A Search for Thionitrosyl Chloride (Cl−N=S) in the Gas Phase

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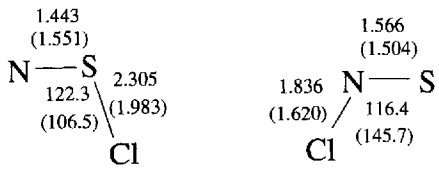
Ab initio MO calculations at the QCISD(T)/6-311++G(3df,2p) + ZPE level show that the thionitrosyl chloride ion, $ClNS^{+\bullet}$, is 36 kJ/mol more stable than the thiazyl chloride ion, $NSCl^{+\bullet}$, whereas neutral NSCl is 77 kJ/mol more stable than ClNS [IE_a (ClNS) = 9.2 ± 0.3 eV, IE_a (NSCl) = 10.5 ± 0.3 eV]. Mild flash-vacuum pyrolysis of the thiazyl chloride trimer $(NSCl)_3$ followed by electron impact ionization resulted in the formation of $[N,S,Cl]^{+\bullet}$ ions (*m/z* 81). The fragments observed in the CA spectrum of these ions indicate the formation of both $NSCl^{+\bullet}$ and $ClNS^{+\bullet}$ ions. A very weak recovery signal is observed in a neutralization-reionization experiment. This signal is tentatively assigned to the neutral thionitrosyl chloride.

In the series of triatomic molecules containing halogen, sulfur, and nitrogen atoms, thiazyl halides having sulfur in the central position (XSN) are well-known and display a rich chemistry[1]. In contrast, the thionitrosyl halide isomers XNS have remained elusive molecules so far[2]. This is in part due to the fact that a XNS molecule has a higher energy content than its XSN counterpart[3].

In this paper we report on some mass spectrometric experiments performed in order to prove the existence of thionitrosyl chloride (Cl−N=S) as a discrete species in the gas phase. These made use of neutralization-reionization (NRMS)[4] in conjunction with collisional activation (CA) experiments[5].

Theoretical results revealed that, while neutral ClNS is thermodynamically much less stable than ClSN, its radical cation $(ClNS)^{+\bullet}$ turned out to be significantly more stable than $ClSN^{+\bullet}$. Such a change in energy order of isomers after ionization makes the ClNS system a suitable target for NRMS experiment which was proven to be a powerful technique for identifying less stable neutral species[4].

Figure 1. (U)MP2/6-311+G(d)-optimized geometries of the neutral and ionized (values in parentheses) [N,S,Cl] isomers. Bond lengths are given in Å and bond angles in degrees



Let us first discuss the relevant thermochemical data of the [Cl,N,S] species obtained from ab initio molecular calculations carried out by using the Gaussian 92 program[6]. Geometry optimizations and harmonic vibrational analyses were conducted at the level of second-order Møller-Plesset perturbation theory with the polarized plus diffuse 6-311+G(d) basis set. Improved electronic energies were then recalculated by using the quadratic configuration interaction method [QCISD(T)] with the larger 6-311+G(3df) basis set with MP2 geometries. For open-shell structures, the unrestricted formalism (UMP2, UQCI) was applied. Calculated results are summarized in Table 1 and Figures 1 and 2.

Table 1. Calculated total (Hartree), zero-point vibrational (ZPE, kJ/mol), and relative (kJ/mol) energies

Species[a]	E[QCISD(T)] /6-311+G(3df)	ZPE[b]	ΔE[QCISD(T)] +ZPE)[c]
NSCl	−912.06840	12.4	0
ClNS	−912.03792	9.9	77
Cl + NS	−911.98296	7.7	213
$NSCl^{+\bullet}$	−911.68219	8.8	0
$ClNS^{+\bullet}$	−911.69753	13.0	−36
$Cl + NS^+$	−911.66943	7.0	32

[a] Based on (U)MP2/6-311+G(d) optimized geometries given in Figure 1. − [b] From (U)MP2/6-311+G(d) harmonic vibrational wavenumbers and scaled by 0.95. − [c] Relative energies including QCISD(T)/6-311+G(3df) energie and ZPE corrections.

Extensive attempts to locate transition structures for chlorine migration between nitrogen and sulfur atoms showed that the transition structures in both neutral and ionized states, if any, should lie much higher in energy than the dissociation limits $Cl^\bullet + NS^\bullet$ and $Cl^\bullet + NS^+$, respectively.

As seen in Figure 1, geometrical parameters of both isomers are markedly changed upon ionization. While in the neutral state the thiazyl NSCl form is 77 kJ/mol more stable

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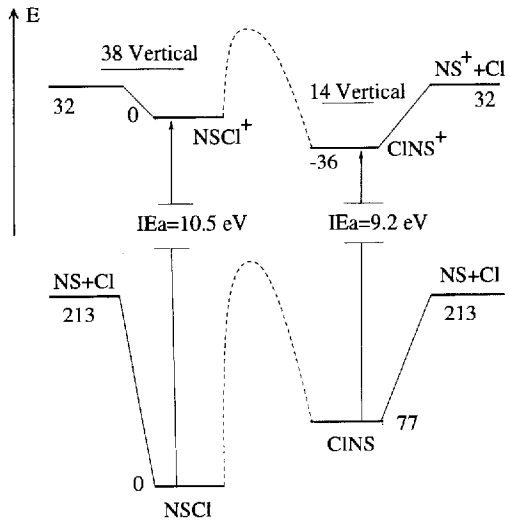
Figure 2. Schematic potential energy curves showing the ionization process of the [N,S,Cl] species. Relative energies within the neutral and ionized systems are given in kJ/mol

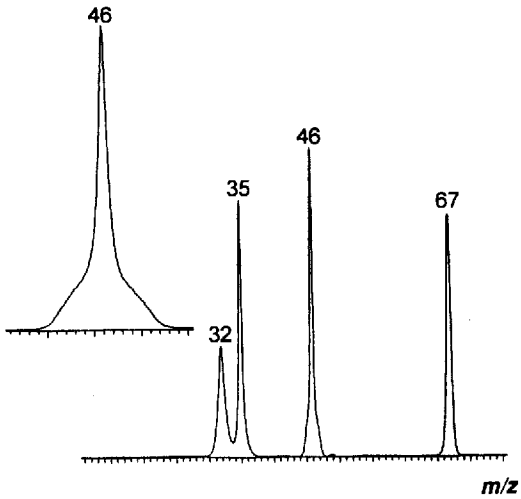


than the thionitrosyl ClNS form, a reversal of the energy order occurs in the ionized state, the thionitrosyl radical cation [ClNS$^{+\bullet}$] being 36 kJ/mol more stable than its thiazyl isomer [NSCl$^{+\bullet}$] (Figure 2). The ionization energies were calculated as follows: IE_a (NSCl) = 10.5 ± 0.3 and IE_a (ClNS) = 9.2 ± 0.3 eV. Due to the large geometrical changes (Figure 1), the differences between vertical and adiabatic ionization energies are quite large amounting to 38 kJ/mol in the case of NSCl and 50 kJ/mol in the case of ClNS. The value for NSCl is even larger than the energy of the dissociation of NSCl$^{+\bullet}$ into NS^+ + Cl$^\bullet$. This implies that the hot vertical [NSCl]$^{+\bullet}$ ion possesses enough internal energy to undergo either dissociation or rearrangement to its more stable [ClNS]$^{+\bullet}$ isomer.

We now turn to the mass spectrometric experiments. The experimental set-up was described in detail in previous papers[7,8]. The electron impact and collisional activation (CA) mass spectra were recorded on a large-scale VG Analytical AutoSpec 6F mass spectrometer having a $E_1B_2E_2E_3B_2E_4$ geometry (E stands for the electric sector and B for the magnetic sector). The ion source of the instrument was equipped with a flash-vacuum pyrolysis (FVP) device[8]. The spectrometer was operated at 8 kV accelerating voltage, 200 μA trap current, and 70 eV accelerating voltage. In the CA experiments, a beam of ions was mass-selected by a combination of three sectors ($E_1B_1E_2$) and subjected to collisional activation with O_2 (80% transmittance). The resolving power of $E_1B_1E_2$ was increased appropriately in order to remove any interferences with isobaric ions. The spectra were recorded by scanning E_3 and collecting the ions in the fifth field-free region.

Thiazyl chloride trimer, $(NSCl)_3$, was employed as the precursor[9]. Mild flashvacuum pyrolysis at ca. 170 °C followed by ionization produces quite abundant [NSCl]$^{+\bullet}$ ions (*m/z* 81). The mass spectra of these ions are shown in Figures 3 and 4. The MIKE spectrum arising from unimolecular fragmentations displays two major fragmentations, namely the loss of a nitrogen atom (*m/z* 67) and the loss of chlorine (*m/z* 46), which are consistent with an N–S–Cl connectivity for the *m/z* 81 ions (Figure 3). Upon collisional activation, the main differences appearing in the spectrum are the increased intensity of the peaks at *m/z* 35 and 32 as well as the composite nature of the peak at *m/z* 46 (Figure 3). The broader component of the composite peak was already suspected without the presence of the collision gas. The formation of $S^{+\bullet}$ ions (*m/z* 32) can hardly be rationalized on the basis of the occurrence of [NSCl]$^{+\bullet}$ ions alone. Due to the fact that [ClNS]$^{+\bullet}$ is more stable than [NSCl]$^{+\bullet}$ (Figure 2), the [NSCl]$^{+\bullet}$ → [ClNS]$^{+\bullet}$ isomerization apparently occurs to some extent after ionization or after collisional activation. A similar behavior was observed in the case of different sulfur-containing radical cations[10]. Thermally induced NSCl → ClNS isomerization before ionization seems unlikely because the CA spectrum of the *m/z* 81 ion remained almost unchanged even when the oven temperature was increased up to 600 °C. This is in line with calculated results given in Figure 2 which point to both thermodynamic and kinetic difficulties for such a reaction.

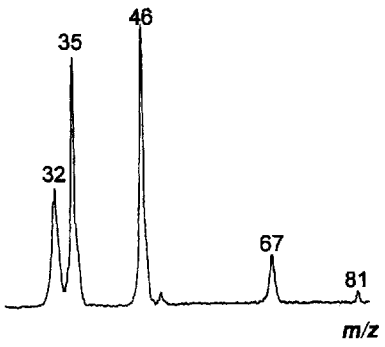
Figure 3. CA (O_2) spectra of [N,S,Cl]$^{+\bullet}$ ions (*m/z* 81); the inset shows the composite shape of the peak at *m/z* 46 [NS]$^{+\cdot}$



The NRMS spectrum of the *m/z* 81 ion displayed in Figure 4 is characterized by the same fragmentations as that observed before the neutralization, even though the recovery signal at *m/z* 81 is very weak. Such a low intensity is no doubt due to the large difference in geometries of both neutral and ionized species; it is difficult for the neutralized species to survive a vertical electron-transfer process when the Frank-Condon factors are unfavorable.

Calculated energies of the vertically neutralized species (NE_v)[11] show that the vertical ionization of ground-state ClSN$^{+\bullet}$ leads to neutral ClSN with an excess of only 30 kJ/mol in internal energy, the vertically neutralized ClSN thus lying about 180 kJ/mol below the Cl$^\bullet$ + NS$^\bullet$ dissociation limit. It can therefore be expected that thiazyl chloride should be able to survive when generated from ClSN$^{+\bullet}$ in an NR experiment and that its formation is manifested by a rather strong recovery signal. In contrast, the vertical ClNS

Figure 4. NR (NH_3/O_2) mass spectrum of $[N,S,Cl]^{+\bullet}$ ions (*m/z* 81)



receives a larger amount of internal energy, namely 97 kJ/mol, an energy level close to the $Cl^{\bullet}$ + $NS^{\bullet}$ dissociation limit (136 kJ/mol relative to the ground state ClNS, Figure 2). Because the vertically neutralized ClNS molecules could easily undergo dissociation, the formation of stabilized ClNS was not expected to be important. Of course, only an appropriate treatment of the Franck-Condon effect on the vibrational populations might give a quantitative information on this matter, which is however beyond the scope of this study. In this context, it is tempting to assign the extremely weak recovery signal detected in the NR spectrum (Figure 4) to neutral thionitrosyl chloride, Cl−N=S, with the assumption that the $ClNS^{+\bullet}$ ions predominate in the cell after collision activation owing to their higher thermodynamic stability. If thionitrosyl chloride exists, it has a life time longer than 1 microsecond, corresponding to the time of flight between both neutralization and reionization cells.

In summary, the present study shows that it is extremely difficult to detect thionitrosyl chloride by means of NRMS techniques, and that it is not due to its inherent kinetic or thermodynamic instability, but rather to the large difference in the geometry of both neutral and ionized structures making the stabilization of the formed neutral species quite unfavorable.

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