Research Project (OTKA K- 101164)

Generation, Spectroscopy, and Structure of Unstable Nitrile Oxides, Nitrile Sulfides, and Nitrile Selenides

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1. Introduction

Covalent pseudohalides, including nitrile oxides, nitrile sulfides and nitrile selenides ($R\text{-}C{\equiv}N{\rightarrow}E$, where E=O, S, Se and R=substituent atom or group), are versatile tools in various chemical transformations and are widely used in various fields of chemistry as building blocks for synthesizing useful chemical products. Synthesizing and characterizing new derivatives is important because it may open the door for further applications. The stability and reactivity of pseudohalides are very varied, and small nitrile oxides, nitrile sulfides and nitrile selenides are known to be reactive and unstable species. Their isolation in the pure state is not possible at ordinary conditions. However, nitrile oxides and nitrile sulfides have become important transient species and reactive intermediates in 1,3-dipolar cycloaddition reactions in solutions, providing routes to several classes of heterocycles accessible only with difficulty by other means. The characterization of unstable pseudohalides is not a routine task, and usually involves gas-phase and matrix isolation techniques. The aim of the project is to find novel routes to nitrile oxides, nitrile sulfides, and nitrile selenides, to characterize them by spectroscopic (UPS, IR) and theoretical means, and to study their cycloaddition reactions. In addition, the synthesis and structural characterization of starting materials used to generate pseudohalides are also aimed during the project.

2. Thermolysis of 1,2,5-oxadiazoles: generation of HCNO, CH_3CNO and NCCNO (ref. [12])

We expected that heterocyclic molecules containing the CNO moiety and a good leaving group, like nitrile, could serve as sources for the generation of nitrile oxides. Small nitrile oxides are unstable due to reactions between molecules, *viz.* dimerization and polimerization, thus their generation was attempted in the dilute gas phase using 1,2,5-oxadiazoles.

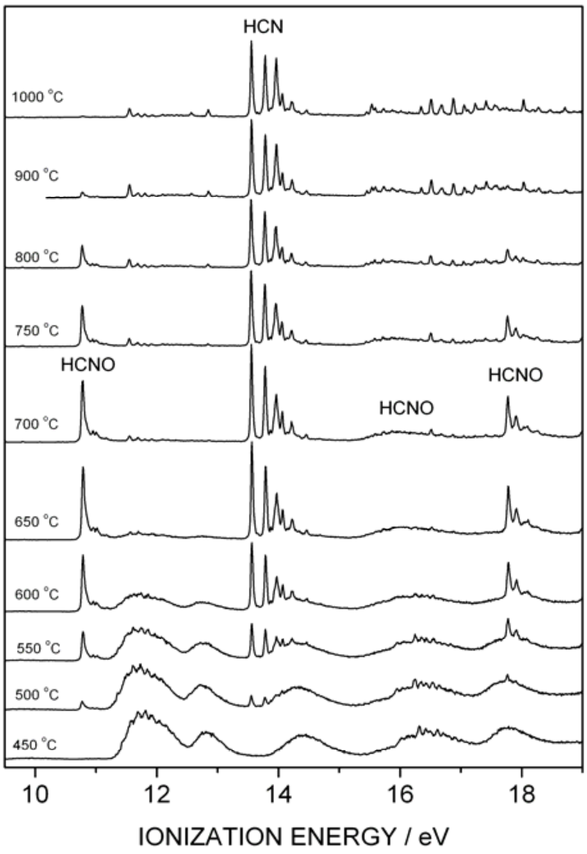
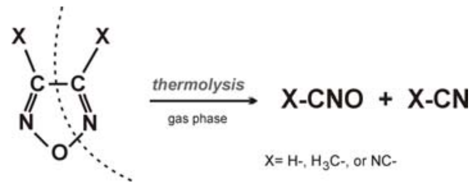


Figure 1.



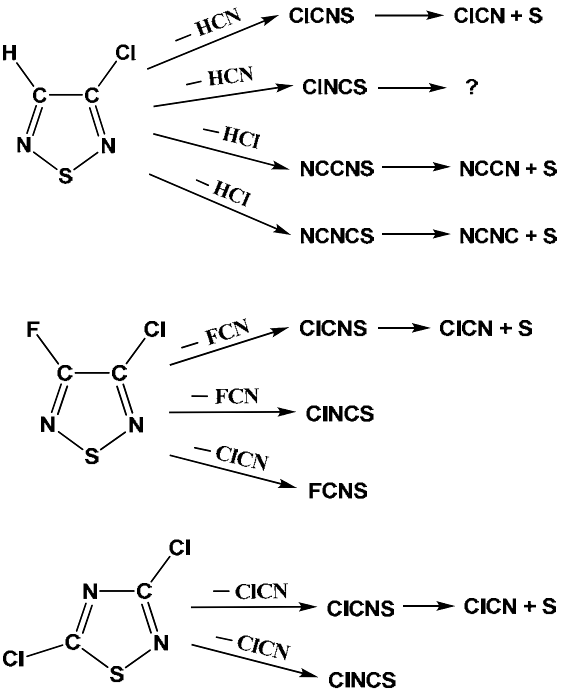
Scheme 1.

Gas-phase thermolysis of 1,2,5-oxadiazoles (Scheme 1) between 500 – 700 °C lead smoothly to nitrile oxide and nitrile, however, higher temperature reduced the nitrile oxide yield. Photoelectron spectra of the pyrolysis products of 1,2,5-oxadiazole are shown in Figure 1, as an example.

Electronic structures of 1,2,5-oxadiazoles ($X_2C_2N_2O$, where X= H, CH_3, CN) have been investigated in the gas phase by He I UV-photoelectron spectroscopy, as well as by calculations at the B3LYP, CCSD(T), and SAC-CI levels using aug-cc-pVTZ basis sets. The ground state geometry of the neutral molecules has been obtained from quantum-chemical calculations at the B3LYP and CCSD(T) levels. Oxadiazoles are predicted to be planar, not considering methyl-group hydrogen atoms, with C_{2v} symmetry. Photoelectron spectroscopy and theory applied to oxadiazoles has provided information on the valence occupied levels, on the ionization energies of neutral molecules, and on the fundamental vibrations of the cations.

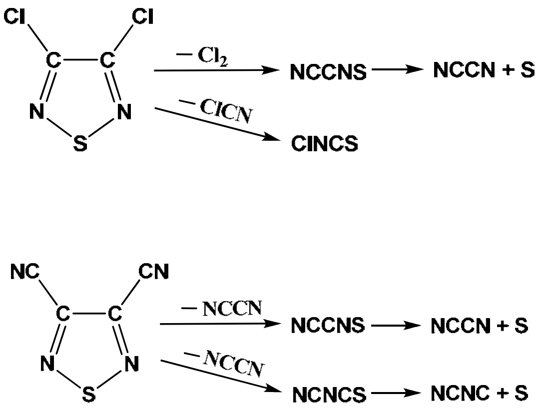
3. Generation and identification of ClCNS, NCCNS, and ClNCS (ref. [7])

Nitrile sulfides are thermally unstable at elevated temperatures and decompose in bimolecular reactions even at room temperature. We have attempted their generation in low-temperature inert noble gas matrices by means of UV irradiation at selected wavelengths of 254 and 280 nm using heterocyclic molecules containing the CNS moiety and the CN leaving group; namely four chloro-substituted thiadiazoles (3,4-dichloro-, 3-chloro- and 3-chloro-4-fluoro-1,2,5-thiadiazole; 3,5-dichloro-1,2,4-thiadiazole) and 3,4-dicyano-1,2,5-thiadiazole. Photochemical decomposition pathways of these thiadiazoles are shown in Scheme 2 and 3. Three pseudohalides, ClCNS, NCCNS, and ClNCS, were identified among photolysis products as new compounds by IR and UV spectroscopy. All of these compounds have been structurally characterised by quantum chemical methods at the CCSD(T) and B3LYP levels. The molecular frame of nitrile sulfides is confirmed as linear, and that of ClNCS as trans-bent. ClCNS, NCCNS and ClNCS are photolabile, and selection of the proper wavelength for photodecomposition of thiadiazole precursors and for the generation



Scheme 2

of ClCNS and NCCNS is of crucial importance. Although ClCNS decomposes at 254 nm, the decomposition is slow enough to support generation of this species at this wavelength for application in solution reactions. The application of 3-chloro-1,2,5-thiadiazole seems to be especially promising due to the relatively fast decomposition and relatively good yield of ClCNS. Formation of NCCNS from 3,4-dichloro-1,2,5-thiadiazole was also observed, likely by Cl_2 elimination.



Scheme 3

4. Generation of FCNS and a matrix isolation and theoretical study of its isomerization (ref. [2,10])

We have synthesized 3,4-difluoro-1,2,5-thiadiazole and studied its photodecomposition and the photoisomerization of the primary product FCNS in cryogenic noble gas matrix (Fig. 2). Upon 365 nm irradiation FCNS isomerizes to FC(NS), and upon 254 nm irradiation a backward reaction takes place, the isomerization of FC(NS) to FCNS. The FCNS↔FC(NS) photoisomerization process is a simple model system for molecular switches, thus we investigated the switching processes by theoretical methods. Vertical excitation energies were computed by the EOMEE-CCSD, MCSCF, and MR-CISD methods. Conical intersections were also searched for. The ring opening and closing processes were simulated by non-adiabatic dynamics propagation with the trajectory surface hopping method. The combined computational and experimental results suggest that upon 365 nm irradiation the ring closure FCNS→FC(NS) occurs under participation of all three conical intersections, while 254 nm

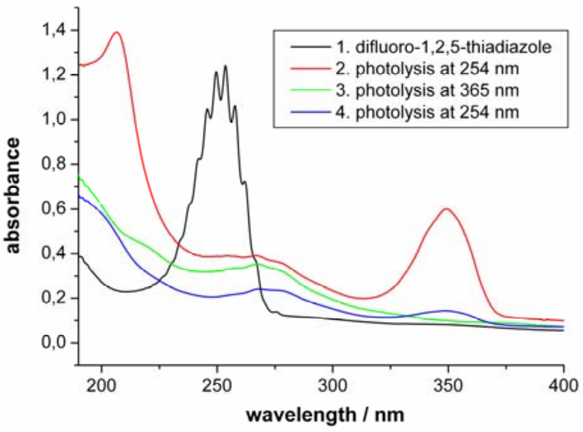


Figure 2.

irradiation causes ring opening FC(NS)→FCNS. Both processes, especially the ring opening, are accompanied by fragmentation into FCN+S.

5. Generation and identification of HCNSe, CH_3CNSe, and NCCNSe (ref. [1,2])

Nitrile selenides are promising dipolarophiles in 1,3-dipolar cycloaddition reactions, however, their chemistry is unknown due to the lack of methods to generate them in solutions. We provided evidence for the existence of HCNSe, CH_3CNSe, and NCCNSe by generating them photolytically in an inert solid argon matrix from the 1,2,5-selenadiazole, 3,4-dimethyl-1,2,5-selenadiazole, and 3,4-dicyano-1,2,5-selenadiazole by 280, 254, and 313 nm UV irradiation, respectively (see selected IR spectrum in Figure 3.). Nitrile selenides are photolabile and the selection of the proper wavelength for photodecomposition of selenadiazoles was of crucial importance. Nitrile selenides were identified and studied by ultraviolet spectroscopy and mid-infrared spectroscopy. Ground state geometries have been obtained from quantum-chemical calculations at the CCSD(T)/aug-cc-pVTZ level. Nitrile selenides are predicted to be linear with a relatively weak N−Se bond. Although the N−Se bond is relatively weak, it is strong enough to support application of these species at room or slightly elevated temperatures.

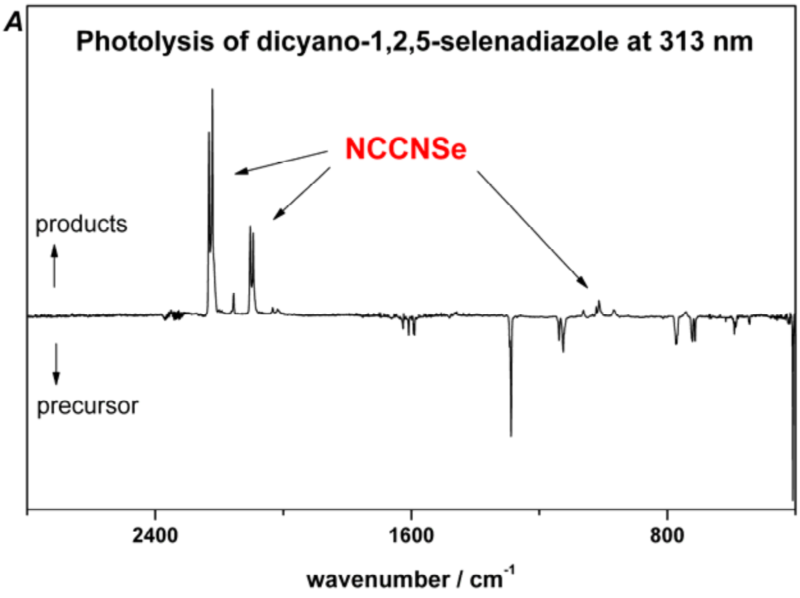


Figure 3.

6. Structure, stability, and cycloaddition reactions of nitrile selenides (ref. [9])

Nitrile selenides are potential 1,3-dipolarophiles for cycloaddition reactions, and they are expected to be key reagents in the production of selenium-containing heterocycles, e.g.

selenazoles, isoselenazolines, and selenadiazoles. However, to date, nitrile selenide chemistry is poorly understood and methods to generate these species in solution are unknown. Nitrile selenides are believed to be unstable. In order to find information about their stability, the equilibrium structure, unimolecular reactions, and bimolecular reactions of nitrile selenides (XCNSe, where X= H, F, Cl, Br, CN, CH_3) have been investigated using CCSD(T), CCSD(T)//B3LYP, and MR-AQCC//UB3LYP quantum chemical methods. Nitrile selenides have been demonstrated to be kinetically stable for unimolecular reactions and application at ambient temperature. In contrast, nitrile selenides are very reactive and decompose quickly in bimolecular reactions even at low temperatures; the decomposition to nitriles and selenium is predicted to be the major decomposition route (see Figure 4).

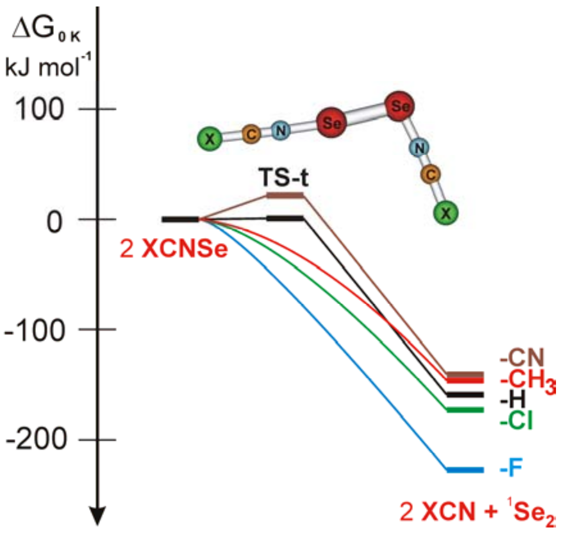


Figure 4

FCNSe and CH_3CNSe cycloaddition with ethynes, ethenes, and nitriles was studied using the MR-AQCC//UB3LYP method. These nitrile selenides readily react with small, sterically not hindered ethynes, ethenes, and nitriles to form selenazoles, isoselenazolines, and selenadiazoles, respectively. Electronegative substituents present in reacting dipolarophiles lower the kinetic energy barrier required for cycloaddition. Calculations suggest that successful application of nitrile selenides as 1,3-dipolarophiles for cycloaddition reactions requires the prevention of unimolecular decomposition processes and bimolecular reactions between nitrile selenides. Therefore, excess amounts of reacting 1,2-dipolarophiles and a relatively low temperature (room temperature or below), depending on the substituent, are required.

7. Generation of SCNNCS and NCSNCS and a theoretical study of their isomers (ref. [3])

Pseudohalogens ([2C, 2N, 2X], X = O, S, Se), derived from the three-membered CNX pseudohalide groups, have larger structural variability than pseudohalides. Pseudohalogens, however, are much less studied than substituted pseudohalides. Considering the [2C, 2N, 2S] isomers, only thiocyanogen (NCSSCN) was synthesized so far. We have investigated the structure and relative stability of twenty three closed-shell singlet [2C, 2N, 2S] isomers (Figure 5), 10 open-chain pseudohalogens, 10 consisting of a three-membered CNS ring, and three with a thiothionyl moiety, using quantum chemical methods at the B3LYP and CCSD(T) levels. According to calculations, the thermodynamically most stable isomer of these species is NCSSCN, which was the only experimentally observed isomer until the present work. According to the calculations, however, several isomers, including isothiocyanato-, thiocyanato-, nitrile sulfide-, thiofulminato-, thiazirine-, and thiothionyl-derivatives, are also expected to be stable and candidates for experimental investigations, especially in inert cryogenic matrices where intermolecular reactions and thermal decomposition do not occur. Anharmonic vibrational wavenumbers, infrared intensities, relative Raman intensities, and UV excitation energies have also been computed to assist their detection. We have synthesized NCSSCN and deposited this molecule into cryogenic noble gas matrices, and characterized it by IR, Raman, and UV spectroscopic methods. The photoisomerization of NCSSCN has also been investigated. We have proved by IR and UV spectroscopy that the UV photolysis of NCSSCN leads to the formation of novel pseudohalogens, namely NCSNCS and SCNNCS.

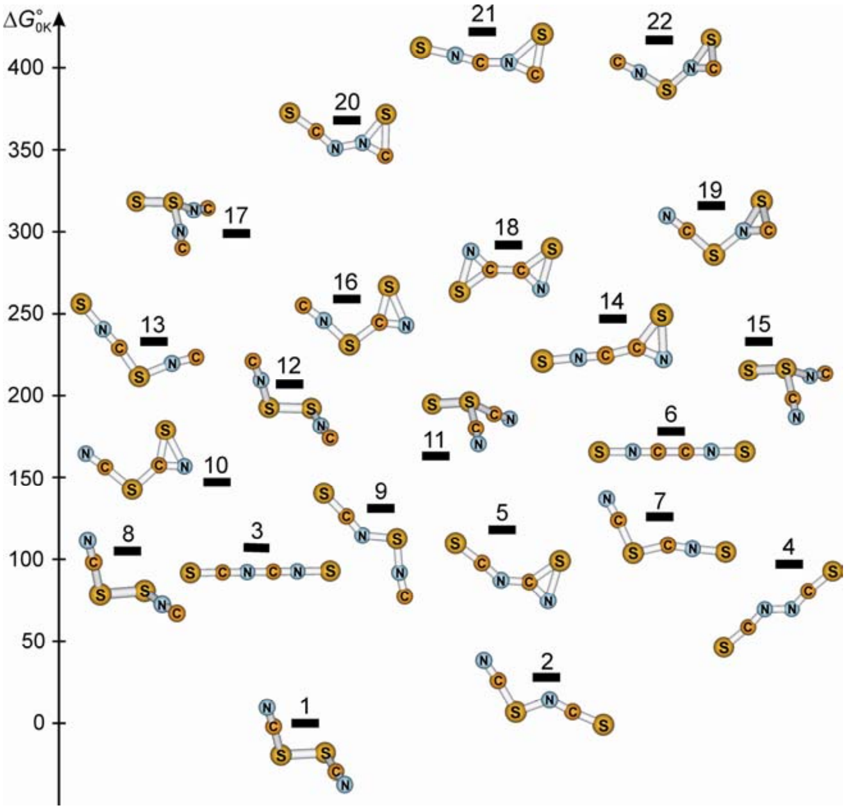
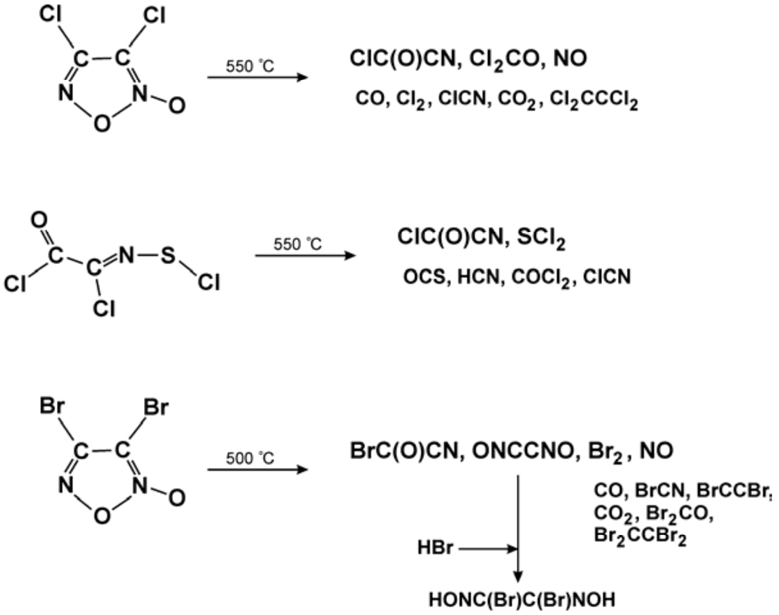


Figure 5.

8. Generation, spectroscopy, and structure of ClC(O)CN and BrC(O)CN (ref. [4])

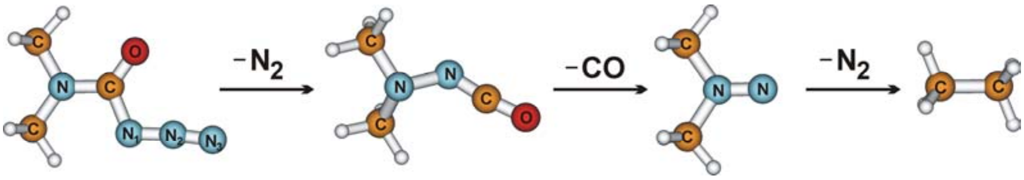
We investigated the thermal decomposition of dihalofuroxans in the gas phase in order to find novel synthetic routes to nitrile oxides, however, nitrile oxide formation was not observed, but we identified new cyanoformyl halides. Cyanoformyl halides, XC(O)CN, are of considerable interest for both synthetic chemistry and spectroscopy/theoretical chemistry. They have the potential to become carbonylating, cyanating, or cyanoformylating agents in organic chemistry. However, their chemistry is largely unexplored to date. In order to isolate and characterize cyanoformyl halides, we used two routes to ClC(O)CN, the gas-phase thermolysis of dichlorofuroxan and 2-chloro-2-(chlorothioimino)acetyl chloride, and one route to BrC(O)CN, the gas-phase thermolysis of dibromofuroxan (see Scheme 4). We isolated ClC(O)CN and BrC(O)CN from these reaction mixtures at low temperature and investigated them in the gas phase by UV photoelectron and mid-infrared spectroscopies. The ground-state geometries of the neutral molecules (planar with C_s symmetry) were obtained from quantum-chemical calculations at the B3LYP and CCSD(T) levels using the aug-cc-pVTZ basis set. The individual spectroscopies provided a detailed investigation into the vibrational and electronic character of the molecules and were supported by quantum-chemical calculations.



Scheme 4.

9. Spectroscopic identification of dimethylamino isocyanate and dimethyl diazene (ref. [8])

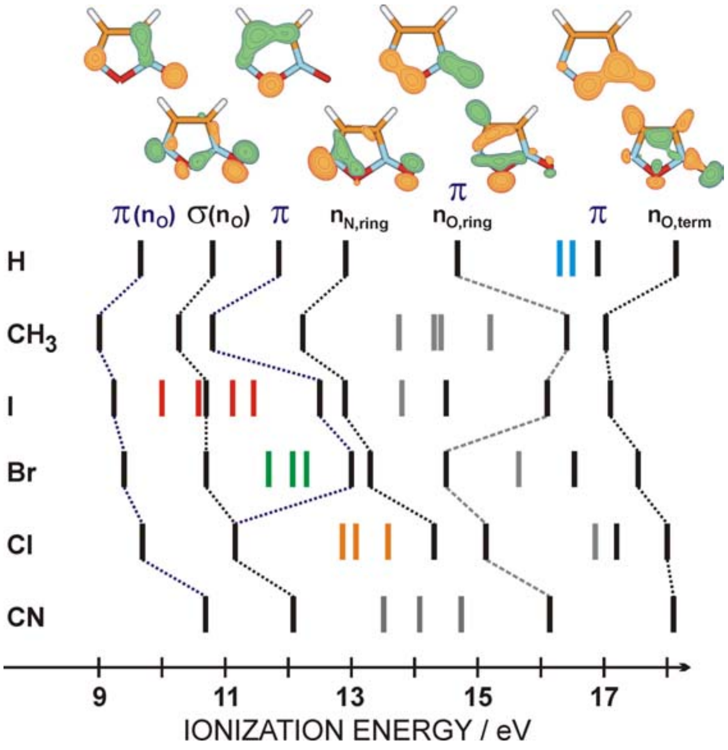
We investigated the UV photochemical decomposition of dimethylcarbamoyl azide in an argon matrix at cryogenic temperatures. The products of the photolysis were identified by infrared spectroscopy supported by quantum-chemical calculations. Sequential formation of dimethylamino isocyanate ($Me_2N{-}NCO$), 1,1-dimethyldiazene ($Me_2N{=}N$), and ethane was established. Therefore, the major decomposition channel (Scheme 5) was identified as $Me_2NC(O)N_3 \rightarrow Me_2N{-}NCO \rightarrow Me_2N{=}N \rightarrow Me{-}Me$, via consecutive N_2, CO, and N_2 eliminations. Ground state geometries, vibrational frequencies, IR intensities, and UV excitation energies of the transient dimethylamino isocyanate and 1,1-dimethyldiazene were computed using the B3LYP and SAC-CI methods and the aug-cc-pVTZ basis set. Both molecules have singlet electronic ground states. $(CH_3)_2N{-}N{=}C{=}O$ has a trans-bent NNCO frame with C_1 molecular symmetry. $(CH_3)_2N{=}N$ has a planar heavy-atom frame with C_{2v} symmetry and a short NN double bond.



Scheme 5

10. Photoelectron spectroscopic investigation of the electronic structure of furoxans (ref. [6])

We investigated the electronic structure of disubstituted furoxans, 1,2,5-oxadiazole-2-oxides ($X_2C_2N_2O_2$, where X= H, Cl, Br, I, CH_3, NC), in the gas phase by He I and He II UV photoelectron spectroscopy. Ionization potentials were determined and the electronic structures were discussed within the frame of molecular orbital theory. The ground-state geometries of the neutral molecules were obtained from quantum-chemical calculations using the B3LYP/cc-pVTZ method. According to calculations, furoxans have a planar ring structure with a short exocyclic N–O bond and a long endocyclic N–O bond. Photoelectron spectroscopy, supported by quantum-chemical calculations at the SAC-CI/cc-pVTZ level, provided a detailed investigation into the electronic character of the molecules and an analysis of the effect of substitution on the orbitals of the parent furoxan. HOMOs of all furoxan derivatives have predominant exocyclic oxygen π lone pair character, therefore the lowest energy ionization potentials are assigned to ionizations from the out-of-plane oxygen lone pair orbitals. Experimental ionization energy correlation diagram for substituted furoxans and schematics of the corresponding molecular orbitals of the parent furoxan is shown in Scheme 6.



Scheme 6

11. Structure and spectroscopy of 3-chloro-4-fluoro-1,2,5-thiadiazole (ref. [5])

We synthesized and investigated the electronic, geometric, and vibrational properties of 3-chloro-4-fluoro-1,2,5-thiadiazole in the gas phase using IR spectroscopy (Figure 6), UV photoelectron spectroscopy, and theoretical calculations. The ground-state geometry of the neutral molecule was obtained from quantum-chemical calculations using the B3LYP/aug-cc-pV(T+d)Z method. According to calculations, the molecule has planar structure and C_S symmetry. IR and photoelectron spectroscopies, supported by quantum-chemical calculations at the B3LYP and SAC-CI/aug-cc-pV(T+d)Z levels, provided information on the fundamental vibrations and on the valence occupied levels of the neutral molecule, and on the sequence and fundamental vibrations of the low-lying cationic states.

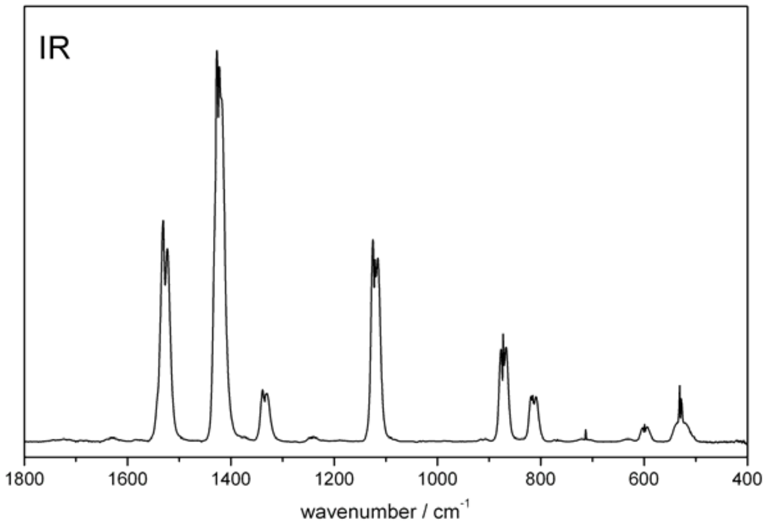


Figure 6.

12. Structure, spectroscopy, and thermal decomposition of 5-chloro-1,2,3,4-thiatriazole (ref. [11])

We investigated the structure and thermal decomposition of 5-chloro-1,2,3,4-thiatriazole in the gas phase for the first time by mid-infrared and He I photoelectron spectroscopy.

The ground-state geometry of the molecule was obtained from quantum chemical calculations at the CCSD(T) and B3LYP levels using aug-cc-pVTZ basis set. According to calculations, the molecule has planar structure and C_S symmetry. Ionization potentials of the molecule were determined. IR and photoelectron spectroscopies, supported by quantum chemical calculations at the B3LYP and SAC-CI levels, provided a detailed investigation into the vibrational and electronic character of the molecule. Thermal stability of 5-chloro-1,2,3,4-thiatriazole was studied both experimentally and theoretically. Flash vacuum thermolysis of the molecule produced fast quantitatively N_2, ClCN, and sulfur (see Figure 7).

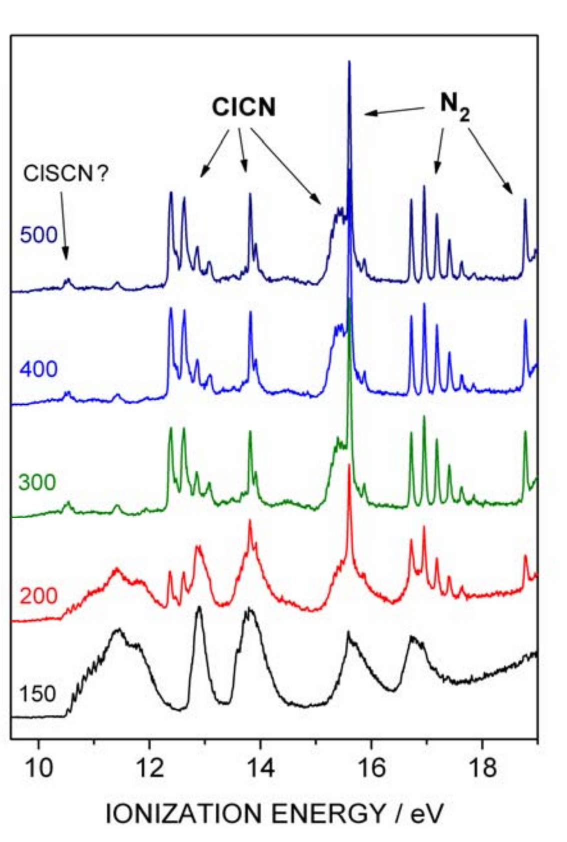


Figure 7.

Theoretical calculations at the CCSD(T)//B3LYP level predicted competitive decomposition routes, starting either with a retro-cycloaddition reaction leading to N_2S and ClCN or with a ring opening to chlorothiocarbonyl azide intermediate, to produce finally N_2, S, and ClCN (Figure 8). Calculations also predicted that N_2S is reactive and decomposes in bimolecular reactions to N_2 and S_2.

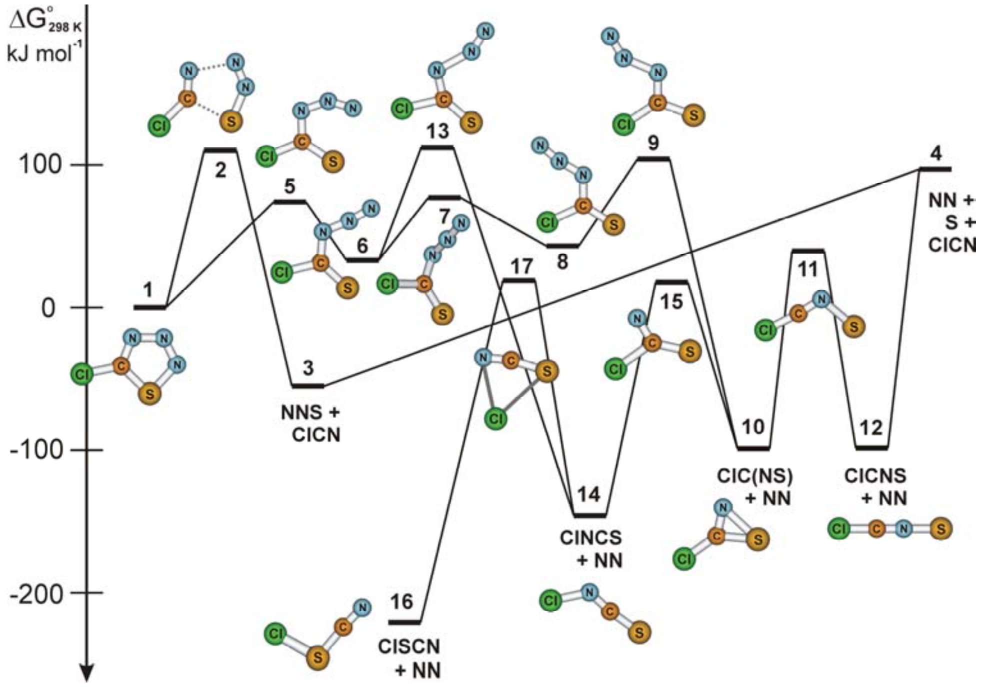


Figure 8.

13. Synthesis, spectroscopy, and structure of 1,2,5-selenadiazoles (ref. [13])

We synthesized the 1,2,5-selenadiazole and its methyl and cyano derivatives, XYC_2N_2Se (X and Y= H, CH_3 or NC), and investigated these molecules in the gas phase by UV photoelectron and mid-infrared spectroscopies, and in the condensed phase by IR and Raman spectroscopies. The ground state geometries of the neutral molecules were obtained from quantum-chemical calculations at the B3LYP and CCSD(T) levels using the aug-cc-pVTZ basis set. The individual spectroscopies provided a detailed investigation into the vibrational and electronic character of the molecules, and were supported by quantum-chemical calculations. Thermal stability of 1,2,5-selenadiazoles were investigated in the gas phase. We found that 1,2,5-selenadiazoles are thermally very stable, with the stability strongly influenced by the substituents. The decomposition of the monomethyl, dimethyl, dicyano, and dihydrogen derivatives commenced at 540, 550, 600, and 675 °C. The decomposition rapidly and quantitatively produced nitriles (HCN, CH_3CN, or NCCN) and red selenium. The He I UPS spectra of investigated selenadiazoles are shown in Figure 9.

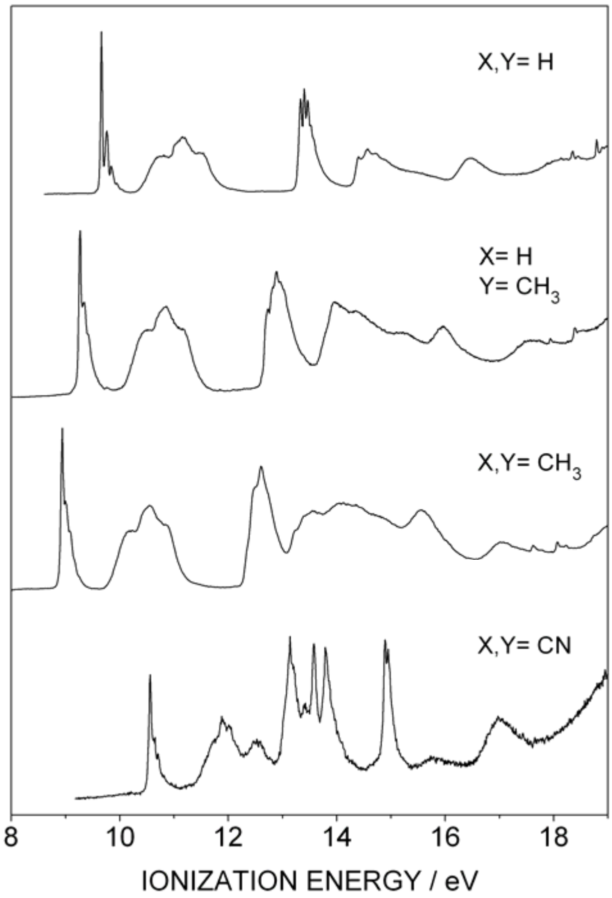


Figure 9.

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