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Communication

QUANTUM-CHEMICAL STUDY ON FORMATION OF THIONITROSO COMPOUNDS FROM *N*-CHLORO-SULFENYL-*N*-TRIMETHYLSILYL AMINES

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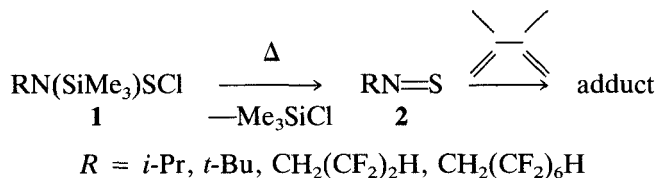
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The MNDO quantum-chemical calculations revealed that the *N*-chlorosulfenyl-*N*-trimethylsilyl amine decomposition scheme may be described as the S—Cl bond weakening and the subsequent trimethylsilyl group transfer to the chlorine atom, with the activation barrier of 260–294 kJ/mol.

Key words: *N*-chlorosulfenyl-*N*-trimethylsilyl amines; thionitroso compounds; MNDO calculations; reaction mechanisms.

INTRODUCTION

Thermolysis of *N*-chlorosulfenyl-*N*-trimethylsilyl alkyl amines and 1,1-dihydro-polyfluoroalkyl amines (**1**) leads to the formation of unstable thionitroso compounds (**2**) proved by isolation of their (4 + 2)-cycloaddition products:^{1,2}



Mechanism of the trimethylsilyl chloride elimination from the compounds **1** is unknown.

RESULTS AND DISCUSSION

We performed the quantum-chemical investigation of the geometrical and electronic structure of molecules $\text{RN}(\text{SiH}_3)\text{SCl}$ (**3a**, $R = \text{Me}$, **3b**, $R = t\text{-Bu}$, **3c**, $R = \text{CH}_2\text{CF}_3$) being models of the compounds **1**. The MNDO method was used with complete geometry optimization. The structure of molecule **3a** is shown in Figure 1(a); differences in geometrical parameters of molecules **3b,c** are insignificant. The nitrogen hybridization is of the sp^2 -type in molecules **3a,b** and close to the sp^2 -type

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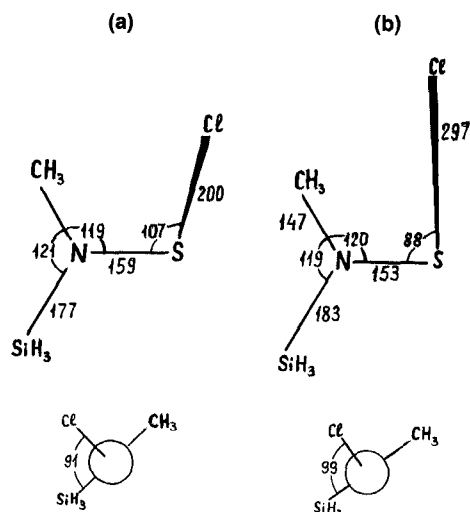


FIGURE 1 Geometrical parameters and Newman projections along the S—N bond for molecule **3a** in the ground state (a) and transition state (b); bond lengths in picometers, valence bond angles in degrees.

in molecule **3c**. The S—N and C—N bonds are simple covalent ones as is evidenced by their lengths and Wiberg indices (Table I). The Si—N bond is strongly polarized as follows from the high positive charge on the silicon atom and the negative charge on the nitrogen atom (another negatively charged centre in molecules **3a–c** is the chlorine atom). The S—Cl bond is practically orthogonal to the CNS plane, its index being very low. Thus, geometrical and electronic structure of molecules **3a–c** suggests the intramolecular rearrangement with the S—Cl bond cleavage.

We studied a theoretical model of this reaction for molecules **3a–c**. The reaction coordinate was the S—Cl bond length ($d_{\text{S-Cl}}$) varied in the range of 200–400 pm. For all systems, enthalpy curve has a maximum at $d_{\text{S-Cl}} = 292\text{--}297$ pm with the simultaneous Si—N bond lengthening, S—N bond shortening and CNS valence bond angle decrease in comparison with the ground state (Figure 2). A comparative analysis of energy values in the vicinity of the obtained enthalpy profile leads to the conclusion that the enthalpy maximum corresponds to the transition states (TS) of molecules **3a–c**. The geometrical parameters of molecule **3a** are presented in Figure 1(b). In TS the maximal negative charge is localized on the chlorine atom;

TABLE I
Charges on atoms and bond indices of molecules **3a–c**

Mole- cule	Charge on atom, e					Bond index			
	S	N	Si	Cl	C ^a	SN	SCI	SiN	CN
3a	+0.29	−0.74	+1.66	−0.27	+0.19	1.06	0.84	0.65	0.95
3a^b	+0.37	−0.54	+1.67	−0.67	+0.13	1.93	0.37	0.55	0.94
3b	+0.28	−0.72	+1.66	−0.27	+0.05	1.07	0.83	0.65	0.93
3c	+0.28	−0.74	+1.67	−0.22	+0.16	1.04	0.89	0.62	0.99

^aAtom C of the C—N bond.

^bTS.

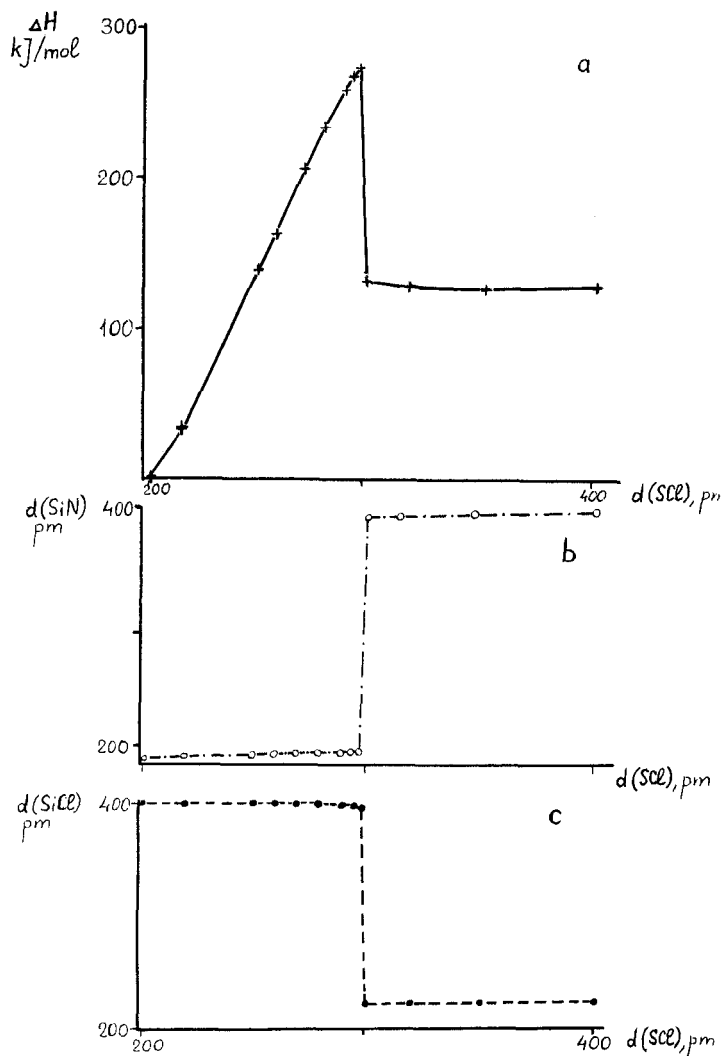


FIGURE 2 Reaction enthalpy profile (a) and changes of interatomic distances $d_{\text{Si-N}}$ (b) and $d_{\text{Si-Cl}}$ (c) versus the reaction coordinate $d_{\text{S-Cl}}$ for the decomposition of compound **3a**.

both the S—Cl and the Si—N bonds are considerably weakened while the S—N bond is strengthened in comparison with the ground state (see Table I). So migration of the electron-deficient SiH_3 group to the chlorine atom is favoured to form SiH_3Cl and a compound **2**. In fact, further growth of the $d_{\text{S-Cl}}$ value causes a drastic increase of the Si—N distance up to 400–420 pm and a decrease of the $d_{\text{Si-Cl}}$ value to 212 pm (Figure 2) giving evidence for the cleavage of the Si—N bond and the formation of the Si—Cl bond. The S—N bond length is simultaneously decreased to the value of 149 pm typical for the compounds **2** in the MNDO calculations.²

Consequently, the decomposition of compounds **3a–c** may be schematically described as the S—Cl bond weakening and the subsequent silyl group transfer to

the chlorine atom. The activation barrier of this process for compounds **3a**, **3b** and **3c** is estimated to be 274, 260 and 294 kJ/mol, respectively, thus increasing for electron-withdrawing substituents. It should be borne in mind, however, that in our investigation only the potential curve of the considered reaction was calculated, while in a complete theoretical study the potential energy surface should be constructed. The latter one is a function of $M = 3N - 6$ independent internal coordinates (nuclear degrees of freedom) where N is the number of nuclei, and a real microscopic reaction pathway includes vibrational and rotational motions within this multidimensional hyperspace. The M value is 27 for the compound **3a** and 54 for **3b**; surely, the required body of calculations would be rather large. Therefore our simplified approach may be acceptable as an overall thermodynamic description for the decomposition process of compounds **3a–c**.

Changes in geometrical and electronic structure of organoelement compounds after substitution of the SiH_3 group by the SiMe_3 group are negligible.³ Thus, our conclusion about the mechanism of the considered reaction may be extended on the compounds **1**, too.

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