ (1.275×10^{-4} M) solution in benzene at $T = 298$ K. 1–6: spectra after 0, 0.1, 0.3, 0.7, 1.3, 5 μs, respectively. The kinetics of the absorbance (b) at 430 and 560 nm.

To determine the spectral and kinetic parameters of the radical $(SBF^{\bullet})Ni(SR)_2$ complex it is necessary to take into account the presence of a competing reaction of S-radial recombination. For the concentrations of S-radical $R(t)$ and radical complex $A(t)$ under condition $R_0 \ll C_0$ (where R_0 and C_0 are the initial concentrations of the S-radical and $Ni(SR)_2$ complex, respectively) one can write the differential equations

$$\frac{\mathrm{d}R(t)}{\mathrm{d}t} = -2k_1R(t)^2 - k_2C_0R(t); \quad \frac{\mathrm{d}A(t)}{\mathrm{d}t} = k_2C_0R(t). \qquad (4)$$

The solutions of these equations are

$$\frac{R(t)}{R_0} = \frac{e^{-k_2C_0t}}{1 + \dfrac{2k_1R_0}{k_2C_0}(1 - e^{-k_2C_0t})}; \quad \frac{A(t)}{R_0} = \frac{k_2C_0}{2k_1R_0}\ln\left[1 + \frac{2k_1R_0}{k_2C_0}(1 - e^{-k_2C_0t})\right] \qquad (5)$$

The absorbance dependence on time in pulsed experiments is described by the following equation:

$$D(t) = \varepsilon_R R(t)l + (\varepsilon_A - \varepsilon_C)A(t)l, \qquad (6)$$

where ε_R, ε_A, and ε_C are the absorption coefficients of the S-radical, the radical complex and initial complex, respectively. This equation takes into account the disappearance of the initial complex absorption upon formation of the radical complex. Concentration of radical complex after the full S-radical disappearance obeys the equation:

$$\frac{A(\infty)}{R_0} = \frac{k_2C_0}{2k_1R_0}\ln\left(1 + \frac{2k_1R_0}{k_2C_0}\right). \qquad (7)$$

Table 1 The wavelength and the absorption coefficient of the optical absorption band of the $^{\bullet}$SBF radical, the rate constants of its recombination and reaction with the RNO$^{\bullet}$ radical in benzene and acetonitrile[14]

Solvent	λ_{max}/nm	ε/M^{-1} cm^{-1}	$2k_1$/×10^{-9} M^{-1} s^{-1}	$k_{^{\bullet}\mathrm{SBF+RNO}^{\bullet}}$/×10^{-9} M^{-1} s^{-1}	k_{diff}/×10^{-9} M^{-1} s^{-1}
Benzene	475	1800 ± 100	3.0 ± 0.4	1.8 ± 0.2	11
Acetonitrile	460	2550	9.5 ± 0.4	1.9 ± 0.2	9.2

Table 2 Spectral and kinetic parameters of radical $(SBF^{\bullet})Ni(NS)_2$ and $(RS^{\bullet})Ni(NS)_2$ complexes[8] in benzene

Radical complex	λ_{max}/nm	ε/M^{-1} cm^{-1}	k_2/×10^{-9} M^{-1} s^{-1}	k_3/×10^{-9} M^{-1} s^{-1}	Reference
$(SBF^{\bullet})Ni(SR)_2$	430	11 600 ± 600	6.0 ± 0.2	2.35 ± 0.55	This work
$(RS^{\bullet})Ni(SR)_2$	460	16 600 ± 500	4.4 ± 0.1	3.1 ± 0.1	8

From these equations we find the ratio between the absorbance at a maximum of the radical complex band at times when its formation is completed (ΔD_∞), and the initial absorbance at a maximum of the S-radical band just after the laser pulse, (ΔD_0).

$$\frac{\Delta D_\infty}{\Delta D_0} = \frac{\varepsilon_A - \varepsilon_C}{\varepsilon_R}\times\frac{k_2C_0}{2k_1R_0}\ln\left(1+\frac{2k_1R_0}{k_2C_0}\right)\xrightarrow{R_0\to 0}\frac{\varepsilon_A-\varepsilon_C}{\varepsilon_R} \tag{8}$$

Fig. 5 shows the experimental dependence of the $\Delta D_\infty/\Delta D_0$ ratio on R_0 (dots) at low initial concentrations of the radical (low laser pulse intensities). The dependence indicates (for $R_0 \to 0$), that $\varepsilon_A = \varepsilon_C + 6\varepsilon_R = 11\,600 \pm 600$ M^{-1} cm^{-1}. The found absorption coefficient allows us to calculate the rate constant k_2 of the coordination of the $^{\bullet}$SBF radical and the $Ni(SR)_2$ complex (Table 2). The table also presents the spectral and kinetic data for the radical $(RS^{\bullet})Ni(SR)_2$ complex in which the coordinated S-radical is a product of 8,8″-diquinolyldisulfide photodissociation.[8]

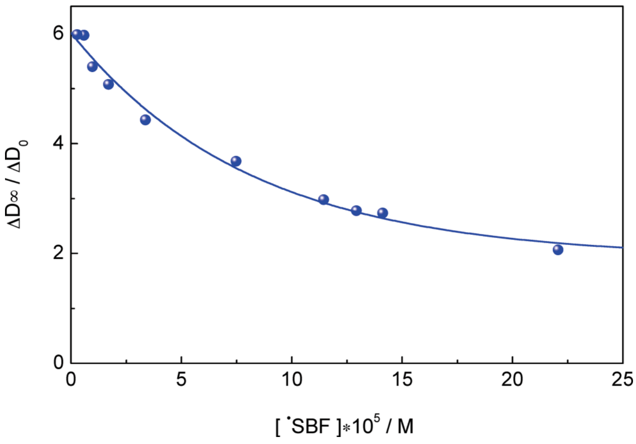

Fig. 5 Determination of the absorption coefficient of the radical $(SBF^{\bullet})Ni(SR)_2$ complex at 430 nm. Dependence of the absorbance ratio of radical complex (ΔD_∞, 20 μs after the pulse) at 430 nm and the initial absorbance of $^{\bullet}$SBF radical at 470 nm (ΔD_0, just after laser pulse) on initial radical concentration. The $(SBF)_2$ (6.25×10^{-4} M) and $Ni(SR)_2$ (1.275×10^{-4} M) solution in benzene at $T = 298$ K. The $\Delta D_\infty/\Delta D_0$ ratio at $R_0 \to 0$ allows us to determine the value $(\varepsilon_A - \varepsilon_C)/\varepsilon_R$ (eqn (8)).

Reaction between the $^{\bullet}$SBF radical and the radical $(SBF^{\bullet})Ni(SR)_2$ complex

The found values of ε_R, ε_A, $2k_1$, and k_2 are used to simulate the kinetics of both the $^{\bullet}$SBF radical disappearance and the appearance of the $(SBF^{\bullet})Ni(SR)_2$ complex by numerical solution of differential equations. At low initial concentrations of R_0 radicals (low laser pulse intensities), when only the reactions of radical recombination (1) and coordination (3) are realized, the simulated kinetics matches the experimental curve.

However, at higher laser pulse intensities (and correspondingly, the initial S-radical concentrations R_0), the calculated kinetics matches only the initial regions of experimental curve and deviate substantially at plateau (the end of radical complex formation). In Fig. 6, smooth curves 1′, 2′, 3′, and 4′ are results of numeric calculation of eqn (6), which predicts much higher absorbance than what was observed in experiments (curves 1–4 with noise). Thus, at high laser pulse intensities, the radical complex disappears in the reaction with one of the particles present in the solution ($^{\bullet}$SBF radical, disulfide, initial $Ni(SR)_2$ complex, radical $(SBF^{\bullet})Ni(SR)_2$ complex). This reaction may not yield a new intermediate because the spectra at 50 μs are not dependent on laser pulse intensity. The only reaction which satisfies these conditions is the reaction between the $^{\bullet}$SBF radical and the radical $(SBF^{\bullet})Ni(SR)_2$ complex which leads to formation of initial disulfide and nickel complex

$$\begin{aligned} {}^{\bullet}\text{SBF} + (\text{SBF}^{\bullet})\text{Ni(SR)}_2 &\rightarrow (\text{SBF-SBF})\text{Ni(SR)}_2 \\ &\rightarrow (\text{SBF})_2 + \text{Ni(SR)}_2,\ (k_3) \end{aligned} \tag{9}$$

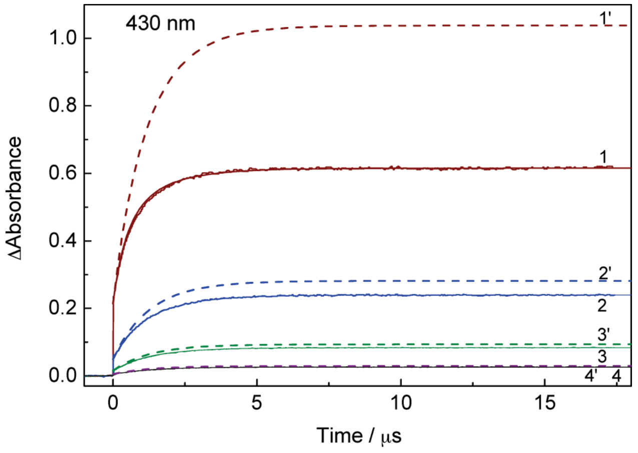

Fig. 6 Kinetic curves of the absorption formation of the radical $(SBF^{\bullet})Ni(SR)_2$ complex at 430 nm for various laser pulse intensities (various initial concentrations of the $^{\bullet}$SBF radical). The $(SBF)_2$ (6.25×10^{-4} M) and $Ni(SR)_2$ (1.275×10^{-4} M) solution in benzene at $T = 298$ K. Curves 1–4 with noise- experimental kinetics. Smooth dashed curves 1′, 2′, 3′, and 4′: simulation of kinetics (eqn (6)) with initial $^{\bullet}$SBF radical concentrations $R_0 \times 10^5 = 13.1$, 3.04, 0.97, and 0.30 M, respectively. Smooth curves 1–4: simulation of kinetics where reaction (9) is taken into account with the same R_0 values.

This reaction continues for tens of microseconds while the concentration of free $^{\bullet}$SBF radical is not close to zero and may run through the formation of the intermediate $(FBS\text{-}SBF)Ni(SR)_2$ complex, in which disulfide is coordinated by a sulfur atom. It is worth noting that similar reaction has been established for the systems containing dithiophosphinate disulfide and dithiophosphinate Ni(II) complex,[7] and 8,8″-diquinolyldisulfide and di(mercaptoquinolinate)Ni(II) complex.[8] Introduction of reaction (9) allows us to achieve a near perfect match between calculated and experimental kinetic curves for all initial S-radical concentrations (smooth curves 1–4 in Fig. 6). The rate constant k_3, found in these calculations is shown in Table 2.

Disappearance of the radical (SBF$^\bullet$)Ni(SR)$_2$ complex

Absorption of the radical (SBF$^\bullet$)Ni(SR)$_2$ complex disappears in a millisecond time range (Fig. 7a). In pulse photolysis experiments at 100 ms the absorption spectrum (Fig. 7b) corresponds to the difference in the spectra recorded in stationary photolysis. In Fig. 7b this difference (the difference between the spectra of the initial complex and after some irradiation period) is denoted by the solid line for spectrum 2. The observed rate constant k_{obs} is linearly dependent on signal amplitude (actually on radical complex concentration) (Fig. 7c). This dependence demonstrates the disappearance of the radical complex in the second-order reaction. The close to zero cut-off in the ordinate (Fig. 7c) indicates the absence of a monomolecular decay of the radical complex into free S-radical and the initial Ni(SR)$_2$ complex ($k_{mono} < 10$ s^{-1}). Variations in the initial complex concentration have no effect on k_{obs}. Thus, the fast processes are over at 100 ms and the system starts to revert slowly (Fig. 2b) to its initial state to complete the cycle of photochromic transformations.

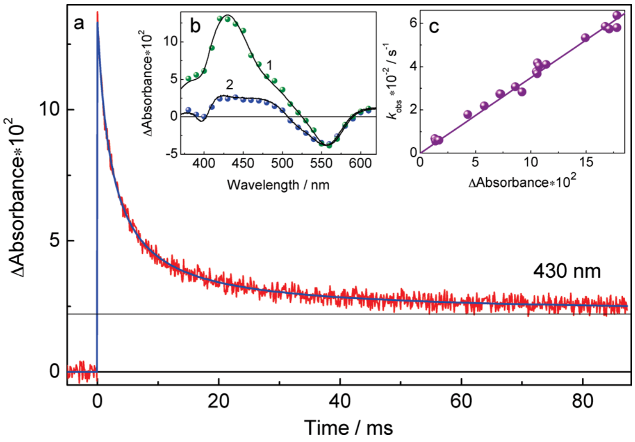

Fig. 7 Kinetics of the absorption disappearance of the radical (SBF$^\bullet$)Ni(SR)$_2$ complex at 430 nm (a) in laser flash photolysis of the (SBF)$_2$ (1.24×10^{-4} M) and Ni(SR)$_2$ (1.78×10^{-5} M) solution in benzene. Flash photolysis was carried out in a microcuvette with a thickness of 1 cm ($2 \times 5 \times 10$ mm). Laser pulse illuminated the entire volume of the cuvette. Smooth curves denote fitting by the second-order kinetic law. Insert (b) shows the initial spectrum of the radical complex (1) and the spectrum after 100 ms (2). Insert (c) shows the linear dependence of the observed rate constant of radical complex disappearance on signal amplitude which is typical of the second-order reaction.

The second-order kinetic law of radical complex disappearance and the appearance of a new intermediate can be explained by the reaction of dimerization only:

$$(^\bullet\mathrm{SBF})\mathrm{Ni(SR)}_2 + (^\bullet\mathrm{SBF})\mathrm{Ni(SR)}_2 \rightarrow [(\mathrm{SBF})\mathrm{Ni(SR)}_2]_2,\ (2k_4) \qquad (10)$$

The slope of the straight line in Fig. 7c determines the value

$$2k_4/(\varepsilon_A - \varepsilon_D) = (3.5 \pm 0.1) \times 10^3\ \mathrm{s}^{-1},$$

where $(\varepsilon_A - \varepsilon_D)$ is the difference between the absorption coefficients of the radical complex and dimer. The ε_A value was determined above (Table 2) and this allows the difference $(\varepsilon_A - \varepsilon_D) = 9300 \pm 800$ M^{-1} cm^{-1} to be determined from the spectra shown in Fig. 7b. Thus, we get the rate constant of radical complex dimerization $2k_4 = (3.3 \pm 0.3) \times 10^7$ M^{-1} s^{-1}, which is about two orders of magnitude less than the diffusion limit in benzene.

The [(SBF)Ni(SR)$_2$]$_2$ dimer is a fairly long-lived particle. The kinetics of its disappearance (450 nm) is shown together with the kinetics of the formation of initial complex absorption (555 nm) in Fig. 2b. Both of the curves are described well by the first-order kinetics with equal rate constants. Fitting these kinetic curves (the solid line in Fig. 2b) yields the lifetime of the dimer 1030 ± 130 s at room temperature (T = 298 K). System reversion to the initial state assumes that the final stage of photochromic transformations is driven by the monomolecular decay of the dimer into disulfide and two initial nickel complexes

$$[(\mathrm{SBF})\mathrm{Ni(SR)}_2]_2 \rightarrow (\mathrm{SBF})_2 + 2\mathrm{Ni(SR)}_2 \qquad (11)$$

Nature of intermediates in photochromic (SBF)$_2$ and Ni(SR)$_2$ system

The flat bivalent nickel complexes with S-ligands can take nitrogen-containing extraligands with an additional Ni–N bond whose energy is in the range of 30–40 kJ mol^{-1}.[9–11,28–32] In photochromic systems containing the flat complexes of bivalent nickel and disulfide,[4–8] extra ligands are S-radicals. When the radical Ni-$^\bullet$SR complex vanishes in the reaction of dissociation, the dependence of the rate constant on temperature allows us to estimate the energy of the Ni–S bond for radical extra ligand. The energy of the dithiocarbamate radical–dithiocarbamate Ni(II) complex bond[4] is ~30 kJ mol^{-1}, which is close to the energy of the bond of nitrogen-containing extra ligands. In the dithiophosphinate radical–dithiophosphinate Ni(II) complex, the bond energy amounts to about 15 kJ mol^{-1}.[7] The perfluorothionaphthyl ($^\bullet$SC$_{10}$F$_7$) radical coordinates with the flat dithiolate Ni(II) complexes with a lower energy in the range 4–10 kJ mol^{-1}, which substantially decreases the lifetime of these particles.[6]

For the (SBF$^\bullet$)Ni(SR)$_2$ complex, which vanishes in dimerization, the rate constant of monomolecular dissociation is small ($k <$ 10 s^{-1} from the estimate of the cut-off in the ordinate of Fig. 7c). Using the expression for the rate constant of monomolecular dissociation ($k_{\mathrm{diss}} = k_0 e^{-\frac{E_{\mathrm{act}}}{kT}} \approx 10^{13} \times e^{-\frac{E_{\mathrm{act}}}{kT}} < 10\ \mathrm{s}^{-1}$), we estimate the activation energy of this reaction $E_{act} \geq 65$ kJ mol^{-1} ($k_0 \approx 10^{13}$ s^{-1}) Since the rate constant of radical complex formation is close to the diffusion limit (Table 2), the energy of diffusion motion activation, $E_{diff} \approx 10$ kJ mol^{-1}, can be taken as the activation energy of the complex formation. In this case, the value $E_{\mathrm{Ni-}^\bullet\mathrm{SBF}} \approx E_{act} - E_{diff} \geq 55$ kJ mol^{-1}, can serve the estimate for the energy of the Ni–$^\bullet$SBF bond.[5–8] In disulfides, the energy of the –S–S– bond is much higher (~230 kJ mol^{-1}).[33,34] Therefore, if the ($^\bullet$SBF)Ni(RS)$_2$ radical complex is exposed to the attack of free $^\bullet$SBF radical, the bond of S atom with nickel ion in radical complex (Ni–S bond) can break to form new S–S bond and FBS-SBF disulfide, resulting in the disappearance of a substantial part of the radical complex. The formation of intermediate (FBS-SBF)Ni(SR)$_2$ complex is probable where the disulfide coordinates with nickel ion. However, the lifetime of such a complex must be short (in nanosecond range).

The recombination of the $^\bullet$SBF radicals and reaction (9) fail to fully block the formation of radical complexes. A substantial part of these particles survives, particularly, at small initial concentrations of the $^{\bullet}$SBF radicals and could slowly vanish through dissociation as in the case for the complexes with other S-radicals.[4–8] However, for a given system, there is another faster channel for radical complex disappearance: the formation of the $[(SBF)Ni(SR)_2]_2$ dimer. In this case we also observe the formation of the disulfide S–S bond which "ties up" two $Ni(SR)_2$ complexes in the dimer.

Dimer dissociation can be two-step process: first one of the Ni–S bonds breaks yielding a disulfide coordinated with only one nickel ion. This intermediate $(SBF\text{-}SBF)Ni(SR)_2$ complex can also appear in the reaction of the second $^{\bullet}$SBF radical with the radical $(^{\bullet}SBF)Ni(SR)_2$ complex (reaction (9)). As mentioned above, this particle is likely to dissociate within the period smaller than one microsecond and energy of the Ni–S bond can be estimated using the preexponential factor ($k_0 \approx 10^{13}$ s^{-1}), as ~30 kJ mol^{-1}. The aforementioned estimates of the dissociation energy of intermediates depend on the value of the preexponential factor. It is believed, however, that they correspond to the real values with an accuracy of ±10 kJ mol^{-1}.

Fig. 8 schematically depicts transformations that are in agreement with the experimental observations. Scheme 1 denotes the process of S-radical coordination. Scheme 2 demonstrates the S-radical attack on the radical complex. Scheme 3 shows the process of the dimerization of two radical complexes and scheme 4 presents dimer dissociation which corresponds to the completion of photochromic transformations after the laser pulse. The geometry of intermediates in Fig. 8 is not optimized and can be determined by quantum-chemical calculations.

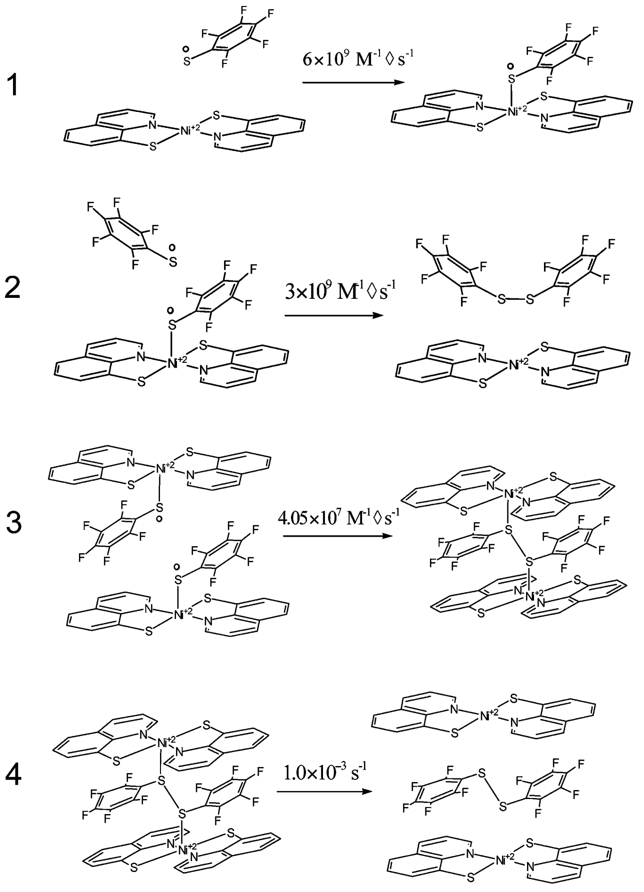

Fig. 8 Scheme of photochemical transformations in the disulfide $(SBF)_2$ and $Ni(SR)_2$ complex solution in benzene. (1) reaction of $^{\bullet}$SBF coordination, (2) reaction between the $^{\bullet}$SBF radical and the radical $(SBF^{\bullet})Ni(SR)_2$ complex, (3) reaction between two radical $(SBF^{\bullet})Ni(SR)_2$ complexes resulting in the $[(SBF)Ni(SR)_2]_2$ dimer, (4) the final reaction of photochromic transformations – dissociation of the dimer yielding disulfide and the initial complexes.

The 8-mercaptoquinolinate complexes of metal ions with a filled d-shell (Zn^{2+}, Cd^{2+}) display two absorption bands at 260 and 380–420 nm which correspond to intraligand transitions.[35,36] Coordination with transition metal ions (Ni^{2+}, Cu^{2+}) complicates the spectrum and leads to the appearance of a series of additional overlapping bands and the bands at longer wavelengths. The high absorption of these bands allows to assign them to the metal to ligand charge transfer.[22,37,38] According to the analysis of the spectra of a series of square flat nickel complexes,[39] the $4p_z$-orbital of a metal ion and four π-orbitals of coordinating ligand atoms form a binding molecular π-orbital which participates in many transitions. In coordination of the nitrogen-containing extra ligand along the axial axis, the $4p_z$-orbital of the nickel ion stops interacting with the π-orbitals of equatorial ligands and the bands of charge transfer disappear.[22] The spectrum of the complex with an adduct becomes similar to that of the complexes of the thioquinolate complexes with the filled d-shell.

There is another explanation of substantial spectrum transformation of the $Ni(SR)_2$ complex after addition of N-adducts. It is assumed that a pair of the electrons of the nitrogen atom adduct fill up the nickel d-shell ($3d^8$) which causes changes in the spectrum.[36] Despite various possible explanations of the nature of spectral changes, the appearance of an additional axial ligand leads to the disappearance of a long-wave absorption band of the $Ni(SR)_2$ complex (560 nm) and the formation of a new band in the 420–440 nm region[22] The $^{\bullet}$SBF coordination also results in the disappearance of the long-wave band of the initial complex and the appearance of a new band shifted to the blue spectral region (a 430 nm band in Fig. 4a). Thus, the radical coordination is assumed to occur also along the axial axis. In sulfur-containing radicals the negative charge and substantial spin density are localized on S atom.[40] Thus it is reasonable to assume that when S-radical collides with $Ni(SR)_2$ complex it coordinates by sulfur atom.

The radical nature of the adduct causes instability of the radical complex which finally finds a way to disappear. For the $(SBF^{\bullet})Ni(SR)_2$ complex the channel of monomolecular dissociation as shown above has a very small rate constant and is dominated by bimolecular reaction (10).

Conclusions

The processes occurring in a novel photochromic system, containing perfluordiphenyl disulfide and a flat di(mercaptoquinolinato)Ni(II) complex are determined. It is shown that the sulfur-containing radicals, resulting from disulfide photodissociation, coordinate with a high rate constant with a complex of bivalent nickel to form the radical $(SBF^{\bullet})Ni(SR)_2$ complexes. Over the microsecond time range when the concentration of free S-radicals is still greater than zero, the part of radical complexes vanishes upon attack by the second S-radical. The remaining radical complexes disappear in the millisecond time range in the second-order reaction to form the $[(SBF)Ni(SR)_2]_2$ dimers in which two nickel ions are bound by disulfide molecule. The dimer lifetime is about 1000 s at room temperature and it slowly dissociates into free disulfide and two initial complexes thus completing the cycle of photochromic transformations.

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