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Transformations of Diphenyl Sulfide and Diphenylamine on Aluminum Chloride

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Abstract—Thianthrene has been synthesized by reacting diphenyl sulfide with $AlCl_3$ in heptane at 98°C for 8 h at a diphenyl sulfide : $AlCl_3$ molar ratio of 2 : 1; the thianthrene yield is 58%. The reaction mechanism proposed previously has been confirmed by quantum-chemical calculations; the reaction is characterized by a low negative value of Gibbs free energy, a low heat of reaction, and a high activation energy of the first step. Diphenyl ether and diphenylamine do not enter the test reaction because of low nucleophilicity of the heteroatoms; diphenylamine dimerizes under the reaction conditions to form *N*,*N*'-diphenylbenzidine.

Keywords: diphenyl sulfide, diphenylamine, aluminum chloride, thianthrene, reaction mechanism

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Previously we found that the reaction of diphenyl sulfide (DPS) with $AlCl_3$ yields thianthrene [1]. Thianthrene and its derivatives have found application as dyes, indicators, pesticides, antioxidants, inhibitors, and polymerization promoters [2]. They are also widely used as stabilizers in the production of polyvinyl chloride and polyvinyl acetyls and as a component of nuclear reactor lubricants. Recent discoveries show that thianthrene is effective in treating *Leismania Donovan*-caused leishmaniasis, the disease that annually affects up to half million people in developing countries [3]. Thianthrene metal complexes having semiconducting properties are studied, opening up the possibility of their use in the microelectronics industry. The use of thianthrene admixtures as a hole conduction agent in LED (light emitting diode) technology for the production of displays also holds promise [4].

The purpose of this work was to study the interaction of $AlCl_3$ with diphenyl sulfide to obtain thianthrene and with its nitrogen- and oxygen-containing analogues diphenylamine (DPA) and diphenyl ether (DPE).

EXPERIMENTAL

The reagents and solvents used in the syntheses were diphenyl sulfide, diphenylamine, diphenyl ether, $AlCl_3$, $AlBr_3$, dimethyl sulfoxide (DMSO), benzene, and nitrobenzene of the "chemically pure" grade. The reaction temperature was varied from 80 to 98°C. The reactor was a three-necked glass flask equipped with a mechanical stirrer, an electric heater, a thermocouple, and a temperature controller. The synthesis procedure is described below.

Synthesis of Thianthrene

The reactor was charged with 50–100 mL of a solvent preliminarily dehydrated over calcium chloride (hydrophyllite). Then 15 mL (0.09 mol) of DPS was poured in, the stirrer was switched on, and 12 g (0.09 mol) of anhydrous aluminum chloride was added. After the formation of a soluble purple complex, another 15 mL (0.09 mol) of DPS was added into the reactor. The reaction mixture was heated to a preset temperature, and the reaction was conducted for 10 h with stirring. Then the brown-colored reaction mixture was cooled to 20°C, 50 mL of distilled water was slowly poured, and the mixture was stirred at this temperature for 1 h. The aqueous layer was neutralized with a 20% sodium hydroxide solution, the reaction mixture was cooled to room temperature, and the aqueous layer was separated from the organic layer.

The latter was evaporated to reduce the volume by three to four times and cooled in a refrigerator to +10°C. The precipitated thianthrene crystals were filtered off on a Buchner funnel, washed with the cold solvent, and recrystallized from a mixture of benzene with ethyl alcohol (1 : 1 by volume). Some syntheses were carried out in a solventless mode in a small excess of DPS. The thianthrene yield was calculated with respect to the theoretical yield defined by the equation:

$$2(C_6H_5)_2S + AlCl_3 \xrightarrow[-HCl]{+H_2O} C_{12}H_8S_2 + Al(OH)Cl_2 + 2C_6H_6.$$

A similar procedure was used to run the reaction with DPA or DPE and the DPS + DPA or DPS + DPE cross-synthesis (see table).

Analysis

The composition and amount of the components of the reaction mixtures were determined by GLC on a Chromatech Kristall 2000 M instrument using a capillary column with $l = 15$ m, $d = 0.32$ mm, and a polymethylsiloxane film thickness of 0.20 μm. The injector and detector temperatures were 290 and 300°C, respectively; the column temperature was programmed as follows: holding for 5 min at 70°C, heating at a rate of 4°C/min to 290°C, and holding at this temperature for 20 min. The carrier gas was helium used at a flow rate of 1.2 mL/min.

IR spectra were recorded on a Perkin-Elmer Spectrum 100 Fourier-transform IR spectrometer in the attenuated total reflectance mode using a Miracle single-reflection ATR accessory—"strong" apodization, 4.00 cm^{-1} resolution. UV spectra were recorded in ethanol with an SF 2000 spectrophotometer over the wavelength range of 200–800 nm. The UV spectrum of thianthrene exhibits an enhanced intensity and a bathochromic shift of the long-wavelength absorption band due to n–π^* transition with $\lambda_{max} = 258$ nm, which is associated with the +M effect of the second sulfur atom having the lone electron pair, as compared with the DPS spectrum. A broad intense absorption band with $\lambda_{max} = 205$ nm corresponds to the HOMO → LUMO π–π^* transition.

To establish the structure of the samples, ^{13}C NMR and ^{1}H NMR spectra in deuterochloroform ($CDCl_3$) were recorded on a Bruker AVACE AV300 instrument operating at 75- and 300-MHz frequencies, respectively, using tetramethylsilane as the standard. The thianthrene structure was confirmed by the UV, IR, and NMR spectral methods. The ^{1}H NMR spectrum of thianthrene displays signals of two groups of aromatic protons as symmetrical double doublets at δ_A 7.460 ppm and δ_B 7.225 ppm. The ^{13}C NMR spectrum exhibits three signals due to tertiary and quaternary carbon atoms at δ_1 135.57 ppm, δ_2 128.75 ppm, and δ_3 127.70 ppm.

In addition, the samples were investigated by the technique of gas chromatography–mass spectrometry (GC–MS) using a Perkin-Elmer chromatograph with a Perkin-Elmer CLARUS 500 mass-selective detector operating in the electron ionization mode (energy, 70 eV). The analysis conditions were as follows: an HP-5MS chromatographic capillary column with $l =$ 30 m, $d = 0.32$ mm, and a polymethylsiloxane film thickness of 0.20 μm; an injector temperature of 280°C, a detector interface temperature of 290°C; the oven temperature programmed as holding for 3 min at 70°C, heating at a rate of 4°C/min to 290°C, and holding at this temperature for 20 min; and a carrier gas (helium) flow rate of 1.0 mL/min. Data acquisition and processing were carried out using the software AMDIS V2.66; chromatographic peaks were identified with the use of NIST 2.0f electronic mass spectra libraries updated on July 23, 2008.

The most intense peaks of fragment ions at m/z 184, 171, 108 in the thianthrene spectrum correspond to cations containing a sulfur atom: $C_{12}H_8S^+$, $C_{11}H_7S^+$, and $C_6H_4S^+$, indicating the dissociation of C–S bonds during the fragmentation of the molecular ion, m/z (I_{rel}, %): 216 (100), 184 (83.9), 171 (23.2), 152 (7.1), 139 (17.9), 127 (3.6), 108 (14.3), 95 (8.9), 86 (7.1), 69 (19.6). Mass spectrum of *o*-di(phenylthio)benzene, m/z (I_{rel}, %): 294 (100), 261 (3.6), 217 (7.1), 185 (78.6), 171 (7.1), 152 (28.6), 139 (10.7), 109 (14.3), 95 (7.1), 77 (26.8). The fragmentation of the molecular ion of bis(phenylthio)diphenyl sulfide involves the elimination of first the thiophenyl and then the phenyl radical followed by the removal of the sulfur atom, m/z (I_{rel}, %): 402 (11.1), 293 (100), 281 (6.7), 216 (55.6), 184 (71.1), 171 (11.1), 152 (13.3), 139 (11.1), 109 (8.9), 96 (6.7), 77 (8.9). In the mass spectrum of phenylthiothianthrene, peaks of fragment ions at m/z = 215, 171, 145 have a high relative abundance, confirming the initial detachment of the thiophenyl radical. Mass spectrum, m/z (I_{rel}, %): 324 (74.5), 290 (17.6), 246 (5.9), 215 (100), 171 (51.0), 145 (49.0), 139 (13.7), 108 (5.9), 95 (9.8), 77 (13.7).

Mass spectrum of dibenzo-1,4,5,8-tetrathioanthracene, m/z (I_{rel}, %): 354 (100), 322 (54.2), 290 (89.6), 277 (18.8), 258 (10.4), 245 (8.3), 214 (4.2), 177 (18.8), 169 (8.3), 160 (27.1), 154 (10.4), 145 (35.4), 138 (43.8), 125 (8.3), 93 (10.4), 69 (25.0).

The melting points of the compounds were determined with a Stuart Scientific SMP30 instrument. The following compounds were identified by the GC–MS technique as impurities in the reaction mixtures of synthesis runs 5, 8, and 9 (wt %): run 5—*o*-di(phenylthio)benzene (4.3, dark brown liquid), phenylthiothianthrene (two isomers, 0.8 and 2.0), and dibenzo-

Synthesis conditions and product yields

Experiment no.	Molar ratio of reactants, solvent	Reaction temperature, °C	Product yield, wt %
1	DPS : $AlCl_3$ = 2.0 : 1.0; benzene	80	Thianthrene, 8.9
2	DPS : $AlCl_3$ = 2.1 : 1.00	95	Thianthrene, 29.0
3	DPA : $AlCl_3$ = 2.1 : 1.00	95	*N*,*N*'-diphenylbenzidine, 24.3
4	DPS : DPA : $AlCl_3$ = 1.0 : 1.1 : 1.0	95	Thianthrene, 11.8 *N*,*N*'-diphenylbenzidine, 16.4
5	DPS : DMSO : $AlCl_3$ = 1.0 : 1.0 : 1.0	85	Thianthrene, 25.8
6	DPE : $AlCl_3$ = 2.1 : 1.0	95	does not react
7	DPS : DPE : $AlCl_3$ = 1.0 : 1.0 : 1.0	95	Thianthrene, 11.7
8	DPS : $AlCl_3$ = 2.1 : 1.0; heptane	98	Thianthrene, 58.0
9	DPS : $AlCl_3$ = 2.1 : 1.0; nitrobenzene	95	*o*-di(phenylthio)benzene, 39.6 thianthrene, 5.8
10	DPA : DPE : $AlCl_3$ = 1.0 : 1.0 : 1.0	95	*N*,*N*'-diphenylbenzidine, 14.9
11	DPE : DPS : $AlBr_3$ = 1.0 : 1.1 : 1.0; heptane	98	Thianthrene, 12.1
12	DPE : DPA : $AlBr_3$ = 1.1 : 1.0 : 1.0; heptane	98	*N*,*N*'-diphenylbenzidine, 14.4

Syntheses 2–7 and 10 were conducted in a solventless mode.

1,4,5,8-tetrathioanthracene (0.8); run 8—thianthrene sulfoxide (4.7), *o*-di(phenylthio)benzene (1.9), phenylthiothianthrene (two isomers, 0.7 and 1.8), *p*-bis(phenylthio)diphenyl sulfide (2.8, dark brown liquid), and dibenzo-1,4,5,8-tetrathioanthracene (0.3); and run 9—phenylthiothianthrene (two isomers, 0.7 and 0.8) and dibenzo-1,4,5,8-tetrathioanthracene (1.0). Thianthrene mp 158.0°C; *N*,*N*'-diphenylbenzidine mp 241.3°C (from toluene).

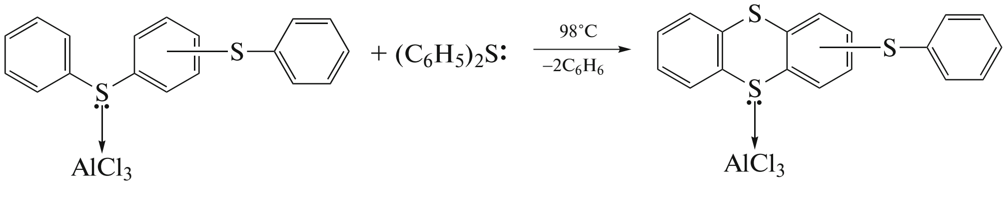
Quantum-chemical calculations were performed using the standard software suite GAUSSIAN'09 [5]. The theoretical study was carried out using the density functional theory (DFT). Calculations performed by the B3LYP hybrid density functional with the Becke exchange functional (B3) [6] and the Lee–Yang–Parr correlation functional (LYP) [7]. To calculate the IR, UV, and NMR spectra, both the all-electron basis set 6-31G(d) and 6-311+G(2d,p) were used for all the atoms. The geometries of the calculated molecules have been fully optimized; the absence of imaginary vibration frequencies confirms their stationary character. Calculations for benzene solution were performed by the same methods using the polarized continuum model (PCM) with optimization [8]. The energies of the calculated compounds were corrected for zero-point vibrational energy (ZPVE) and reduced to standard conditions (298.15 K, 1 atm) using the thermal correction to the enthalpy and free energy. Optimized geometry was also used to calculate the total energy of the molecules in the gas phase with the software package ADF'2004 (Amsterdam density functional) [9]. We used the exchange functional OPTX paired with the correlation functional PBE, employing the all-electron triple-ζ polarization basis set of Slater orbitals.

RESULTS AND DISCUSSION

At a temperature above 70°C, diphenyl sulfide reacts with aluminum chloride to form thianthrene, byproducts, and impurities.

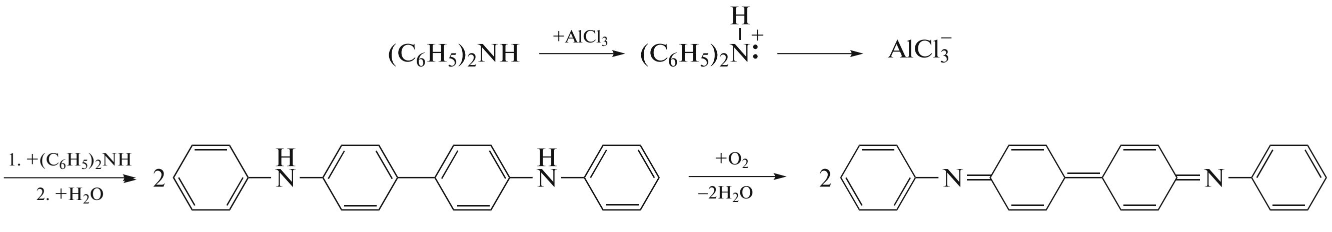
The yield of thianthrene in run 8 reaches 58% at a molar ratio of DPS : $AlCl_3$ = 2.0 : 1.0, a reaction temperature of 98°C (boiling heptane), and a reaction time of 8 h (Fig. 1).

Two isomers, 2-phenylthiothianthrene and 4-phenylthiothianthrene, are formed as impurities in the similar reaction of the di(phenylthio)benzene complex with DPS:



There is no experimental evidence that direct hydride-ion substitution occurs in the thianthrene complex with aluminum chloride.

As compared to diphenyl sulfide, diphenyl ether and diphenylamine form stronger donor–acceptor complexes with aluminum halides, having the enthalpy of formation of 104.0–125.0 kJ/mol and a p–π-conjugation energy of 46.8–61.9 kJ/mol (for DPS, $-\Delta H = 98.2$ and $E_{p\pi} = 35.5$ kJ/mol), values that cause their low reactivity in the reaction of interest (run nos. 3, 4, 6, 7, 10–12) [10]. Reacting with $AlCl_3$, diphenylamine partially undergoes oxidative dehydrogenation to give the dimerization product N,N'-diphenylbenzidine (run nos. 3, 4, 10, 12), which is slowly oxidized in air to yield Diphenylamine Blue:



$$(C_6H_5)_2NH \xrightarrow{+AlCl_3} (C_6H_5)_2\overset{H}{\overset{|\,+}{N}}\!: \longrightarrow AlCl_3^-$$

The aprotic solvents DMSO (run 5) and nitrobenzene (run 9) reduce the reaction selectivity for thianthrene to increase the yield of di(phenylthio)benzene to 39.6% and other compounds with a higher molecular weight formed by the reaction of oxidative dehydrogenation of DPS.

The quantum-chemical calculations gave fairly reliable linear correlations (Eqs. (1), (2)), suggesting that the calculations of sulfur compounds by the B3LYP/6-31G(d) and VR86/TZ2P+ methods correctly describe not only the geometry, but also thermodynamic parameters, in particular, the dissociation energy (D_0). The dissociation energy of the sulfur compounds was determined as the difference between the energy of a compound and the energies of its constituent atoms with allowance for the enthalpy of formation. The calculated dissociation energies divided by the number of bonds were compared with the experimental average sulfur–element bond energies. As a result, correlation equations were obtained on the basis of both the GAUSSIAN and ADF calculation data.

$$\begin{gathered}\text{GAUSSIAN}: D_0\,(\text{exp.}) = -38 + 0.73\,D_0\,(\text{calc.})\\ r = 0.981;\ s = 35;\ n = 6,\end{gathered} \tag{1}$$

$$\begin{gathered}\text{ADF}: D_0\,(\text{exp.}) = -61 + 0.74\,D_0\,(\text{calc.})\\ r = 0.984;\ s = 32;\ n = 6,\end{gathered} \tag{2}$$

where r is the coefficient of correlation, s is the standard deviation, and n is the number of compounds.

The correlation equations obtained indicate that the thermodynamic parameters calculated by different methods for the sulfur compounds are sufficiently close to each other and to the experimental values, and the error of calculation by the ADF method is no more than 8%.

According to crystal structure data, the thianthrene molecule is bent along the S···S axis by 127° and 128° at 163 and 295 K, respectively. The C–S–C bond angle is approximately 100°, differing insignificantly from that in diphenyl sulfide (103.4°); thus, bending along the S···S axis allows the sulfur atoms to retain their inherent bond angle. However, the C–S bond length, which is 1.76 Å, is substantially less than the normal value of 1.81 Å, indicating p–π conjugation. Breslow and Skolnik [2] estimated the character of the C–S bond at 25% of a double bond. Our calculations for the gas phase showed that the energetically favorable conformation is C_2 and the geometric parameters are quite close to the experimental values. Namely, the C–S–C bond angle was found to be 103.7° in DPS and 101.4° in thianthrene. The C–S bond length appeared to be 1.787 Å using the 6-31G(d) basis set or 1.756 Å with the 6-311+G (2d,p) basis set. In terms of the valence bond theory, the total Wiberg bond index for each sulfur atom in thianthrenyl is 2.4; i.e., each C–S bond has an order of 1.2, which is consistent with

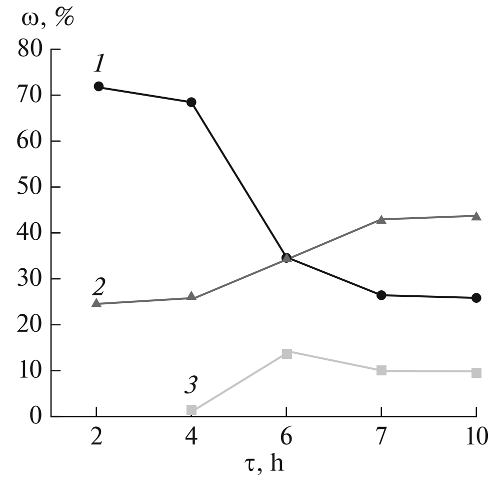


Fig. 1. Changes in the concentration of the reaction mixture (experiment 8): (*1*) diphenyl sulfide, (*2*) thianthrene, and (*3*) di(phenylthio)benzene.

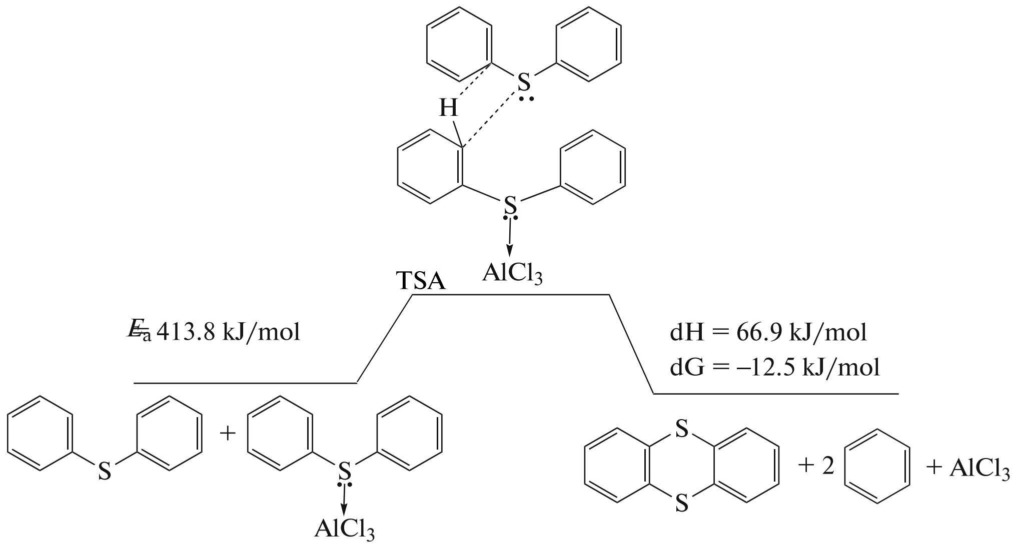


Fig. 2. Energy diagram of the reaction of nucleophilic displacement of hydrogen in diphenyl sulfide in the gas phase.

the assumption of 25% of its double bond character. The diphenyl sulfide molecule is not planar, the angle in the *o*-positions relative to the sheet plane is 35°. The sulfur atom bears two lone electron pairs, of which one is on the hybrid $sp^{0.5}$ orbital (population 1.97e) and the other is on the nonhybridized p orbital (population 1.86e) that is involved in π–p conjugation with the π-electron system of the benzene ring. Thus, sulfur is a donor of electron density and increases the negative charge on the carbon atoms of both the benzene rings. This is indicated by the form of the highest occupied molecular orbital, where the most of the electron density is concentrated on the benzene ring along with the lone electron pair of the sulfur atom.

In the DPS–$AlCl_3$ complex, the positive charge on the sulfur atom is increased and the total charge of the $AlCl_3$ molecule is negative, so that the planar structure of the $AlCl_3$ molecule is disturbed. The sulfur atom retains two unshared electron pairs, one pair on the $sp^{1.55}$ hybridized orbital (population 1.95e) and the other on the $sp^{2.7}$ hybrid orbital (population 1.72e). The reduced population of the second lone electron pair of the sulfur atom indicates interaction with the acceptor orbital of the aluminum atom. The positively charged sulfur atom pulls the π electrons of the aromatic ring; thus, sulfur becomes an electron acceptor and the negative charge on the carbon atoms of the benzene rings decreases. The C–S–C angle slightly increases to 105°, the C–S bond length increases to 1.81Å, the aromatic rings are rotated by the repulsion of hydrogen atoms, and the angle in the *o*-positions relative to the ring plane increases to 51°. The free DPS molecule attacks a carbon atom in the *o*- or *p*-position by the nucleophilic sulfur atom.

Small positive values of the enthalpy and the activation energy of the reaction and a small negative value of the Gibbs energy explains the need for heating during the reaction:

$$AlCl_3SPh_2 + SPh_2 \rightarrow \text{Thianthrene} + AlCl_3 + 2BZ$$

$$(\Delta H = +66.9 \text{ kJ/mol}, \Delta G = -12.5 \text{ kJ/mol},$$

$$\Delta E = +8.4 \text{ kJ/mol}, \Delta H^{BZ} = +58.5 \text{ kJ/mol},$$

$$\Delta G^{BZ} = -12.5 \text{ kJ/mol}).$$

The reaction of nucleophilic displacement of hydrogen goes through transition state A (Fig. 2), which has been optimized with the use of the Berny algorithm and the synchronous transit-guided quasi-Newton (STQN) method for benzene solution (PCM model). The transient nature of the resulting structure shows the presence of a negative vibrational frequency (-1267 cm^{-1}), which is due to the bending vibration of the proton in the direction from the sulfur atom to the phenyl leaving group. Our analysis using the natural orbital bond method also shows that the formation of this transition state increases the charge on the sulfur atom of diphenyl sulfide (+0.549), one of the lone electron pairs of which is involved in the formation of a new bond with the hydrogen atom that migrates from the *o*-position of the benzene ring of the reactant complex.

The Wiberg index of this new S–H bond is 0.812. Note that sulfur bonding to the carbon of the leaving phenyl group is weakened in this case—the Wiberg index is 0.401—and a weak bond between the sulfur atom and the carbon of the reactant complex is formed, having a Wiberg index of 0.635. The other lone electron pair remains on the sulfur atom is the $sp^{0.7}$ hybridized orbital (population 1.96e). The activation energy of the reaction, as calculated on the basis of this transition state, is 413.8 kJ/mol.

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