

Ab initio calculations of $\text{Cl}_2\text{SO} \cdot n\text{AlCl}_3$ complexes ($n = 1, 2$)

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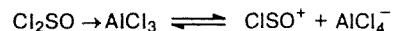
Fragments¹ of the potential energy surfaces (PES) for the $\text{SOCl}_2 \cdot n\text{AlCl}_3$ ($n = 1, 2$) complexes were calculated by the *ab initio* MO LCAO method using the RHF approximation for the STO-3G basis set and adding a 3d-AO for the S atom, as well as by the semiempirical MNDO method. Two local minima, assigned to the donor-acceptor complex $\text{Cl}_2\text{SO} \rightarrow \text{AlCl}_3$ (**1a**) and to $\text{Cl}_3\text{SOAlCl}_2$ (**1b**) were located on the PES at $n = 1$. Two local minima corresponding to two donor-acceptor complexes $\text{Cl}_2\text{SO} \rightarrow \text{Al}_2\text{Cl}_6$ and $\text{Cl}_3\text{SO} \rightarrow \text{AlCl}_2 \cdots \text{AlCl}_2 \cdots \text{Cl}$, were also located on the PES at $n = 2$. An analysis of the enthalpies of cation formation in the $\text{SOCl}_2 + n\text{AlCl}_3$ ($n = 1-3$) systems calculated by the *ab initio* method shows that the enthalpy of formation of the SOCl_2^+ cation at $n = 2$ is 17 kcal mol⁻¹ less than that at $n = 1$; the structure of the $\text{Cl}_2\text{SOAlCl}_2^+$ cation with two strong electrophilic centers at the Al and S atoms becomes more favorable energetically at $n = 3$. The results of calculations for $\text{Cl}_2\text{SO} \cdot n\text{AlCl}_3$ complexes by the MNDO method are in agreement with those obtained by the *ab initio* method except for the geometry of complexes containing the Cl_3SO fragment and the charge values on the S atoms.

Key words: *ab initio* calculations, MNDO method; thionyl chloride, aluminum chloride, complexes.

Recently we have found that the systems $\text{SOCl}_2 \cdot n\text{AlX}_3$ ($n = 2, 3$; X = Br, Cl), containing thionyl chloride in combination with aluminum bromide or chloride, are efficient initiators in cracking C_5 – C_{10} *n*-alkanes at ~20 °C. They are highly competitive in their activity with the strongest protonic superacids. Thus, octane under the action of the $\text{SOCl}_2 \cdot 2\text{AlBr}_3$ with the molar ratio $[\text{C}_8\text{H}_{18}] : [\text{SOCl}_2 \cdot 2\text{AlBr}_3] = 10$ is converted (70 %) into its cracking products in 10 min. In the presence of Al_2Br_6 and under the same conditions the conversion is only 17 %. Systems containing thionyl chloride also show a high activity in the initiation of octane cracking. For instance, $\text{SOCl}_2 \cdot 3\text{AlCl}_3$ catalyzes nearly quantitative conversion of octane into its cracking products and the process is completed in 30 min, while $\text{SOCl}_2 \cdot 2\text{AlCl}_3$ results in 71 % conversion. The equimolar $\text{SOCl}_2 \cdot \text{AlCl}_3$ complex and Al_2Cl_6 are inactive under the same conditions.

As follows from Fig. 1, the activity of $\text{SOCl}_2 \cdot n\text{AlCl}_3$ systems in octane cracking (octane conversion under standard conditions is accepted as the measure of activity) increases sharply with increasing n . Under the chosen conditions the conversion of octane into cracking products when treated with $\text{SOCl}_2 \cdot 2\text{AlCl}_3$ is twice that in the presence of $\text{SOCl}_2 \cdot 1.5\text{AlCl}_3$, while the equimolar complex $\text{SOCl}_2 \cdot \text{AlCl}_3$ is completely inactive.

Several works^{1–3} have been dedicated to thionyl chloride complexes with aluminum chloride, $\text{SOCl}_2 \cdot \text{AlCl}_3$ (**1**), and $\text{SOCl}_2 \cdot 2\text{AlCl}_3$ (**2**). Thus, complex **2** was obtained nearly 50 years ago² (by boiling AlCl_3 in SOCl_2 with the subsequent elimination of SOCl_2) as a colored oil-like liquid with b.p. 215 °C. Heating adduct **2** *in vacuo* resulted in the equimolar complex **1**; the structure of **1** with a donor-acceptor bond, $\text{Cl}_2\text{SO} \rightarrow \text{AlCl}_3$, was assigned³ on the basis of its Raman spectra. Conductometric and potentiometric studies have shown that complex **1** is very slightly ionized in solution ($K_i = 10^{-4}$ mol L⁻¹).¹



The conclusion that adduct **2** is complex **1** weakly coordinated to the second AlCl_3 molecule was drawn³ from the Raman spectra of **2**. However, the authors³ give no detailed explanation of the nature of that bonding.

The present work is a quantum-chemical study of the complexes that can be generated in $\text{SOCl}_2 \cdot n\text{AlCl}_3$ systems where $n = 1-3$. The calculations were carried out by the *ab initio* MO LCAO method in the RHF/STO-3G and RHF/STO-3G* approximations using the GAMESS⁴ program package, as well as by the semiempirical MNDO method.

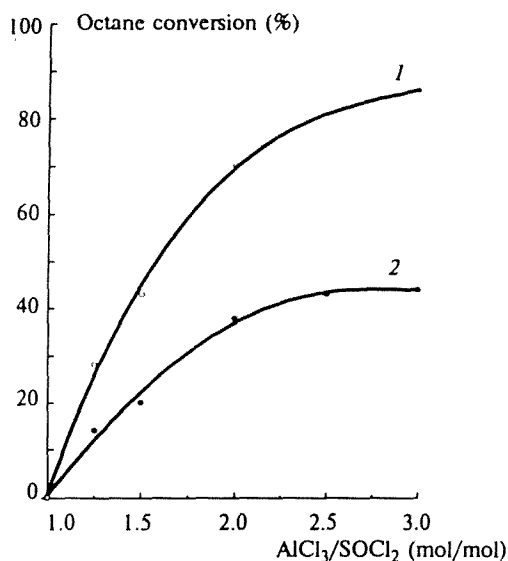


Fig. 1. The activity of $\text{SOCl}_2 \cdot n\text{AlCl}_3$ systems in octane cracking at 20 °C: octane conversion after 20 min (1) and 10 min (2); $[\text{C}_8\text{H}_{18}] : [\text{SOCl}_2 \cdot n\text{AlCl}_3] = 10 : 1$, in CH_2Cl_2 (4.2 mL CH_2Cl_2 per 1 mole AlCl_3).

Results and Discussion

SOCl_2 (3), AlCl_3 (4), and Al_2Cl_6 (5) molecules. The results of our calculations of the components of complexes 1 and 2 (molecules 3–5) by the *ab initio* MO LCAO SCF method in the RHF approximation are presented in Table 1. The calculations were carried out using

Table 1. Total energies (E_t), main bond lengths (d), and bond angles for the SOCl_2 , AlCl_3 , Al_2Cl_6 molecules and AlCl_4^- and Al_2Cl_7^- anions

Molecule, ion	$-E_t$ (au)	$d/\text{\AA}$			S—O—Cl /deg
		S—O	S—Cl	Al—Cl	
SOCl_2	1376.025434 ^a	1.741 ^a	2.126 ^a		105.6 ^a
	1376.182200 ^b	1.440 ^b	2.069 ^b		109.2 ^b
		1.443 ^c	2.076 ^c		106.3 ^c
AlCl_3	1603.016129 ^a			2.087 ^a	
				2.06 ^c	
				2.083 ^a	
Al_2Cl_6	3206.124818 ^a			2.267 ^a	
				2.07 ^c	
				2.25 ^c	
AlCl_4^-	2057.689067 ^a			2.153 ^a	
Al_2Cl_7^-	3660.781361 ^a			2.126 ^a	
				2.270 ^a	

Note. Calculated charges at the S atom in the SOCl_2 molecule are equal to 0.33^a and 0.54^b, respectively.

^a Calculated by the RHF/STO-3G method.

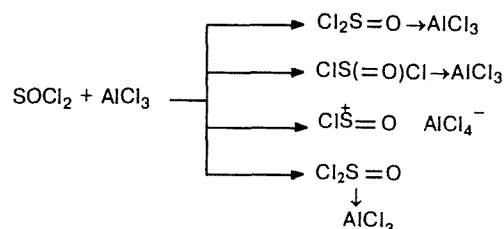
^b Calculated by the RHF/STO-3G* method.

^c Experimental data.

two basis sets — 3G and 3G*; the latter was obtained from the 3G basis set by adding the diffuse d-orbitals of the S atom. As can be seen from Table 1 the geometric characteristics of AlCl_3 and Al_2Cl_6 molecules are fairly well described in the 3G basis set; however, calculations of SOCl_2 carried out in the 3G basis set, unlike those in the 3G* basis set, result in a S—O bond length that differs essentially from the experimental one. Therefore, the 3G* basis set was used in further calculations of neutral and cationic complexes containing a S atom.

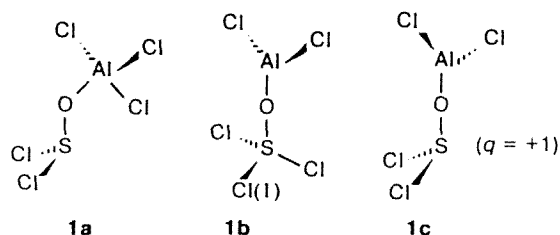
$\text{Cl}_2\text{SO} \cdot \text{AlCl}_3$ (1) complex. There are four nucleophilic centers in the SOCl_2 molecule. In principle, formation of the following four simplest complexes is possible if the molecule is attacked by the AlCl_3 electrophile (Scheme 1).

Scheme 1



Two local minima were found from the analysis of the PES fragments of system 1 calculated using the RHF/STO-3G* approximation; structures **1a** and **1b** presented in Scheme 2 correspond to these minima. Adduct **1a** is a donor-acceptor complex with an O→Al bond, while **1b** can be considered as its isomer formed through migration of the chlorine atom from aluminum to sulfur. Structure **1a** appeared to be more favorable energetically. The difference between the heats of formation of **1a** and **1b** ($\Delta_f H$) is ~67 kcal mol⁻¹.

Scheme 2



Structures **1a** and **1b** have C_s symmetry; the symmetry plane in complex **1a** passes through the S, O, and Al atoms, while in isomer **1b** it passes through the S, O, and Cl(1) atoms. It can be seen from Table 2 that the formation of complex **1a** from the starting molecule by coordination of the Al atom at the O atom is accompanied

Table 2. Total energies (E_t), main bond lengths (d) and bond angles (ω), effective charges (q) at the S and Al atoms, and dipole moments (μ) for the $\text{SOCl}_2 \cdot n\text{AlCl}_3$ ($n = 1, 2$) and $\text{SOCl}^+ \cdot m\text{AlCl}_3^+$ ($m = 0-2$) systems

Structure	$-E_t$ (au)	$d/\text{\AA}$			ω/deg			q_{Al} (au)	q_{S} (au)	μ/D
		S—O	Al—O	S—Cl	Al—O—S	Cl—S—Cl	Cl—S—O			
SOCl^+	921.689066	1.449	—	1.972	—	—	—	—	0.77	—
1a	2979.260735	1.486	1.879	2.033	130.4	98.3	105.3	0.72	0.61	7.9
1b	2979.151735	1.539	1.640	2.159	176.3	174.9	88.2	0.93	0.60	0.9
1c	2524.411336	1.493	1.718	2.023	176.0	100.2	104.8	0.94	0.65	—
2a	4582.327185	1.473	1.795	2.033	157.0	98.2	98.2	0.81	0.66	9.7
2b	4582.312182	1.486	1.879	2.170	123.1	171.3	85.8	0.74	0.42	6.2
2c	4127.488045	1.497	1.795	2.027	142.5	99.5	106.3	0.82	0.62	—

by lengthening of the S—O bond and a significant increase in the dipole moment. This is a characteristic feature of donor-acceptor complexes formed by AlCl_3 with esters, ketones, and nitro compounds.⁵ In isomer **1b** the S—O bond length is longer and the Al—O distance is shorter than those in isomer **1a**.

The effective charges at the S atoms (q_{S}) in complexes **1a** and **1b** are positive and exceed the charge at the S atom in the SOCl_2 molecule by ~ 0.06 au. It should be noted that the positive charges at the Al atoms in complexes **1a** and **1b** are also significant; q_{Al} in isomer **1b** is larger than that in **1a** by about 0.2 au. The corresponding local minima on the PES were not found for the other potentially feasible complexes depicted in Scheme 1 (donor-acceptor complexes with the coordination bonds $\text{Cl} \rightarrow \text{AlCl}_3$ or $\text{S} \rightarrow \text{AlCl}_3$).

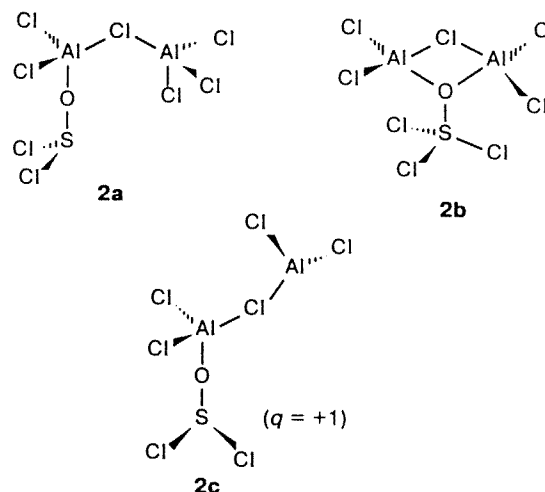
The calculations for the SOCl^+ (**6**) and $\text{Cl}_2\text{SOAlCl}_2^+$ (**1c**) cations were also carried out by the RHF/STO-3G* method with full optimization of geometry. Cation **6** can be formed by heterolytic abstraction of Cl^- from SOCl_2 (see Scheme 1); cation **1c** is formed as a result of the analogous dissociation of complex **1b**. It is obvious that formation of cation **1c** requires participation of more than 1 mole of AlCl_3 .

The effective charge at the S atom in cation **6** appeared to be 0.16 au, larger than that in complexes **1a** and **1b**. The effective charge at the S and Al atoms in cation **1c** is larger than those in complexes **1a** and **1b**, though the charge at the S atom is smaller than the q_{S} value for the SOCl^+ cation by 0.12 au. We also note that the geometric parameters of the SOCl_2 fragment in cation **1c** are close to the relevant characteristics of the same fragment in complex **1a**.

$\text{Cl}_2\text{SO} \cdot 2\text{AlCl}_3$ (2**) complexes.** The number of complexes whose formation appears to be possible in the reaction of 2 moles of AlCl_3 with SOCl_2 is essentially larger than that indicated in Scheme 1. However, for complexes of composition 1 : 2 calculated in the RHF/STO-3G* approximation, only two minima assigned to the structures **2a** and **2b** (Scheme 3) were found on the PES. Adduct **2a** is a classic donor-acceptor complex with $\text{O} \rightarrow \text{Al}$ bond, analogous to complex **1a**; the only difference is that in this case the coordination bond is formed with participation of the dimeric Al_2Cl_6 molecule instead of

monomeric AlCl_3 . Despite the fact that the S—O and S—Cl bond lengths in structures **2a** and **1a** differ insignificantly (the S—O bond in **2a** is shorter), the positive charges at the Al and S atoms are larger in complex **2a**.

Scheme 3



The donor-acceptor complex **2b** is formed by migration of a Cl atom from aluminum to sulfur and the addition of a coordinatively unsaturated Al atom to the O atom. There is a symmetry plane passing through the O, S, and Cl(1) atoms in the structure of complex **2b**. The symmetry of the $\text{SO} \cdots \text{AlCl}_2 \cdots \text{Cl}$ fragment is described by group C_{2v} ; the bridging O and Cl atoms lie on the symmetry axis.

In structure **2b** the lengths of the bridging Al—Cl bonds in the Al—Cl—Al fragment appeared to be nearly the same as those in the Al_2Cl_6 molecule (2.283 Å). The replacement of a Cl atom in Al_2Cl_6 with the O atom makes little change in the type of bonding. However, the charges at the S and Al atoms in complex **2b** are much smaller than in complexes **2a**, **1b**, and **1c**.

Table 3. Enthalpies (ΔH) of possible reactions in the $\text{SOCl}_2 + n\text{AlCl}_3$ ($n = 1-3$) mixtures calculated by the RHF/STO-3G* method

Reaction	Equation	ΔH /kcal mol ⁻¹
(1)	$\text{SOCl}_2 + 1/2 \text{Al}_2\text{Cl}_6 = \text{Cl}_2\text{SO} \rightarrow \text{AlCl}_3$ 1a	-10.0 (-8.0)*
(1')	$\text{SOCl}_2 + 1/2 \text{Al}_2\text{Cl}_6 = \text{Cl}_3\text{SO} \rightarrow \text{AlCl}_2$ 1b	56.7
(2)	$\text{Cl}_2\text{SO} \cdot \text{AlCl}_3 + 1/2 \text{Al}_2\text{Cl}_6 = \text{Cl}_2\text{SO} \cdot 2\text{AlCl}_3$ 1a 2a	-2.5 (-6.4)*
(2')	$\text{Cl}_2\text{SO} \cdot \text{AlCl}_3 + 1/2 \text{Al}_2\text{Cl}_6 = \text{Cl}_2\text{SO} \cdot 2\text{AlCl}_3$ 1a 2b	7.0
(3)	$\text{Cl}_2\text{SO} \cdot \text{AlCl}_3 = \text{ClSO}^+ + \text{AlCl}_4^-$ 1a	150.7
(4)	$\text{Cl}_2\text{SO} \cdot \text{AlCl}_3 + 1/2 \text{Al}_2\text{Cl}_6 = \text{ClSO}^+ + \text{Al}_2\text{Cl}_7^-$ 1a	131.8
(5)	$\text{Cl}_2\text{SO} \cdot 2\text{AlCl}_3 = \text{ClSO}^+ + \text{Al}_2\text{Cl}_7^-$ 2a	134.5
(6)	$\text{Cl}_2\text{SO} \cdot \text{AlCl}_3 + 1/2 \text{Al}_2\text{Cl}_6 = \text{Cl}_2\text{SOAlCl}_2^+ + \text{AlCl}_4^-$ 1a 1c	139.8
(7)	$\text{Cl}_2\text{SO} \cdot 2\text{AlCl}_3 = \text{Cl}_2\text{SOAlCl}_2^+ + \text{AlCl}_4^-$ 2a 1c	142.3
(8)	$\text{Cl}_2\text{SO} \cdot \text{AlCl}_3 + \text{Al}_2\text{Cl}_6 = \text{Cl}_2\text{SOAlCl}_2^+ + \text{Al}_2\text{Cl}_7^-$ 1a 1c	117.3
(9)	$\text{Cl}_2\text{SO} \cdot 2\text{AlCl}_3 + 1/2 \text{Al}_2\text{Cl}_6 = \text{Cl}_2\text{SOAl}_2\text{Cl}_5^+ + \text{AlCl}_4^-$ 2a 2c	133.3
(10)	$\text{Cl}_2\text{SO} \cdot \text{AlCl}_2^+ + 1/2 \text{Al}_2\text{Cl}_6 = \text{Cl}_2\text{SOAl}_2\text{Cl}_5^+$ 2c	-9.0

*Values obtained by the MNDO method are listed in parentheses.

The enthalpies (ΔH) of reactions (1)–(10), which can proceed in the $\text{SOCl}_2 \cdot n\text{AlCl}_3$ systems, calculated in the RHF/STO-3G* approximation are listed in Table 3. Obviously, the solvation and aggregation effects, particularly for the ionic forms, can essentially decrease the energies of the complexes. And though the energy values calculated for the gas phase, strictly speaking, cannot be extended to the reactions in solutions, an analysis of the ΔH values found seems to be helpful in judging which cationic forms in the $\text{SOCl}_2 \cdot n\text{AlCl}_3$ ($n = 1-3$) systems are preferable and with which isomers the superelectrophilic properties of these systems at $n > 1$ are most likely associated.

The fact that the $\text{SOCl}_2 \cdot \text{AlCl}_3$ ($n = 1$) system does not initiate alkane cracking allows one to state that the easily formed donor-acceptor complex **1a** (reaction (1)) detected by Raman spectroscopy³ does not react with alkanes under mild conditions, as does the less energetically favorable isomer **1b**, which has a more electrophilic Al atom (reaction (1')). At the same time 151 kcal mol⁻¹ are required for generating the ionic form when $n = 1$, and therefore such a system is unlikely to occur. It is unlikely that the activity of the $\text{SOCl}_2 \cdot n\text{AlCl}_3$ systems when $n = 2$ is associated with the participation of donor-acceptor complexes **2a** and **2b** that form with a release or small consumption of energy (reactions (2) and (2')), since structures **2a** and **2b** are not more electrophilic than

complexes **1a** and **1b**. We point out that the enthalpy of formation of the SOCl^+ cation in reactions (4) and (5) at $n = 2$ is 17 kcal mol⁻¹ less than that at $n = 1$ (reaction (3)). A further increase in the molar fraction of AlCl_3 to $n = 3$ results in the fact that structure **1c**, with two strong electrophilic centers at the S and Al atoms, becomes more favorable energetically (the energy gain is 15 kcal mol⁻¹, reaction (8)) than the SOCl^+ cation. Therefore, it can be assumed that cation **1c** along with SOCl^+ will also participate in cracking initiation at $n > 2$.

In conclusion, it should be noted that $\text{SOCl}_2 \cdot n\text{AlCl}_3$ complexes ($n = 1, 2$) were also calculated by the semiempirical MNDO method with full optimization of geometry. The MNDO and RHF/STO-3G* approximations were found to result in close values of structural parameters for the more stable isomers **1a** and **2a**. Additionally, the MNDO method, as well as the RHF/STO-3G* approximation, adequately reflect the qualitative difference between the stabilities of complexes **2a** and **1a** (see Table 3). Essential deviations were found for the structural parameters of the Cl_3SO fragment in complexes **2a** and **1a**. Thus, as found by the MNDO method, the Cl_3SO group has a trigonal pyramidal configuration; however, as follows from the *ab initio* calculations in the RHF/STO-3G* approximation, the structure of this fragment is similar to that of the SF_4 molecule shaped as a

trigonal bipyramid,⁶ where one equatorial position is occupied by the lone electron pair of the S atom. In addition, the charges at S atoms calculated by the MNDO method are essentially larger than those calculated in the RHF/STO-3G* approximation. Thus, for instance, in the case of the SOCl⁺ cation, q_s is 1.30 au (MNDO) and 0.77 au (*ab initio* method).

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