Photochromic transformations in solutions of 8,8´-diquinolyl disulfide and di(mercaptoquinolinato)nickel(II)

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The nature of intermediate species and their reactions were studied by laser pulse photolysis for a photochromic system consisting of 8,8´-diquinolyl disulfide (RSSR) and a planar $\mathrm{Ni^{II}}$ complex di(mercaptoquinolinato)nickel(II) ($\mathrm{Ni(SR)_2}$) in toluene and benzene solutions. Under exposure to laser radiation, disulfide RSSR dissociates to two $\mathrm{RS^{\bullet}}$ radicals, whose spectrum has an intense absorption band with a maximum at λ = 400 nm (ε = 8400 L mol^{-1} cm^{-1}). The radicals disappear by recombination ($2k_{\mathrm{rec}} = 4.6 \cdot 10^9$ L mol^{-1} s^{-1}). In the presence of the $\mathrm{Ni(SR)_2}$ complex, coordination of the radical ($k_{\mathrm{coord}} = 4.4 \cdot 10^9$ L mol^{-1} s^{-1}) competes with recombination to form a radical complex $\mathrm{RS^{\bullet}Ni(SR)_2}$ having an intense absorption band with a maximum at 460 nm (ε = 16 600 L mol^{-1} cm^{-1}). This species decays in the second-order reaction ($2k = 4.6 \cdot 10^4$ L mol^{-1} s^{-1}). Since the photochromic system returns to the initial state, the reaction of two radical complexes is assumed to produce radical recombination and reduction of the disulfide and $\mathrm{Ni(SR)_2}$ complex. Analysis of the kinetic data showed that some $\mathrm{RS^{\bullet}}$ radicals decay in the microsecond time interval due to the reaction with the $\mathrm{RS^{\bullet}Ni(SR)_2}$ radical complex ($k = 3.1 \cdot 10^9$ L mol^{-1} s^{-1}).

Key words: photochemistry, nickel(II) complexes, sulfur-containing radicals, laser pulse photolysis, optical spectra.

Photodissociation of disulfides affords sulfur-containing radicals (S radicals), which recombine rapidly (rate constant is close to the diffusion limit).[1—4] In the presence of planar $\mathrm{Ni^{II}}$ dithiolate complexes, some S radicals reversibly coordinate to the metal atom.[5—7] Reversibility of coordination provides good photochromic properties of these systems, which sustain many transformation cycles without degradation. The S radicals resemble some heterocyclic extraligands, for example, pyridine, by the ability to reversible coordination with nickel ions.[8—14]

For instance, dithiocarbamate ($\mathrm{dtc^{\bullet} = {}^{\bullet}S_2CNAlk_2}$) and perfluorothionaphthyl ($\mathrm{{}^{\bullet}SNF = {}^{\bullet}SC_{10}F_7}$) radicals generated by the photodissociation of disulfides $\mathrm{(S_2CNAlk_2)_2}$ and $\mathrm{(SC_{10}F_7)_2}$,[15,16] respectively, react rapidly and reversibly with the planar dithiocarbamate, xanthogenate, and dithiophosphate complexes of bivalent nickel ($\mathrm{Ni(dtc)_2}$, $\mathrm{Ni(xan)_2}$, and $\mathrm{Ni(dtp)_2}$, respectively) to form the intermediate radical complexes $\mathrm{(dtc^{\bullet})Ni(dtc)_2}$,[5,15] $\mathrm{({}^{\bullet}SNF)Ni(dtc)_2}$, $\mathrm{({}^{\bullet}SNF)Ni(xan)_2}$, and $\mathrm{({}^{\bullet}SNF)Ni(dtp)_2}$.[6] These complexes dissociate with radical escape from the coordination sphere in the micro- and millisecond time ranges. In the solvent bulk, the radical can disappear due to recombination to form disulfide. However, a low concentration of the radicals increases the probability of repeated coordination with the initial complex. For this reason, the lifetime of the radical complexes can elongate by two—three orders of magnitude. In the case of the dithiophosphinate radical ($\mathrm{Bu^i{}_2PS_2{}^{\bullet}}$) and planar complex with dithiophosphinate ligands $\mathrm{Ni(S_2PBu^i{}_2)_2}$, the biradical complex $\mathrm{(Bu^i{}_2PS_2{}^{\bullet})_2Ni(S_2PBu^i{}_2)_2}$ is formed due to the coordination of the second radical with the primary radical complex $\mathrm{(Bu^i{}_2PS_2{}^{\bullet})Ni(S_2PBu^i{}_2)_2}$.[7] In most cases, the system returns to the initial state due to the recombination of S radicals.[5—7,15]

In the present work, we studied photochemical processes that occur in solutions of 8,8´-diquinolyl disulfide (RSSR) and di(mercaptoquinolinato)nickel(II) ($\mathrm{Ni(SR)_2}$) in toluene and benzene. The photodissociation of RSSR generates S radicals having two heteroatoms (S and N)

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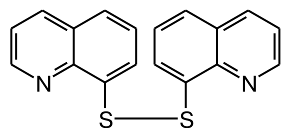
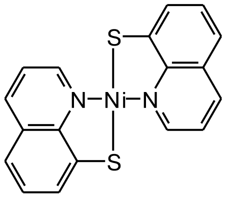
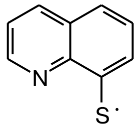
capable of coordinating with a metal atom. This coordination can increase considerably the lifetime of the radical complex, which makes it possible to organize a photochromic system in which the forward and backward reactions are photoinitiated. The choice of the complex is caused by the capability of reversible adding extraligands of the type of pyridine and amines and by the presence of an intense absorption band in the visible spectral region.[16,17] This band allows one to monitor transformations of the complex upon laser pulse photolysis.



RSSR



Ni(SR)$_2$



RS$^{\cdot}$

Experimental

Laser pulse photolysis was carried out on a setup with a XeCl excimer laser (308 nm, 15 ns, 30 mJ, surface area of the laser pulse cross section on a sample 10 mm^2).[18] Exciting and probing light pulses were directed to a 2—10-mm cell at a small angle (~2°) to each other. All experiments were conducted at 25 °C. To study slow processes in the millisecond and second time intervals, special quartz microcells were used (volume 50 mm^3, surface area 10 mm^2, thickness 5 mm) in which the solution volume was transmitted with a laser beam and the photoreaction kinetics was not violated by convective flows. When microcells were used at long measurement times, we applied a less powerful halogen incandescent lamp, whose emission was passed through narrow-band interferential filters, instead of the powerful xenon lamp to decrease the effect of the probing light. Selected experiments were carried out on a similar laser pulse photolysis equipment[19] with the perpendicular geometry of the exciting and probing light beams.

Optical absorption spectra were recorded on HP 8453 and Shimadzu UV-2501 spectrophotometers. Spectrally pure solvents (Merck) were used to prepare solutions. The intensities of laser pulses were measured by the triplet-triplet absorption of anthracene at 431 nm in an oxygen-free benzene solution (quantum yield of the triplet state is 0.53, and the molar absorption coefficient of the T—T absorption band is 42 000 L mol^{-1} cm^{-1}).[20] A specially developed program based on the Runge—Kutta method of the fourth order was used in numerical calculations of the decay kinetics of the intermediate optical absorption to solve differential equations. The Ni(SR)$_2$ complex was synthesized according to a known procedure.[16] 8,8´-Diquinolyl disulfide (Reagent corp., Russia) was used as received.

Results and Discussion

Photochemistry of solutions of 8,8´-diquinolyl disulfide. The Ni—S and Ni—N distances in the Ni(SR)$_2$ complex are 2.40 and 2.06 Å, respectively, and the bond lengths in the quinoline ring vary from 1.33 to 1.47 Å.[21] The optical absorption spectrum of the Ni(SR)$_2$ complex in benzene contains charge-transfer bands[16] with maxima at 554, 396, 336, and 308 nm (Fig. 1) and molar absorption coefficients of 900, 7240, 12270, and 11970 L mol^{-1} cm^{-1}, respectively. The spectrum of a solution of the disulfide in benzene has an absorption band with a maximum at 324 nm (ε = 11490 L mol^{-1} cm^{-1}) and ε = 9400 L mol^{-1} cm^{-1} in the wavelength region of XeCl laser radiation (308 nm).

The energy of the S—S bond in disulfides is ~100 kJ mol^{-1} and, hence, these molecules dissociate to two sulfur-containing radicals in a high quantum yield upon absorption of photons from a XeCl laser with an energy of 400 kJ mol^{-1}.[2,22—25] For a benzene solution of 8,8´-diquinolyl disulfide after a laser pulse, an intermediate absorption was detected, whose spectrum contains bands with maxima at ~364 (shoulder), 384, 404, 560, and 605 nm (Fig. 2, *a*, curve *1*). At wavelengths <345 nm, the absorbance decreases (bleaching) after a laser pulse, which is caused by the disappearance of the starting disulfide that absorbs in this spectral region (see Fig. 1).

The absorption, whose spectrum is shown in Fig. 2, *a*, belongs to the 8-mercaptoquinoline radical (RS$^{\bullet}$). The disappearance of the intermediate absorption obeys the

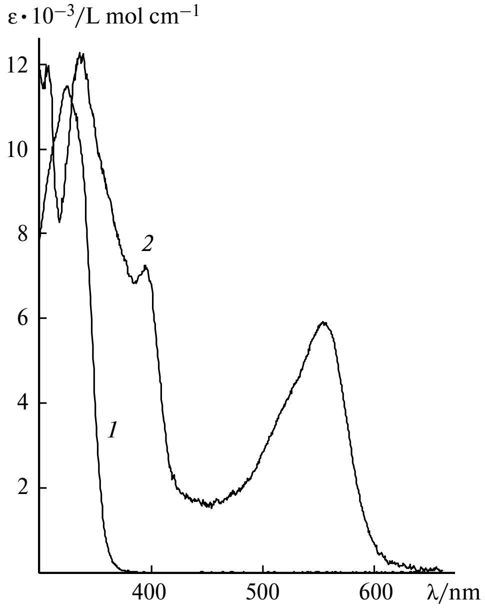


Fig. 1. Optical absorption spectra of RSSR (*1*) and Ni(SR)$_2$ (*2*) in benzene.

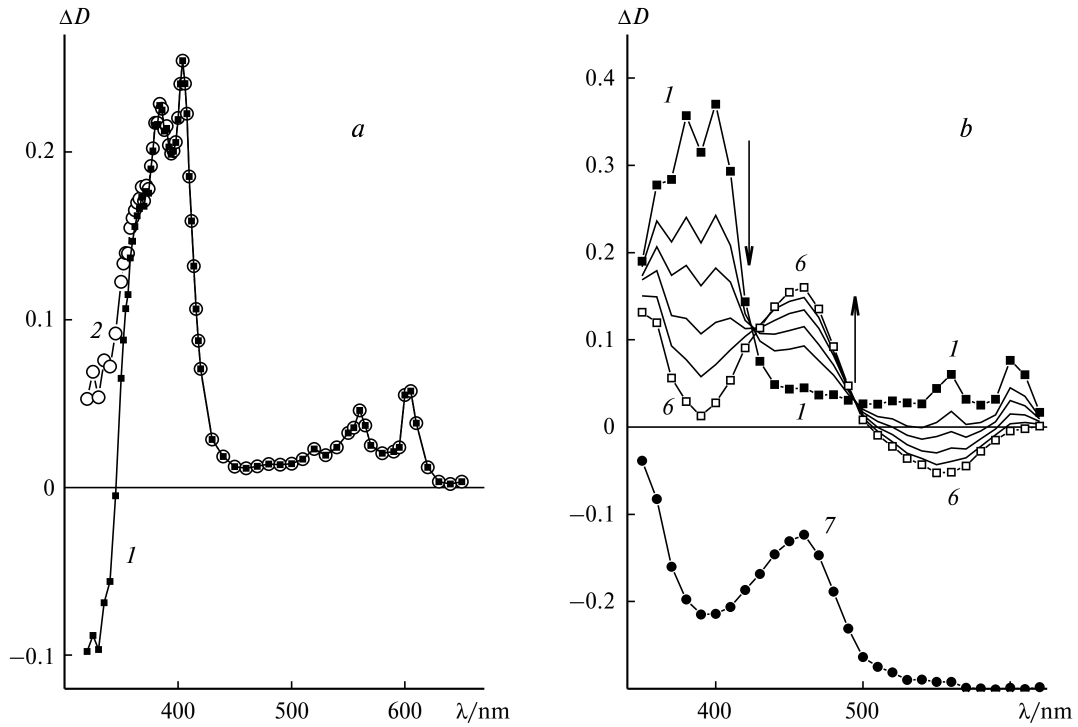


Fig. 2. Optical spectra of the RS$^•$ radical (*a*) and RS$^•$Ni(SR)$_2$ radical complex (*b*) detected by laser pulse photolysis: *a*, spectrum of a solution of RSSR ($1.4 \cdot 10^{-4}$ mol L^{-1}) in benzene after a laser pulse (50 ns) (*1*); spectrum corrected for the absorption of disulfide (*2*); *b*, spectra of a solution of RSSR ($3.3 \cdot 10^{-4}$ mol L^{-1}) and Ni(SR)$_2$ ($4.1 \cdot 10^{-5}$ mol L^{-1}) in benzene after 0 (*1*), 0.8 (*2*), 1.6 (*3*), 3.2 (*4*), 6.4 (*5*), and 44 μs (*6*); spectrum of the RS$^•$Ni(SR)$_2$ radical complex obtained from the spectrum (*6*) with allowance for the disappearance of absorption of the starting complex and disulfide (*7*) (shifted down by 0.3 for clarity).

second order kinetics and is associated with radical recombination to form the starting disulfide.

$$\mathrm{RS^\bullet + RS^\bullet \xrightarrow{k_1} RSSR} \quad (1)$$

The observed rate constant of radical decay at room temperature (298 K) is $k_{\mathrm{obs}} = (2k_{\mathrm{rec}}/\varepsilon) \cdot (\Delta D/l) = 3 \cdot 10^5$ s^{-1}, where ΔD is the absorbance of the radical after a pulse, and l is the cell thickness.

To determine the recombination rate constant ($2k_{\mathrm{rec}}$), it is necessary to know the molar absorption coefficient of the RS$^•$ radical. These parameters were determined in experiments using the reaction of the RS$^•$ radical with the stable nitroxyl radical (RNO$^•$),[3] which gives intense absorption bands in the UV (λ_{max} = 342 nm, ε = 14000 L mol^{-1} cm^{-1}) and visible (λ_{max} = 600 nm, ε = 1000 L mol^{-1} cm^{-1}) spectral regions. The reaction RS$^•$ + RNO$^•$ proceeds with the rate constant close to the diffusion limit, which allows it to compete successfully with the recombination of the RS$^•$ radicals. The molar absorption coefficient of the absorption band of the RS$^•$ radical with a maximum at 400 nm measured by this method is 8400±900 L mol^{-1} cm^{-1}. Using this value, we calculated the recombination rate constant ($2k_{\mathrm{rec}}$ = $4.6 \cdot 10^9$ L mol^{-1} s^{-1} in benzene) and determined the absorption spectrum of the RS$^•$ radical at 320—370 nm (see Fig. 2, *a*, curve *2*).

Appearance of intermediate absorption in solutions of RSSR and Ni(SR)$_2$ under laser irradiation. The absorption of the RS$^•$ radical appears in a solution of the disulfide RSSR and complex Ni(SR)$_2$ after a laser pulse (see Fig. 2, *b*, curve *1*). This absorption rapidly changes with retention of two isosbestic points at 425 and 495 nm, and a new absorption band with a maximum at 460 nm appears in the spectrum in 20 μs (see Fig. 2, *b*, curve *6*). In the region of 500—620 nm, the absorbance decreases (bleaching) due to the disappearance of the long-wave absorption band of the starting complex. The new spectrum disappears within several hundreds of milliseconds.

Coordination of the S radicals with the dithiolate complexes, which has been found earlier[5—7,15] for a number of systems, and the ability of the planar nickel complexes to add extraligands[8—14] suggest that the new band at 460 nm belongs to the radical complex RS$^•$Ni(SR)$_2$, which is formed due to the coordination of the RS$^•$ radical with the Ni(SR)$_2$ complex.

$$\mathrm{RS^\bullet + Ni(SR)_2 \xrightarrow{k_2} RS^\bullet Ni(SR)_2} \quad (2)$$

This reaction agrees with the disappearance of the long-wave absorption band of the starting Ni(SR)$_2$ complex with a maximum at 560 nm (see Fig. 2, *b*). Only reactions (1) and (2) occur at short times after a laser pulse ($\tau < 1/(k_2 \cdot C_0)$, where C_0 is the initial concentration of the $Ni(SR)_2$ complex). Further other reactions involving the radical complex $RS^{\bullet}Ni(SR)_2$ can occur. For instance, the complex can add the second radical to form a biradical complex.[7] In terms of the scheme of reactions (1) and (2), the following expressions can be written for the time plots of the concentrations of the radical and radical complex ($R(t)$ and $A(t)$, respectively):

$$R(t) = R_0\{e^{-k_2C_0t}/[1 + R_0(2k_1/k_2C_0)(1 - e^{-k_2C_0t})]\}, \quad (3)$$

$$A(t) = R_0(k_2C_0/2k_1R_0)\ln[1 + (2k_1R_0/k_2C_0)(1 - e^{-k_2C_0t})], \quad (4)$$

where R_0 is the initial concentration of the radical after a laser pulse. These equations make it possible to determine the ratio of the absorbance of the radical complex at long times (ΔD_∞) to the initial absorbance (ΔD_0) of the radical after a laser pulse (in the band maximum at 400 nm)

$$\Delta D_\infty/\Delta D_0 = [(\varepsilon_A - \varepsilon_C)/\varepsilon_R](k_2C_0/2k_1R_0) \cdot \ln[1 + (2k_1R_0/k_2C_0)] \xrightarrow{R_0\to 0} (\varepsilon_A - \varepsilon_C)/\varepsilon_R, \quad (5)$$

where ε_A and ε_C are the molar absorption coefficients of the radical complex and initial complex, respectively, at the wavelength of measurements. The plot of the $\Delta D_\infty/\Delta D_0$ ratio *vs.* initial concentration R_0 measured at 460 nm is shown in Fig. 3. It is seen that ratio (5) at $R_0 \to 0$ tends to the $(\varepsilon_A - \varepsilon_C)/\varepsilon_R$ value, which allows one to determine the molar absorption coefficient of the absorption band of the radical complex at 460 nm (ε_A = 16 600±500 L mol^{-1} cm^{-1}).

The rate constant of coordination of the radical (k_2) was determined at its low initial concentrations when the recombination is suppressed and other possible reactions are absent. The initial region (1—2 μs) of the kinetic absorption curve at 460 nm was processed by an equation of the first order and determined the observed rate constant (k_{obs}). Using Eq. (4), we find

$$k_{obs}(A_\infty/R_0) = k_2C_0. \quad (6)$$

The concentrations A_∞ and R_0 can be calculated from the absorbances at 460 and 400 nm, because the molar absorption coefficients of the absorption bands of the radical and radical complex were determined above. The linear plot of $k_{obs}(A_\infty/R_0)$ *vs.* C_0, whose slope ratio determines the rate constant $k_2 = (4.4\pm0.1) \cdot 10^9$ L mol^{-1} s^{-1}, is presented in Fig. 4.

After the molar absorption coefficients and rate constants of recombination and radical coordination were determined, we can consider a possibility of participation of the radical and radical complex in other reactions. The experimental kinetic curves at 400, 460, and 560 nm at maxima of the absorption bands of the $RS^{\bullet}$ radical, $RS^{\bullet}Ni(SR)_2$ radical complex, and $Ni(SR)_2$ complex are presented in Fig. 5. Curve *4* (see Fig. 5) is the calculation for 460 nm in terms of reactions (1) and (2), which agrees with the experimental curve only in the initial region (0—3 μs). At long times, the experimental kinetic curve runs much lower than the calculated one. Thus, a considerable amount of the radical complexes decays in the parallel process.

The yield of the radical complex at different concentrations of the starting complex, depending on the initial radical concentration (variation of the laser pulse intensity), is shown in Fig. 6 (points). Line *1* corresponds to the hypothetical case of coordination of all radicals (no recombination and no parallel processes). Smooth

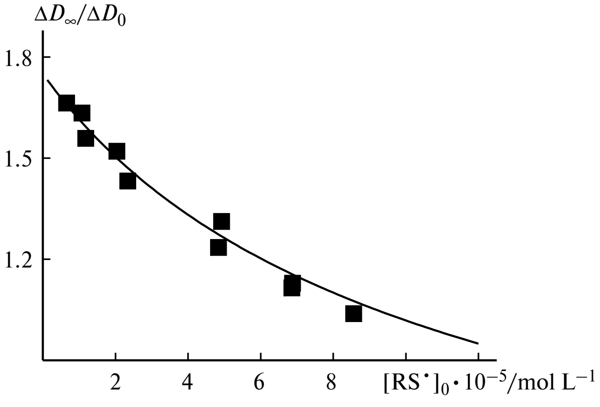


Fig. 3. Ratio of the absorbance of the radical complex at 460 nm (ΔD_∞, time 30—50 μs) to the initial absorbance of the radical at 400 nm (ΔD_0, immediately after a laser pulse) *vs.* initial concentration of the radical ($[RS^{\bullet}]_0$); solution of RSSR ($2.6 \cdot 10^{-4}$ mol L^{-1}) and $Ni(SR)_2$ ($14.8 \cdot 10^{-5}$ mol L^{-1}) in benzene.

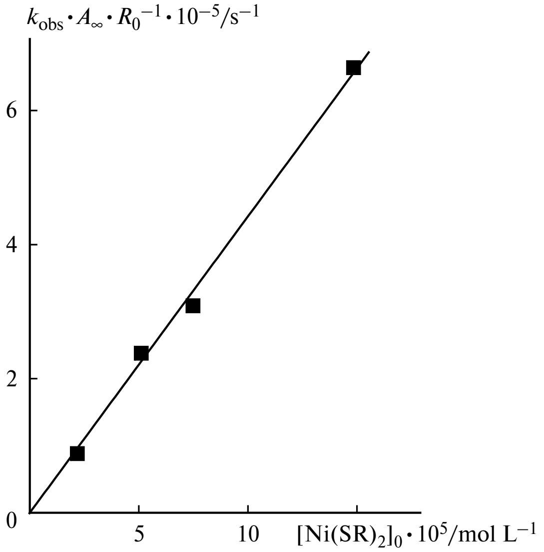


Fig. 4. Parameter $k_{obs}(A_\infty/R_0)$ *vs.* initial concentration of the complex ($[Ni(SR)_2]_0$) (k_{obs} and A_∞ were determined at low concentrations of the radical ($R_0 < 10^{-5}$ mol L^{-1})); solution of RSSR ($1.7 \cdot 10^{-4}$ mol L^{-1}) and $Ni(SR)_2$ in benzene.

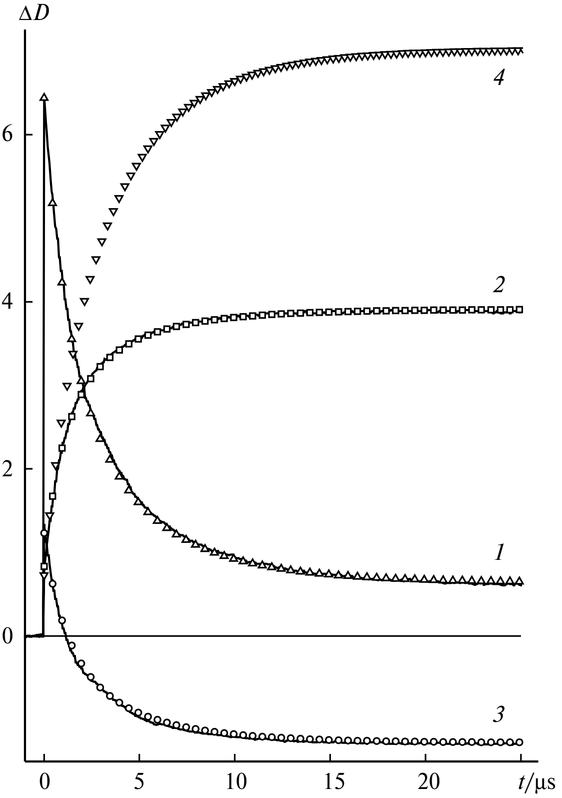


Fig. 5. Kinetic curves of a change in the intermediate absorption during laser pulse photolysis of a solution of RSSR ($1.3 \cdot 10^{-4}$ mol L^{-1}) and $Ni(SR)_2$ ($5.1 \cdot 10^{-5}$ mol L^{-1}) in benzene: experiment (*1—3*, lines) and calculation (*1—3*, points) at 400 (*1*), 460 (*2*), and 560 nm (*3*) (calculation was performed for reactions (1), (2), and (7), for molar absorption coefficients and rate constants, see Tables 1 and 2); the kinetic curve was calculated with allowance for reactions (1) and (2) at 460 nm (*4*).

curves *2—4* show the yield calculated by the above obtained rate constant with allowance for reactions (1) and (2). Points (*5—7*) present the experimental results. At $R_0 < 10^{-5}$ mol L^{-1}, all calculated curves and experimental data approach to line *1*. However, a substantial divergence begins at $R_0 > 10^{-5}$ mol L^{-1}. Inconsistency between the calculated and experimental yields of the radical complex increases considerably with a decrease in the concentration of the starting $Ni(SR)_2$ complex. Thus, at high initial concentrations of the radical, an additional process develops in the system and results in the disappearance of the radical complex. This process ceases together with the radical decay, because the absorption of the radical complex formed within 30—50 μs further remains unchanged. The decay of the latter is much slower (during several hundreds of milliseconds) without changing the shape of the spectrum. Therefore, we can exclude the monomolecular decay of $RS^{\bullet}Ni(SR)_2$ to the free radical and starting complex.[5—7,15] No coordination of the second radical occurs to form a biradical complex,[7] because the shape of the intermediate spectrum remains unchanged (see isosbestic points in Fig. 2, *b*). All above-listed conditions correspond to the following reaction, which also agrees with the photochromic properties of the system:

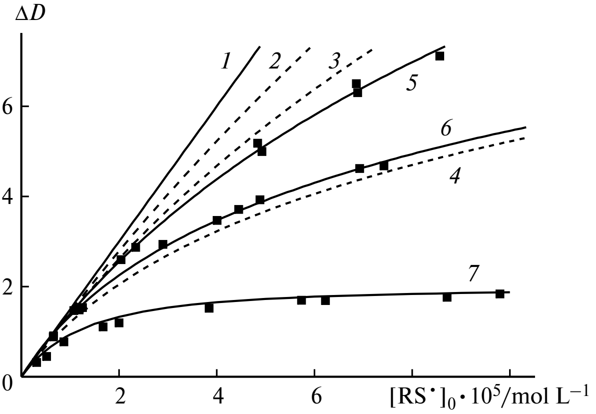


Fig. 6. Absorption of the $RS^{\bullet}Ni(SR)_2$ radical complex at 460 nm (30—50 μs after a pulse) *vs.* initial concentration of the $RS^{\bullet}$ radical (absorption at 400 nm immediately after a pulse): *1*, calculation for coordination of all radicals with the complex (no recombination and reaction (7)); *2—4*, calculation for occurrence of reactions (1) and (2) only at $[Ni(SR)_2] \cdot 10^5$ = 14.8 (*2*), 7.5 (*3*), and 2.2 mol L^{-1} (*4*); *5—7*, calculation for the same concentrations of the complex for occurrence of reactions (1), (2), and (7). Points are experimental values at the indicated concentrations. For parameters of calculation, see Tables 1 and 2.

$$RS^{\bullet} + RS^{\bullet}Ni(SR)_2 \xrightarrow{k_3} RSSR + Ni(SR)_2. \qquad (7)$$

This reaction produces no new species that could transform the optical spectrum of the radical complex. At high radical concentrations, reaction (7) decreases substantially the concentration of the radical complex. After the radical decay, this reaction is completed, and the "survived" radical complexes can disappear rather slowly. Reaction (7) can include the step of coordination of the second radical to form a biradical complex. However, its lifetime should be sufficiently short (must not exceed several hundreds of nanoseconds) to have no effect on the rate and spectrum of the intermediate absorption.

Reactions (1), (2), and (7) make it possible to calculate the kinetic curves, which agree well with the experimental data (see Fig. 5), with the single varied parameter $k_3 = (3.1\pm0.1) \cdot 10^9$ L mol^{-1} s^{-1}. Smooth curves *5—7* (see Fig. 6) represent the calculated absorption of the radical complex (460 nm) using the determined k_3 value, which coincides with the experimental points for different initial concentrations of the $Ni(SR)_2$ complex. The molar absorption coefficients of species and the reaction rate constants are given in Tables 1 and 2. Thus, reactions (1), (2), and (7) considered as a whole provide the complete ex-

Table 1. Molar absorption coefficients (ε/L mol^{-1} cm^{-1}) for the initial and intermediate species under study in benzene

λ/nm	Ni(SR)$_2$	RS$^\bullet$	RS$^\bullet$Ni(SR)$_2$
400	6630	8400±900	8800±300
460	1620	800±100	16600±500
560	5620	1500±200	800±100

Table 2. Rate constants of the reactions under study (k_1—k_4) in benzene and toluene

Solvent	$2k_1 \cdot 10^{-9}$	$k_2 \cdot 10^{-9}$	$k_3 \cdot 10^{-9}$	$2k_4 \cdot 10^{-4}$
	L mol^{-1} s^{-1}			
Benzene	4.6±0.1	4.4±0.1	3.10±0.1	—
Toluene	4.5±0.7	4.7±0.6	2.8±0.8	4.6±0.1

planation of all kinetic transformations for solutions of the disulfide and nickel complex that occur in the microsecond time interval.

Decay of radical complex RS$^\bullet$Ni(SR)$_2$. At room temperature, the RS$^\bullet$Ni(SR)$_2$ radical complex decays in the millisecond time interval accompanied by the appearance of the absorption bands of the initial complex Ni(SR)$_2$ and disulfide RSSR. Thus, this system possesses photochromic properties, which allow it to repeat multiply phototransformation cycles. In the case of several similar systems,[5—7,15] the complexes of sulfur-containing radicals with the dithiolate NiL$_2$ complexes decay through monomolecular dissociation with radical escape from the coordination sphere. The lifetime of these species lies in the micro- or millisecond time intervals. The repeated coordination of the radical elongates the effective lifetime of the radical complex by two—three orders of magnitude.[5—7,15] The repeated coordination exerts an especially pronounced effect on an increase in the lifetime of the radical complex with an increase in the concentration of the NiL$_2$ complex.[5]

The curve of changing the concentration of the radical complex (absorption at 460 nm), which corresponds to the reaction of the second order, is presented in Fig. 7 (corresponding anamorphosis is shown in insert). Numerical simulation shows that kinetic curves of the second order can be obtained in different reaction schemes. For instance, for reversible coordination of a radical, the disappearance of the radical complex occurs finally due to radical recombination, which usually results in the kinetics similar to the second order.

To reveal the mechanism of decay of the RS$^\bullet$Ni(SR)$_2$ radical complex, we studied the dependence of the observed rate constant on the amplitude of the signal (variation of the laser pulse intensity) in a wide range of concentrations of the starting Ni(SR)$_2$ complex (Fig. 8). The linear character of the curve that passes through the origin indicates that the radical complex decays only due to reactions of the second order. The decay rate constants coincide for the Ni(SR)$_2$ complex concentrations differing by an order of magnitude, which makes it possible to exclude the monomolecular decomposition of the radical complex and repeated coordination of the radical. Since the system returns to the initial state, the reaction products are the starting disulfide and complex. All these data suggest that the radical complex disappears through the reaction

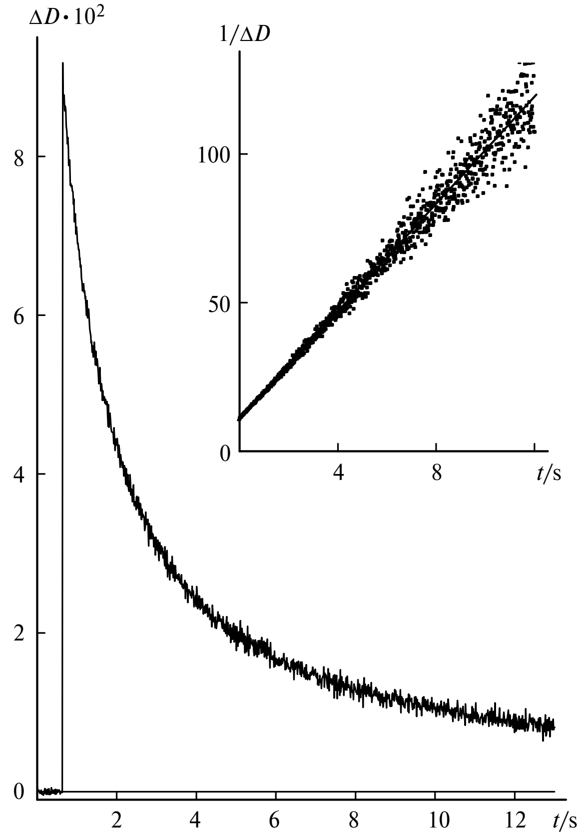


Fig. 7. Absorption decay kinetics of the RS$^\bullet$Ni(SR)$_2$ radical complex at 460 nm under laser pulse photolysis of a solution of RSSR ($1.0 \cdot 10^{-4}$ mol L^{-1}) and Ni(SR)$_2$ ($3.5 \cdot 10^{-5}$ mol L^{-1}) in toluene. The anamorphosis of the second-order kinetics is shown in insert.

$$\mathrm{RS^\bullet Ni(SR)_2 + RS^\bullet Ni(SR)_2 \xrightarrow{k_4} RSSR + 2\,Ni(SR)_2}. \quad (8)$$

Since the molar absorption coefficient of the absorption band of the radical complex was determined above (see Table 1), the data presented in Fig. 8 make it possible to calculate the second order rate constant ($2k_4 = (4.6\pm0.1) \cdot 10^4$ L mol^{-1} s^{-1}).

Reaction (8) can proceed in either one step or *via* a complicated mechanism. The latter can include, for example, the step of radical transfer from the coordination

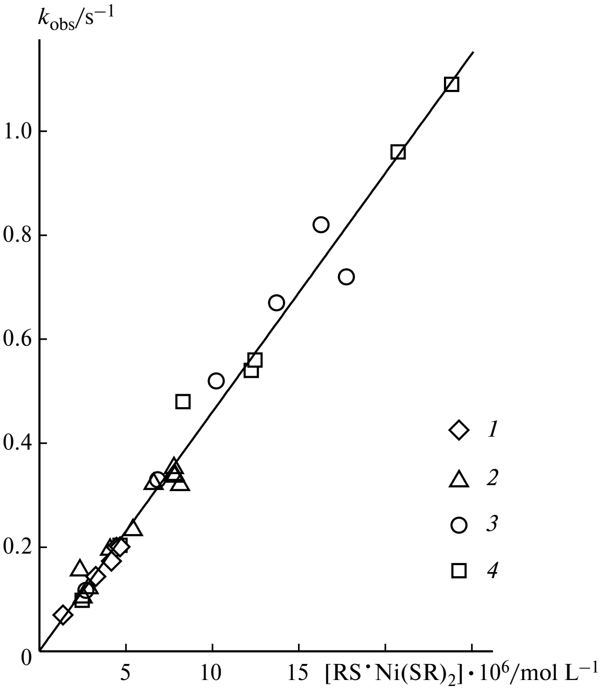


Fig. 8. Observed rate constant (k_{obs}) of the absorption decay of the RS$^•$Ni(SR)$_2$ radical complex at 460 nm *vs.* its concentration: [Ni(SR)$_2$]•10^5 = 0.67 (*1*), 1.53 (*2*), 3.58 (*3*), and 7.1 mol L^{-1} (*4*); [RSSR] = 1.7•10^{-4} mol L^{-1}.

sphere of one complex to the sphere of another complex to form a biradical complex (RS$^•$)$_2$Ni(SR)$_2$.

$$\mathrm{RS^{\bullet}Ni(SR)_2 + RS^{\bullet}Ni(SR)_2 \longrightarrow Ni(SR)_2 + (RS^{\bullet})_2Ni(SR)_2 \longrightarrow RSSR + 2\,Ni(SR)_2} \quad (9)$$

If the first step of radical transfer is rate-determining, then the whole reaction would obey the second order kinetics. The question about the mechanism of reaction (8) coincides with the same problem for reaction (7). In both cases, the biradical complex can be an intermediate species. Since no formation of this species was detected in the microsecond time region, it can rapidly decompose, indeed, in the nanosecond range.

Temperature plot of the rate constants of reactions involving radical and radical complex. Laser pulse photolysis of solutions of RSSR and Ni(SR)$_2$ in a wide temperature range (230—350 K) and processing of the obtained kinetic curves made it possible to determine the temperature plots for the rate constants of all reactions (Fig. 9). The calculated activation energies and pre-exponential factors are given in Table 3. These parameters have similar values for reactions (1) and (2) (radical recombination and coordination, respectively) and reaction (7). The rate constants of the listed reactions are lower than the diffusion limit by 2—3 times (k_{diff} = $8RT/3000\eta$ = 1.1•10^{10} L mol^{-1} s^{-1}), most likely, due to the steric factor. In these cases, the activation energies are similar to the activation energy of diffusion motion determined by the temperature dependence of the solvent viscosity.

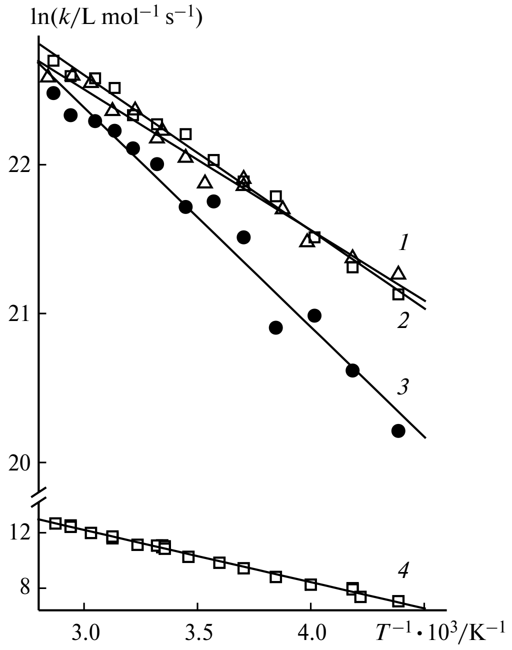


Fig. 9. Temperature plots of the rate constants of recombination (*1*), coordination of the RS$^•$ radical with the initial complex (*2*) and the radical complex (*3*), and the reaction of two radical complexes (*4*).

The activation energy of reaction (8) is substantially higher than that for the other reactions and comparable with the activation energy of monomolecular dissociation of RS$^•$NiL$_2$ radical complexes.[5—7] This similarity of activation energies can serve as an argument in favor of a complicated mechanism including radical transfer (reac-

Table 3. Activation energies (E_a) and pre-exponential factors (logk_0) of the reaction rate constants for the RSSR + Ni(SR)$_2$ system in toluene

Reaction	E_a/kJ mol^{-1}	log(k_0/L mol^{-1} s^{-1})
RS$^•$ + RS$^•$ → RSSR (1)	7.7±0.4	11.0±0.1
RS$^•$ + Ni(SR)$_2$ → RS$^•$Ni(SR)$_2$ (2)	8.7±0.3	11.2±0.1
RS$^•$ + RS$^•$Ni(SR)$_2$ → RSSR + Ni(SR)$_2$ (7)	12.3±0.7	11.6±0.1
2 RS$^•$Ni(SR)$_2$ → RSSR + 2 Ni(SR)$_2$ (9)	31.4±0.6	10.2±0.1

tion (9)). In this case, the RS$^{\bullet}$—Ni bond in one of the complexes should be cleaved, and the energy of this bond can determine the energetics of the whole process. For the planar NiL_2 dithiolate complexes, the energy of homolytic cleavage of the Ni—S bond is about 200 kJ mol^{-1} [26] and, hence, the energy of radical coordination is much lower than the bonding energy of the dithiolate ligand. It is known[27] than many planar nickel complexes reversibly add nitrogen-containing compounds (amines, pyridine, and picoline) as extraligands, which are coordinated by the nitrogen atom at the fifth coordination site. The activation energies of decomposition of these extra complexes lie in a range of 30—40 kJ mol^{-1},[27,14] which agrees well with the dissociation energy of the complexes of sulfur-containing radicals with nickel(II) dithiolate complexes (~30 kJ mol^{-1}).[5]

Rather high activation energy induces a substantial decrease in the rate constant of reaction (8) and an increase in the lifetime of the radical complex. For instance, at 230 K and the initial concentration $[RS^{\bullet}Ni(SR)_2] \approx 10^{-5}$ mol L^{-1}, the time of decay of the radical complex is ~100 s, which allows one to detect steady-state optical spectra. The spectra of a solution of RSSR and $Ni(SR)_2$ in cooled toluene at 230 K before and after irradiation with pulses of a XeCl laser (λ = 308 nm) are shown in Fig. 10. The spectra were recorded on an HP 8453 spectrophotometer with a diode array (time of recording the full spectrum is 5 s). After irradiation, the intensity of the band of the starting complex decreases with the simultaneous appearance of a new band with a maximum at 460 nm. The differential spectrum coincides with that observed in pulse photolysis (see Fig. 2, *b*). Taking into account the disappearance of absorption of the starting $Ni(SR)_2$ complex and disulfide RSSR, one can plot the optical spectrum of the $RS^{\bullet}Ni(SR)_2$ radical complex (see Fig. 10, curve *4*). Thus, the spectrum of this species has two intense absorption bands with maxima at 458 and 353 nm, being, in fact, the long-lived species, whose lifetime in cooled solutions can achieve several tens and hundreds of seconds.

Structure and nature of optical spectrum of radical complex. Depending on the pH value, free 8-mercaptoquinoline in aqueous solutions can exist as protonated (RSH^{2+}), thiol (RSH), zwitterionic ($RSH^{\pm}$), and ionized (RS^{-}) species. Each of them has different optical absorption spectra.[28—33] In nonpolar organic solvents, 8-mercaptoquinoline usually exists in the thiol form, which is characterized (in benzene) by absorption bands at 250 and 324 nm (ε = 22000 and 4500 L mol^{-1} cm^{-1}, respectively). Coordination compounds contain the ionized form as a ligand, whose free state in aqueous solutions exhibits absorption bands with maxima at 260 and 367 nm (ε = 22 300 and 4300 L mol^{-1} cm^{-1}, respectively).[31] The zwitterionic form is characterized by an absorption band in the visible part of the spectrum. The spectrum of this species in water (at pH 5.2, the content is 96%) has a band with a maximum at 446 nm ($\varepsilon \approx$ 2000 L mol^{-1} cm^{-1}). In polar solvents without a hydroxyl group, the content of the zwitterionic form decreases, and the maximum of its long-wave absorption band shifts toward 550—605 nm, which imparts violet color to solutions of 8-mercaptoquinoline.[31—33]

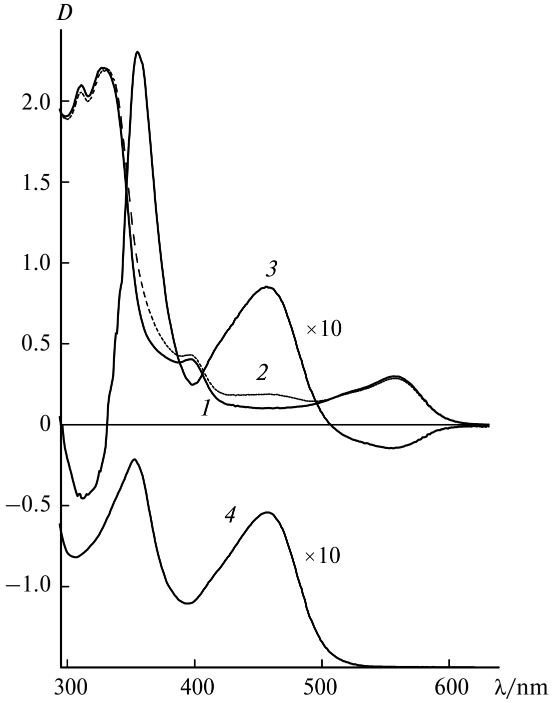


Fig. 10. Steady-state photolysis of a solution of RSSR ($1.3 \cdot 10^{-4}$ mol L^{-1}) and $Ni(SR)_2$ ($5.1 \cdot 10^{-5}$ mol L^{-1}) in cooled (230 K) toluene (1-cm cell): optical spectra before (*1*) and after (*2*) irradiation (10 pulses of a XeCl laser), the difference of spectra *1* and *2* (*3*), and the optical spectrum of the $RS^{\bullet}Ni(SR)_2$ radical complex (*4*) (obtained with allowance for the absorption decay of the $Ni(SR)_2$ complex and RSSR disulfide).

The spectra of the 8-mercaptoquinoline complexes of metal ions with the filled d-shell (Zn^{2+}, Cd^{2+}, *etc.*) exhibit two absorption bands at 260 and 380—420 nm.[31] The position and intensity of these bands are similar to the absorption parameters of the free ligand RS^{-}. Thus, the bands in the spectra of these complexes correspond, most likely, to intraligand transitions. Coordination with transition metal ions (Ni^{2+}, Cu^{2+}) complicates the spectrum giving a series of overlapped bands and additional bands in a lower-frequency region of the spectrum. The greater intensity of these bands makes it possible to attribute them to metal—ligand charge-transfer bands.[16,17] According to analysis of the spectra of several square planar nickel complexes,[34] the $4p_z$-orbital of the metal ion and four π-orbitals of the coordinating atoms of the ligands, form a bonding molecular π-orbital involved in many transitions. For coordination of the nitrogen-containing extraligand along the axial axis, the $4p_z$-orbital of the nickel ion stops interacting with the π-orbitals of the equatorial ligands, and the charge-transfer bands disappear.[16] The spectrum of the adduct resembles the spectra of the thioquinolate complexes with the filled d-shell.

There is another explanation of a considerable transformation of the spectrum of the $Ni(SR)_2$ complex upon the addition of nitrogen-containing compounds. A pair of electrons of the nitrogen atoms of the extraligand is assumed[31] to complete the d-shell of the nickel ion ($3d^8$), which changes the spectrum. In the framework of these concepts, the optical spectrum of the complexes with the unfilled d-shell is determined by a greater contribution of the zwitterionic form of the ligand. On going to the filled d-shell, the ligand structure becomes similar to the thiol one.[31] Despite different explanations of the nature of spectrum changing, it is shown in many studies that the appearance of an additional axial ligand results in the disappearance of the long-wave absorption band of the $Ni(SR)_2$ complex at 560 nm and formation of a new band at 420—440 nm.

In the case of coordination of the $RS^{\bullet}$ radical, the long-wave band of the starting complex also disappears and a new band with a maximum at 460 nm appears. This suggests that the radical is also coordinated at the axial coordinate. At the moment of collision of the radical and complex, the coordination occurs, most likely, due to the sulfur atom on which a negative charge and a significant spin density are usually localized in sulfur-containing radicals.[4] Quinoline (molecular analog of the $RS^{\bullet}$ radical containing no sulfur atom but with the nitrogen atom) exerts no effect on the spectrum of the $Ni(SR)_2$ complex (the quinoline concentration is $4 \cdot 10^{-1}$ mol L^{-1}, and that of the complex is $2 \cdot 10^{-5}$ mol L^{-1}).

It cannot be excluded that after coordination with the sulfur atom the radical is additionally bonded through the nitrogen atom as well. The distortion of the planar structure of the complex upon adduct formation can favor this process.[31] In this case, the $RS^{\bullet}Ni(SR)_2$ radical adduct can be presented as an octahedral complex of the trivalent nickel ion with three equivalent $Ni(SR)_3$ ligands.

The radical nature of the adduct results in instability of the radical complex as a whole, which finally decomposes. For the $RS^{\bullet}Ni(SR)_2$ complex, the monomolecular dissociation channel has, most likely, a low rate constant (absence of a cut on the ordinate axis gives an estimate of $k_{\mathrm{diss}} < 10^{-2}$ s^{-1} (see Fig. 8)), and this channel is blocked by bimolecular reaction (8). If the radical is coordinated due to the two atoms (S and N), the disulfide in reaction (8) can be formed from species that earlier were ligands in the coordination sphere of the ion. A possibility of this process is indicated by a small shift of the maximum and an increase in the intensity of the long-wave absorption band of the starting complex under prolong irradiation (Fig. 11). These changes can be caused by the formation of complexes in which the sulfur atoms of two ligands are in the *cis*-position to each other.

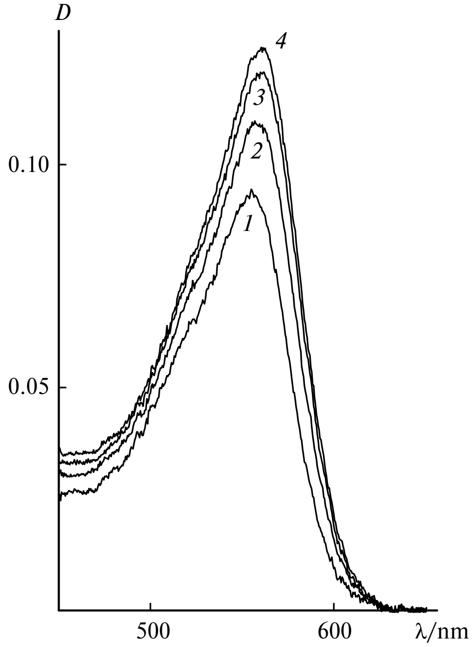


Fig. 11. Change in the long-wave absorption band of the $Ni(SR)_2$ complex during steady-state photolysis of a solution of RSSR ($1.3 \cdot 10^{-4}$ mol L^{-1}) and $Ni(SR)_2$ ($7.5 \cdot 10^{-5}$ mol L^{-1}) in toluene (2-mm cell): 0 (*1*), 40 (*2*), 220 (*3*), and 460 pulses of a XeCl laser (*4*).

Thus, the primary process in photochromic transformations in solutions of 8,8′-diquinolyl disulfide and di(mercaptoquinolinato)nickel(II) in toluene and benzene is the photodissociation of the disulfide to two sulfur-containing radicals. In the presence of the nickel complex, the radicals decay in competing recombination and coordination reactions, which proceed with the rate constants similar to the diffusion limit. The coordination of the radical produces the radical complex $RS^{\bullet}Ni(SR)_2$, which is consumed in two reactions with considerably different rate constants. At high initial concentrations of the radicals (high intensities of a laser pulse) in the microsecond time region, some amount of the radical complex disappears due to the reaction with the $RS^{\bullet}$ radicals, which have no time yet to recombine or disappear in the coordination reaction. In a region of much longer times (intervals of seconds), two radical complexes disproportionate to regenerate disulfide molecules and the starting nickel complex, thus completing the cycle of photochromic transformations.

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