Inorg. Chem. **2004**, *43*, 4799–4801

Inorganic Chemistry
Communication

Reaction of AgN_3 with $SOCl_2$: Evidence for the Formation of Thionyl Azide, $SO(N_3)_2$

Zeng Xiaoqing,[†,‡] Liu Fengyi,[†,§] Sun Qiao,[†,‡] Ge Maofa,*[,†] Zhang Jianping,[†] Ai Xicheng,[†] Meng Lingpeng,[§] Zheng Shijun,[§] and Wang Dianxun*[,†]

State Key Laboratory for Structural Chemistry of Unstable and Stable Species,
Institute of Chemistry, Chinese Academy of Science, Beijing 100080, China,
Open Laboratory of Computational Quantum Chemistry, Hebei Normal University,
Shijiazhuang 050091, China, and Graduate School of Chinese Academy of Sciences,
Beijing 100039, P. R. China

Received April 29, 2004

Pure thionyl azide $SO(N_3)_2$, which is the only gaseous reaction product, has been generated in a vacuum by the heterogeneous reaction of $SOCl_2$ vapor with AgN_3 at room temperature at a $SOCl_2$ vapor pressure of 1×10^{-3} Torr. Evidence for the formation of $SO(N_3)_2$ is given by on line photoelectron spectroscopy (PES) combined with outer valence Green's function (OVGF) calculations with the 6-311++G(2df) basis set. The good agreement between the PES experiment and the OVGF calculation shows that $SO(N_3)_2$ has C_1 symmetry. The first ionization energy of $SO(N_3)_2$ is 10.18 eV.

Since the discovery of azides in 1864, the chemistry of these species has been attracting intense interest, owing not only to their widespread use as building blocks in organic and heterocyclic syntheses,[1−3] but also to their potential use as environmentally friendly high-energy density materials.[4] Although a number of azidosulfonic acids have been reported,[5] until now, there has been no report on thionyl azide $SO(N_3)_2$.

Our laboratory has demonstrated the ability to generate a continuous flowing beam of short-lived species via the pyrolysis of suitable precursors, allowing us to perform photoelectron spectroscopy (PES) studies.[6] Recently, pure XN_3(X = F, Cl, Br, I) compounds have been prepared by us and then characterized by on line PES experiments combined with outer valence Green's function (OVGF) calculations.[7,8] New convenient reactions to prepare pure INCO, ISCN, and the hitherto unknown ISeCN have been also reported by us.[9]

In this paper, we report vacuum preparation of the hitherto unknown thionyl azide $SO(N_3)_2$, and its characterizations by PES in combination with OVGF calculations with 6-311++G(2df) basis set.

Caution: *AgN_3 is highly explosive, especially as a pure dry powder, so appropriate safety precautions should be taken.*

The preparation of $SO(N_3)_2$ is carried out in the PES spectrometer by the heterogeneous reaction of $SOCl_2$ vapor with freshly prepared AgN_3 at room temperature:

$$2AgN_3(s) + SOCl_2(g) \rightarrow SO(N_3)_2(g) + 2AgCl(s) \quad (1)$$

For the PES measurement, the freshly prepared AgN_3 powder[10] was loosely filled into a quartz inlet tube and supported on quartz wool. Pure $SO(N_3)_2$ is easily formed by passing the $SOCl_2$ vapor at a pressure of 1×10^{-3} Torr over

---

* To whom correspondence should be addressed. E-mail: wangdx@iccas.ac.cn.

[†] State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Chinese Academy of Science.

[‡] Graduate School of Chinese Academy of Sciences.

[§] Hebei Normal University.

(1) Nguyen, M. T.; Flammang, R. *Chem. Ber.* **1996**, *129*, 1373 and references cited therein.

(2) Scriven, E. V. F.; Turnball, K. *Chem. Rev.* **1988**, *88*, 298.

(3) (a) Tornieporth-Oetting, I. C.; Klapötke, T. M. *Angew. Chem.* **1995**, *107*, 559; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 511. (b) Klapötke, T. M.; Schulz, A. *Polyhedron* **1996**, *15*, 1407.

(4) (a) Lucien, H. W. *J. Am. Chem. Soc.* **1958**, *80*, 4458. (b) Schulz, A.; Tornieporth-Oetting, I. C.; Klapötke, T. M. *Angew. Chem.* **1993**, *105*, 1697; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1610. (c) Klapötke, T. M.; Schulz, A.; Tornieporth-Oetting, I. C. *Chem. Ber.* **1994**, *127*, 2181. (d) Engelke, R. *J. Am. Chem. Soc.* **1993**, *115*, 2961. (e) Klapötke, T. M.; Schulz, A. *Chem. Ber.* **1995**, *128*, 201.

(5) (a) Shozda, R. J.; Vernon, J. A. *J. Org. Chem.* **1965**, *4*, 359. (b) Curtius, T.; Schmidt, F. *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 1571. (c) Abramovitch, R. A.; Davis, B. A. *Chem. Rev.* **1964**, *64*, 149. (d) Ruff, J. K. *Inorg. Chem.* **1965**, *4*, 567. (e) Lehman, H.; Holznagel, W. Z. *Anorg. Allg. Chem.* **1958**, *293*, 314.

(6) (a) Zhu, X. J.; Ge, M. F.; Wang, J.; Sun, Z.; Wang, D. X. *Angew. Chem., Int. Ed.* **2000**, *112*, 2016. (b) Sun, Z.; Wang, J.; Zhu, X. J.; Ge, M. F.; Wang, D. X. *Chem. Eur. J.* **2001**, *14*, 2995. (c) Wang, J.; Sun, Z.; Zhu, X. J.; Yang, X. J.; Ge, M. F.; Wang, D. X. *Angew. Chem., Int. Ed.* **2001**, *40*, 3055.

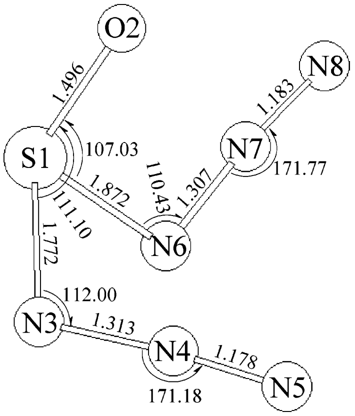
(7) Che, H. J.; Bi, H. M.; Zeng, Y. L.; Meng, L. P.; Zheng, S. J.; Wang, D. X. *ChemPhysChem* **2003**, *3*, 300.

(8) Niessen, Von W.; Schirmer, J.; Cederbaum, L. S. *Comput. Phys. Rep.* **1984**, *1*, 57.

(9) Li, Y. M.; Qiao, Z. M.; Sun, Q.; Zhao, J. C.; Li, H. Y.; Wang, D. X. *Inorg. Chem.* **2003**, *42*, 8446.

(10) Tornieporth-Oetting, I. C.; Buzek, P.; Schleyer, R. von P.; Klapötke, T. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1338.

10.1021/ic049442s CCC: $27.50



O2-S1-N3-N4	49.18
O2-S1-N6-N7	53.06
S1-N3-N4-N5	170.92
S1-N6-N7-N8	165.96
N4-N3-S1-N6	-58.99

Figure 1. Fully optimized MP2 geometry of $SO(N_3)_2$.

the AgN_3 (0.5 g) at room temperature, because in the high pressure of $SOCl_2$ vapor the PE spectrum of $SOCl_2$ will appear in the PE spectrum of the reaction products.

$SOCl_2$ was bought from the ACROS Company, and its purity is better than 99.5%. The PE spectrum of $SOCl_2$ is the same as that reported.[11]

The PE spectrum of $SO(N_3)_2$ is recorded on a double-chamber UPS-II machine[6] which was built specifically to detect transient species at a resolution of about 30 meV as indicated by the $Ar^+(^2P_{2/3})$ photoelectron band. Experimental vertical ionization energies (I_v in eV) are calibrated by simultaneous addition of a small amount of argon and methyl iodide to the sample.

OVGF calculations using the 6-311++G(2df) basis set and frozen core MP2 optimized geometry of the gauche-conformer have been performed on the ground and ionic states corresponding to ionization of the electron from different molecular orbitals with the C_1 symmetry. The results are used to assign the PES bands.

The geometry of $SO(N_3)_2$ was optimized by both a frozen core MP2 and DFT B3LYP methods with the 6-31+G(d) basis set, because no experimental geometry has been reported. Three conformers were located by both methods. The *cis*-conformer with C_{2v} symmetry was shown to be a transition state by the frequency analysis (NIMAG = 1). The other two minima of $SO(N_3)_2$ have C_1 symmetry with the trans conformer being 1.175 kcal/mol higher in energy than the gauche one at the CCSD/6-311G(d) level. A frozen core MP2 fully optimized geometry for the gauche conformer is shown in Figure 1.

Figure 2 gives the PE spectrum of the product obtained by the above-mentioned reaction 1. An expanded PE spectrum in the low ionization energy region (<14.00 eV) for reaction 1 is shown in Figure 3.

The assignment of the observed PE spectrum of $SO(N_3)_2$ is supported by the OVGF calculation with 6-311++G(2df) basis set and on the basis of the Koopmans theorem.[12] Table 1 gives PES vertical ionization energies (I_v in eV) and ionization energies (E_v in eV) calculated by the OVGF method for the $SO(N_3)_2$ molecule. The character of the ionized orbital corresponding to the PES band is also listed in Table 1.

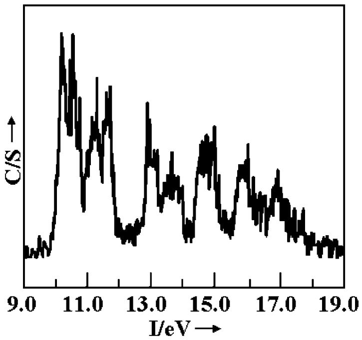


Figure 2. Complete HeI photoelectron (PE) spectrum of $SO(N_3)_2$.

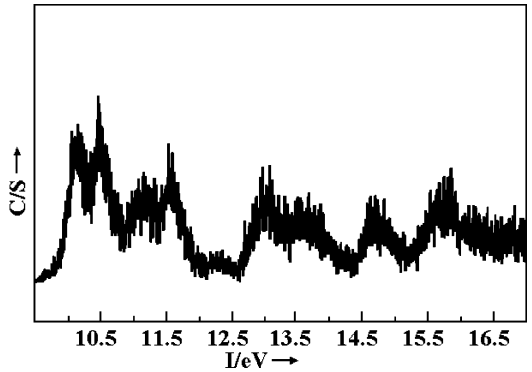


Figure 3. Expanded PE spectrum of $SO(N_3)_2$ in the low ionization energy region (<14.00 eV).

Table 1. PES Ionization Energies (IP in eV) and Computed Ionization Energies (E_v in eV) by the OVGF Calculation with 6-311++G(2df) Basis Sets and Molecular Orbital-Ionized Character for $SO(N_3)_2$

IP (eV)	E_v (eV)	MO character
10.18	10.244(33)	$\pi_{N_6-N_7-N_8}{}^*$
10.50	10.616(32)	$\pi_{N_6-N_7-N_8}{}^*$
11.15	10.769(31)	$\pi_{N_3-N_4-N_5}{}^*$
11.48	11.441(30)	$\pi_{N_3-N_4-N_5}{}^*$
13.08	13.519(29)	$\sigma_{S-O}{}^*$, $\sigma_{N_3-N_4}$
13.59		
14.94	14.226(28)	π_{S-O}, $\pi_{N_7-N_8}$
15.69	15.163(27)	π_{S-O}, $\pi_{N_4-N_5}$

From Table 1, it is clearly seen that the good agreement between the experimental PES and the calculated OVGF ionization energies provides evidence that the new compound is the hitherto unknown $SO(N_3)_2$. Of particular interest are the four separated PES bands in the low ionization energy region (<14.00 eV), which embody mainly the two dominant N_3 groups in the molecule. The first band at 10.18 eV results from the ionization of the electron from the highest occupied molecular orbital (HOMO) whose dominant character is $\pi_{N_6-N_7-N_8}$. The second band at 10.50 eV corresponds to ionization of the electron from the second HOMO (SHOMO) which also has the dominant character of $\pi_{N_6-N_7-N_8}$. Ionization of the electrons from the orbital embodying the second

---

(11) Chadwick, D.; Frost, D. C.; Herring, F. G.; Katrib, A.; McDowell, C. A.; McLean, R. A. N. *Can. J. Chem.* **1973**, *51*, 1893.

(12) Koopmans, T. *Physica* **1934**, *1*, 104.

azide $\pi_{N_3-N_4-N_5}$ group in the $SO(N_3)_2$ molecule lead to the third and fourth bands at 11.15 and 11.48 eV, respectively.

The PES bands in the high ionization energy region (>13.00 eV) involve mainly the contribution of the SO group (see Table 1).

The first appearance of the contribution of the dominant $N_6-N_7-N_8$ group in the HOMO and SHOMO of the $SO(N_3)_2$ molecule shows that the $N_6-N_7-N_8$ group is closer to the SO group than $N_3-N_4-N_5$ group, because the geometry of the species studied could be deduced from its PE spectrum.[6] The gauche conformer with C_1 symmetry (See Figure 3) is in excellent agreement with the PES results. The distance 2.884 Å between the S_1 and N_7 atoms is closer than that of 3.001 Å between the S_1 and N_4 atoms in the MP2/6-31+G(d) geometry, suggesting that electronic interaction between the SO and $N_6-N_7-N_8$ groups is stronger than that between the SO and the $N_3-N_4-N_5$ group.

Besides, all calculated ionization energies using the same method for the possible species $SO(N_3)Cl$ are 0.4−0.6 eV higher than that of the $SO(N_3)_2$ molecule. That is, PES experimental ionization energies of the reaction product have larger differences with respect to the calculated results of the possible $SO(N_3)Cl$ species. In particular, for the $SO(N_3)Cl$ species there is no PES band corresponding to the calculated ionization energy of 12.177 eV, which has the character of a dominant contribution of the Cl atom in the molecule. So, $SO(N_3)_2$ is the only gaseous reaction product.

An X-ray diffraction analysis showed that the solid residue in the reactor inlet tube was AgCl(s).[13] This fact further supports that the heterogeneous reaction of $SOCl_2$ vapor with AgN_3 at room temperature at a $SOCl_2$ vapor pressure of 1×10^{-3} Torr leads to the formation of the only gaseous compound $SO(N_3)_2$.

In summary, the hitherto unknown thionyl azide $SO(N_3)_2$ was prepared by the heterogeneous reaction of $SOCl_2$ vapor with freshly synthesized AgN_3 at room temperature at a $SOCl_2$ vapor pressure of 1×10^{-3} Torr. The only gaseous product, $SO(N_3)_2$, has been characterized on line by a combination of PES and OVGF calculations. The good agreement between the PES experiment and OVGF calculation shows that $SO(N_3)_2$ has C_1 symmetry and a first ionization energy of 10.18 eV. The discovery of a ready synthesis method for $SO(N_3)_2$ might facilitate studies of its properties and applications.

Acknowledgment. This project was supported by the National Natural Science Foundation of China (Contract 50372071). Zeng Xiaoqing and Sun Qiao thank the Chinese Academy of Sciences, Liu Fengyi thanks the Beijing University of Chemical Technology for scholarships during the period of this work, and Prof. M. F. Ge would like to thank the foundation of Chinese Academy of Sciences (Hundred Talents).

Supporting Information Available: Additional tables and figure. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049442S

---

(13) Zeng, X. Q. Ph.D. Thesis, 2004.