Registry No. $K_4[Pt_2(pop)_4]$, 80011-26-3; $K_4[Pt_2(pop)_4Cl_2]$, 85335-49-5; $K_4[Pt_2(pop)_4Br_2]$, 82135-55-5; $K_4[Pt_2(pop)_4I_2]$, 85335-50-8; $K_4[Pt_2(pop)_4Cl]$, 85553-26-0; $K_4[Pt_2(pop)_4Br]$, 98875-97-9; $K_4[Pt_2(pop)_4I]$, 85553-25-9.

Contribution from the Institutes of Inorganic Chemistry, University of Frankfurt, Niederurseler Hang, D-6000 Frankfurt (Main) 50, West Germany, and University of Göttingen, Nikolausberg, D-3400 Göttingen, West Germany

Gas-Phase Reactions. 52.[1] Pyrolysis of S_4N_4[§]

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Received December 21, 1984

The potentially explosive title compound is thermally decomposed in a controlled way by using a flow system under reduced pressure and PE spectroscopic gas analysis. The two reaction channels to 2 SN at lower and to $N_2 + S_2$ at higher temperature are rationalized by semiempirical hypersurface calculations. Our report containing information on both the decomposition conditions and the products formed may be useful for the polymerization to superconducting $(SN)_x$. The interesting dynamics of the S_2N_2 system will hopefully stimulate further theoretical work employing e.g. correlated wave functions.

Tetrasulfur tetranitride, S_4N_4, a cage with a square set of N atoms and a bisphenoid of S atoms, forms thermochromic crystals and must be handled with care, since friction, percussion, or rapid heating can cause it to explode.[2] When this compound is pumped through silver wool heated to 490 K, colorless crystals of square-planar S_2N_2, another explosive,[2,3] can be isolated, which at room temperature polymerize to the golden, lustrous, superconducting $(SN)_x$.[2,3] In the gas phase at pressures below 10^{-2} mbar the following sulfur nitrides have been identified and characterized by their photoelectron spectra: $(SN)_4$,[4a] $(SN)_2$,[4a,b] and SN.[4c] On the basis of above prior knowledge[2-4] and our experience concerning the controlled thermal decomposition[5] of hazardous compounds like azides[1,5,6] in flow systems using PE spectroscopic real-time analysis,[5] we have pyrolyzed S_4N_4 at 10^{-2} mbar pressure and temperatures up to 1100 K (Figure 1).

The PE spectra recorded during the S_4N_4 pyrolysis over silver wool (Figure 1) exhibit a marked temperature dependence: nitrogen evolution starts already at about 800 K, presumably due to the reaction of S_4N_4 with the silver surface to form Ag_2S as the decomposition catalyst.[3] At 900 K all S_4N_4 is converted (Figure 1, peak at 9.36 eV has vanished) predominantly into S_2N_2

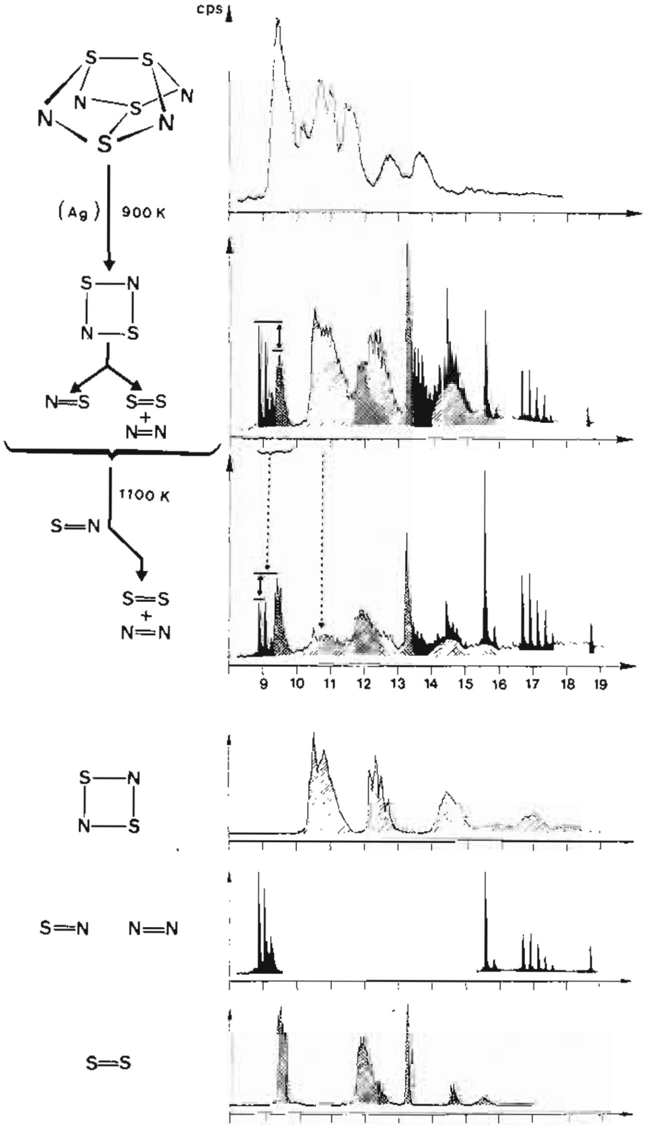

Figure 1. He I PE spectra of S_4N_4, its pyrolysis products formed over silver wool at 900 K and at 1100 K, and reference molecules S_2N_2 (hatched),[4b] SN (black),[4c] N_2 (black), and S_2 (cross-hatched).[7] Instrumentation: Leybold Heraeus UPG 200[5] PE spectrometer equipped with a short-pathway decomposition furnace with additional electron bombardment heating.[8] Calibration: $^2P_{3/2}$ (Ar) at 15.76 eV.

[†] University of Frankfurt.

[‡] University of Göttingen.

[§] Dedicated to Professor M. Schmidt on the occasion of his 60th birthday.

(1) Part 51: Bock, H.; Solouki, B.; Rosmus, P.; Dammel, R.; Hänel, P.; Hierholzer, B.; Lechner-Knoblauch, U.; Wolf, H.-P. "Abstracts of Papers", 7th International Symposium on Organosilicon Chemistry, Kyoto, Japan; Ellis Horwood Ltd.: Chichester, England, 1985; pp 45–74.

(2) Cf. e.g.: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; pp 515–518, and literature quoted therein.

(3) Mikulski, C. M.; Russo, P. J.; Saran, M. S.; McDiarmid, A. G.; Garito, A. F.; Heeger, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6358 and literature quoted therein.

(4) (a) Findlay, R. H.; Palmer, M. H.; Downs, A. J.; Egdell, R. G.; Evans, R. *Inorg. Chem.* **1980**, *19*, 1307 and references given especially to numerous other calculations on S_4N_4, S_2N_2, and SN. (b) Frost, D. C.; Le Geyt, M. R.; Paddock, N. L.; Westwood, N. P. *J. Chem. Soc., Chem. Commun.* **1977**, 217. (c) Dyke, J. M.; Morris, A.; Trickle, I. R. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 147.

(5) For a review on "Photoelectron Spectra and Molecular Properties: Real-Time Gas Analysis in Flow Systems", cf.: Bock, H.; Solouki, B. *Angew. Chem.* **1981**, *93*, 425; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 427.

(6) Refer to the following references for the compounds mentioned: (a) Methyl azide: Bock, H.; Dammel, R.; Horner, L. *Chem. Ber.* **1981**, *114*, 220. (b) Vinyl azide: Bock, H.; Dammel, R.; Aygen, S. *J. Am. Chem. Soc.* **1983**, *105*, 7681. See also ref 5. (c) Allyl azide: Herrmann, W. A.; Kriechbaum, G. W.; Dammel, R.; Bock, H. *J. Organomet. Chem.* **1983**, *254*, 219. (d) $H_5C_6Si(N_3)_3$: Bock, H.; Dammel, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 111; *Angew. Chem.* **1985**, *97*, 128.

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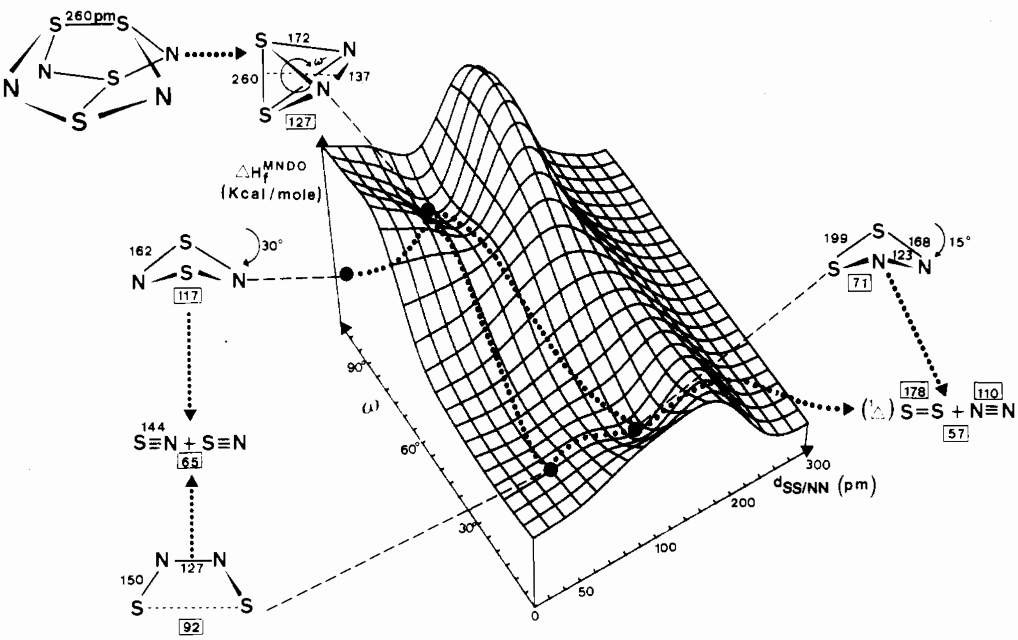

Figure 2. Exploratory singlet MNDO hypersurface for the deformation of an ensemble S_2N_2 projected onto the distance between SS and NN subunits in a tetrahedral arrangement as well as onto the dihedral angle ω defined with respect to this axis (see text). For the indiviudal species, which are partly located outside the truncated cut through the six-dimensional hyperspace shown here, the MNDO-optimized structural data are included as well as the approximate ΔH_f^{MNDO} values (positive, in kcal/mol) obtained for their minima.

(Figure 1, peak at 10.5 eV has developed to maximum intensity). Although not all of the bands in the 900 K PE spectrum can be assigned unequivocally to individual molecules in the complex product mixture (Figure 1, e.g. the needle at 14.5 eV), comparison with known ionization patterns clearly demonstrate that two consecutive reaction channels are already populated: one leading to the monomer SN and a second one unexpectedly producing SS (Figure 1, peak marked ↔ at 900 K). At 1100 K the PE band intensity ratio SN:SS starts to reverse: although absolute ionization cross sections are unknown, this observation clearly shows that at higher temperatures SS is the preferred decomposition product (Figure 1, peak marked ↔ at 1100 K).

In order to rationalize in a rather qualitative way the PE spectroscopic observation that S_2N_2 decomposes preferentially into two SN molecules at lower temperatures, whereas SS and NN are favored at higher temperatures, a crude MNDO hypersurface study[9] has been undertaken under the following specific assumptions: (i) when it is heated over silver wool, S_4N_4 first forms S_2N_2; (ii) the resulting fragments S_2N_2 with six degrees of freedom can be approximated by starting from a tetrahedral arrangement and by projecting its deformation onto only two coordinates,[9] i.e. the distance between SS and NN subunits as well as the dihedral angle ω between them defined with respect to this axis. Despite the crudeness of this approach,[9] which neglects e.g. multiplicities or population of vibrational levels,[10] the resulting exploratory singlet MNDO hypersurface reflects the PE spectroscopic findings.

For the assumed S_2N_2[10] tetrahedral arrangement a rather shallow local minimum is calculated in contrast to the more pronounced ones for the two four-membered ring isomers. Without embarkment on a discussion of the values ΔH_f^{MNDO} reflecting their stabilities within the crude approximation chosen, these two isomers possibly can transform into each other by a "wagging" vibration crossing the tetrahedral arrangement (Figure 2, left-hand side). The SN alternating isomer—by definition of the $d_{SS/NN}$ distance coordinate necessarily located outside the hypersurface cut presented here—presumably slightly distorted from planarity (C_{2v}) should dissociate preferentially into two SN molecules. Another SN-producing pathway could include the SNNS species with an elongated S···S bond, for which a shallow minimum is predicted on the $d_{SS/NN}$ vs. ω hypersurface (Figure 2) and which on a break of the NN bond also would yield two SN molecules as observed by PE spectroscopy (Figure 1) at lower temperatures. The other four-membered ring isomer of C_2 symmetry with SS and NN subunits (Figure 2, right-hand side) would be a likely precursor for $S_2 + N_2$ fragmentation. In reference to the experimental results of the S_4N_4 pyrolysis (Figure 1), it is imaginable that the latter reaction channel requires the crossing of a saddle point higher in energy although its products, SS + NN, are predicted to be thermodynamically more stable than two SN molecules. Altogether, despite the numerous neglects specified, the two-dimensional hypersurface cut for the S_2N_2 ensemble (Figure 2) indicates considerable fluxionality between the individual species involved and thus would invite a more rigorous theoretical treatment.[10]

Experimental Section

S_4N_4 was prepared from S_2Cl_2 and ammonia according to ref 11 and purified by recrystallization from $HCCl_3$. After 10 h of solvent evaporation at room temperature the compound was sublimed at 10^{-4} mbar and its purity checked by PE spectroscopy.[4a]

Photoelectron spectra were recorded on a Leybold Heraeus UPG 200 PE spectrometer[5] at $\sim 10^{-2}$ mbar vapor pressure and calibrated with use of the argon double peaks $^2P_{3/2,1/2}$ at 15.76 and 15.94 eV, respectively. A resolution of 20 meV and a count rate of 10^3 counts s^{-1} were maintained throughout the experiments.

Pyrolysis was carried out with use of an electron-impact high-temperature oven[8] with a short pathway distance of about 4 cm between the end of the heating zone and the target chamber of the PE spectrometer. S_4N_4 was mixed with silver wool, and after its PE spectrum was recorded at 400 K, the oven temperature was raised in 100 K steps up to the pyrolysis temperature of 1100 K.

MNDO calculations were performed at our VAX 11/750 with the MNDO program, kindly provided by M. J. S. Dewar and modified by Roth,[13] which uses a Davidson–Fletcher–Powell subroutine for optimi-

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(7) Cf.: Dyke, J. M.; Golob, L.; Jonathan, N.; Morris, A. *J. Chem. Soc., Faraday Trans. 2* **1974**, *71*, 1026. Berkowitz, J. *J. Chem. Phys.* **1975**, *62*, 4674.

(8) Cf.: Solouki, B.; Bock, H.; Appel, R.; Westerhaus, A.; Becker, G.; Uhl, G. *Chem. Ber.* **1982**, *115*, 3747.

(9) For a review on "Molecular State Fingerprints and Semiempirical Hypersurface Calculations—Useful Correlations to Track Short-Lived Molecules", cf.: Bock, H.; Dammel, R.; Roth, B. "Rings, Clusters and Polymers of the Main Group Elements"; Cowley, A. H., Ed.; American Chemical Society: Washington, DC, 1983; ACS Symp. Ser. No. 232, pp 139–165.

(10) For a VB rationalization of the S_2N_2 diradical and a summary of the preceding MO calculations, cf.: Skrezenek, F. L.; Harcourt, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3934.

(11) Cf.: Goehring, M. *Spec. Publ.—Chem. Soc.* **1957**, *10*, 45.

(12) Cf.: Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.

(13) Roth, B. Ph.D. Thesis, University of Frankfurt, 1983.

zation of each individual structure. The two-dimensional hypersurface cut for S_2N_2 with its six degrees of freedom was based on the simplifying assumption[9] that the S_2N_2 dissociation can be projected on the distance between SS and NN subunits as well as the dihedral angle ω. The distance $d_{SS/NN}$ has been varied between 0 and 300 pm in 25-pm steps and the dihedral angle ω between 0 and 90° in 7.5° steps.

Registry No. N_4S_4, 28950-34-7; S_2N_2, 25474-92-4; SS, 23550-45-0; NN, 7727-37-9; SN, 12033-56-6; Ag, 7440-22-4.

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Gas-Phase Reactions. 53.[1,2] Pyrolysis of F_2HCN_3

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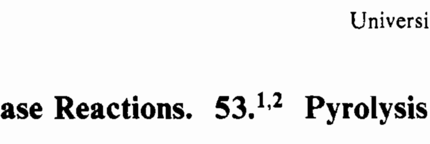
The potentially explosive title compound is thermally decomposed in a controlled way by using a flow system under reduced pressure and PE spectroscopic gas analysis. The partly surprising reaction pathway to N_2 + FCN + HF, which might be useful to prepare pure FCN, is discussed on the basis of semiempirical hypersurface calculations. Our report, containing information on both the decomposition conditions and the products formed, will hopefully stimulate further experimental and theoretical work: the presumed intermediate nitrene F_2HCN exhibits interesting dynamics and is small enough to be treated e.g. by correlated calculations.

The thermal decomposition of azides, attractive from synthetic as well as mechanistic points of view,[2,3] can be studied safely in a flow system by using photoelectron (PE) spectroscopic gas analysis both to continuously follow the temperature-dependent changes and to unequivocally identify the main products by their ionization patterns.[4] Thus the N_2 splitoff from saturated[5] aliphatic azides requires rather high temperatures, above 600 K, and the open-chain[5] and cyclic[6] alkylimines formed via a synchronous[6] 1,2-hydrogen shift are detected as intermediates:[2,4-7]



(1)

A consecutive reaction channel, increasingly populated at higher temperatures, produces the thermodynamically stable final products HCN or H_3CCN, respectively.[5,6] The intermediate alkylimines can be trapped at low temperatures.[6,7] Essential features of the reaction pathways (1) such as the 1,2-hydrogen shift or the ring closure are comprehensible from semiempirical hypersurface studies.[2,5,6,8]

Here we report the pyrolysis of the acceptor-substituted difluoromethyl azide[9] to cyanogen fluoride

$$F_2HC-Cl \xrightarrow[-NaCl]{+NaN_3} F_2HC-N_3 \xrightarrow[-N_2]{>720K} FC{\equiv}N + HF \qquad (2)$$

as well as attempts to rationalize the N_2 and HF extrusion by geometry-optimized MNDO calculations.

Experimental Part

F_2HCN_3[9] was prepared by bubbling 28 g (0.15 mol) of F_2HCCl (Frigen 22) within 2 h through a solution of 6.5 g (0.1 mol) of activated NaN_3,[10] 5.6 g (0.1 mol) of KOH in 25 mL of H_2O, and 30 mL of dioxane at 70 °C. All gases were collected in a dry ice/methanol-cooled trap, the temperature of which was raised to 0 °C after connection to a −30 °C reflux column. The remaining liquid (3.5 g) was purified by multiple trap-to-trap condensation, and 2 g (38%) of 96% pure F_2CHN_3 with bp 9–10.5 °C was obtained. Mass spectroscopic control ($m/e = 93$) showed that an analytically pure sample can be obtained by pumping off the excess F_2HCCl at −80 °C. Purity has been checked by ^1H NMR (δ = 5.83 (t), J_{HF} = 32.5 Hz), and F_2HCN_3 has been further characterized by its PE spectrum (Figure 1: $IE^v{}_1$ = 11.00 eV (π_{N_3}, a″, ν^+ = 720 cm^{-1}), $IE^v{}_2$ = 12.12 eV (σ_{N_3}, a′), and $IE^v{}_3$ = 14.84 eV (σ_{F_2CH}, a′); followed by fluorine lone pair ionizations at 15.93 and 16.01 eV).

Photoelectron spectra were recorded on a Leyboldt Heraeus spectrometer UPG 200[4] equipped with a molybdenum tube furnace.[11] The resolution was 20 meV; all spectra were calibrated by the N_2 ($^2\Sigma_g{}^+$) and Ar ($^2P_{3/2}$) peaks at 15.60 and 15.76 eV, respectively.

MNDO calculations were performed with the MOPAC program package[12] with full geometry optimization for all compounds. For the saddle-point determinations the systematic location procedure was used, and the obtained approximate transition-state geometries were refined by gradient norm minimization. By diagonalization of the Hessian matrix, a single negative eigenvalue (imaginary force constant) has been found for each transition state.

Results and Discussion

PE Spectroscopically Monitored Pyrolysis. Following the temperature-dependent changes of the F_2HCN_3 ionization fingerprints (Figure 1), one recognizes that above 720 K the characteristic peaks of FCN,[13] of N_2, and of HF[14] emerge. The pyrolysis (2) is complete at 940 K.

Relative to the parent azide, H_3CN_3,[5] difluoro substitution raises the decomposition temperature by about 100 K. Whereas the

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(1) Part 52: Bock, H.; Solouki, B.; Roesky, H. W. *Inorg. Chem.*, preceding paper in this issue.

(2) Taken from: Dammel, R. Ph.D. Thesis, University of Frankfurt, 1985.

(3) Cf. e.g.: Brown, R. F. C. "Pyrolytic Methods in Organic Chemistry", Academic Press: New York, 1980. Wentrup, C. "Reaktive Zwischenstufen"; Thieme Verlag: Stuttgart, West Germany, 1979, and literature cited therein.

(4) For a summary cf.: Bock, H.; Solouki, B. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 427–444; *Angew. Chem.* **1981**, *93*, 425–442.

(5) Bock, H.; Dammel, R.; Horner, L. *Chem. Ber.* **1981**, *114*, 200 and literature cited therein.

(6) Bock, H.; Dammel, R.; Aygen, S. *J. Am. Chem. Soc.* **1983**, *105*, 7681 and literature cited therein.

(7) Cf. also: Guillemin, J.-C.; Denis, J.-M.; Lasne, M.-C.; Ripoll, J.-L. *J. Chem. Soc., Chem. Commun.* **1983**, 238.

(8) Bock, H.; Dammel, R.; Roth, B. *ACS Symp. Ser.* **1983**, *No. 232*, 139–165.

(9) Difluoromethyl azide was first prepared by : Ginsburg, V. L.; Gitel, P. O.; Didina, I.M. U.S.S.R. Pat. 375 287 (cf.: *Otkrytiva, Izobret., Prom. Obraztsy, Tovarnye Znaki* **1973**, *50* (16), 50; *Chem. Abstr.* **1973**, *79*, 41895*f*.

(10) Cf., e.g.: Jacox, M. E.; Milligan, D. E.; Moll, N. G.; Thompson, W. E. *J. Chem. Phys.* **1965**, *43*, 3734.

(11) Solouki, B.; Bock, H.; Appel, R.; Westerhaus, A.; Becker, G.; Uhl, G. *Chem. Ber.* **1982**, *115*, 3748.

(12) The MOPAC program package has kindly been provided by M. J. S. Dewar.

(13) Bieri, G. *Chem. Phys. Lett.* **1977**, *46*, 107. Cf. also: Stafast, H.; Bock, H. In "The Chemistry of the Cyanogen Group"; Patai, S., Ed.; Wiley: Chichester, England, 1983; pp 146, 152, and literature cited therein.

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