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.

Contribution from the Institute of Inorganic Chemistry,
University of Frankfurt, Niederurseler Hang, D-6000 Frankfurt (Main) 50, West Germany

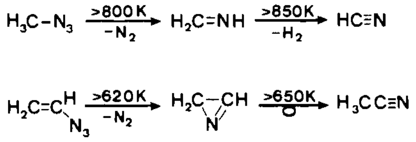
Gas-Phase Reactions. 53.[1,2] Pyrolysis of F_2HCN_3

HANS BOCK* and RALPH DAMMEL

Received December 12, 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 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

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

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 ($\delta = 5.83$ (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″, $\nu^+ = 720$ 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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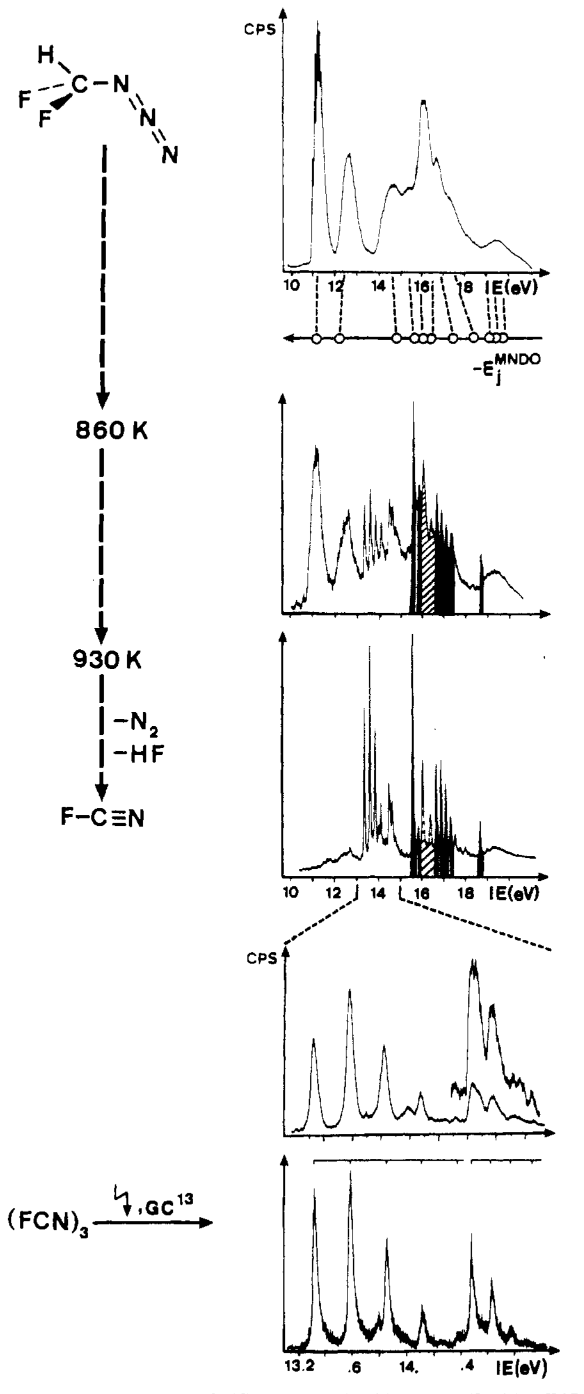

Figure 1. He I PE spectra of difluoromethyl azide at 300 K with MNDO Koopmans correlation, $IE^v_n = -\varepsilon_j^{MNDO}$, at 860 and 930 K ($N_2$ peaks solid black, HF peaks shaded). The enlarged section shows the PE spectrum of FCN between 13 and 15 eV recorded at an expanded scale and compared to the one obtained by monomerization of $(FCN)_3$ in an electrical discharge and subsequent gas chromatographic purification.[13]

formation of FCN is proven beyond doubt by PE spectra comparison[13] (Figure 1), no ionization bands for the expected intermediate difluoromethanimine, predicted by MNDO at about 12.3 eV (π_{CN}, a″), 13.0 eV (n_N, a′), and above 16 eV (n_F), can be detected at any pyrolysis temperature.

In order to rationalize the unexpected course of the F_2HCN_3 thermolysis, exploratory MNDO calculations with geometry optimization have been performed to obtain approximate heats of formation ΔH_f^{MNDO} (kJ/mol) for the species considered and the saddle points between them as located by gradient norm minimization (Figure 2).

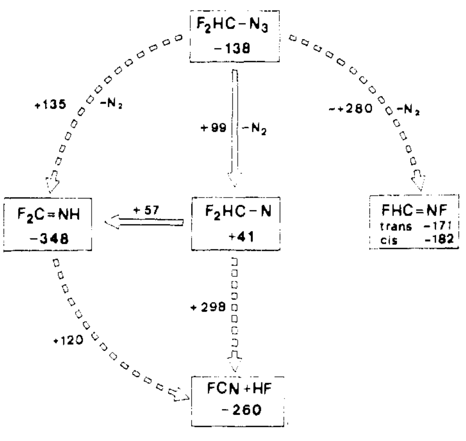

Figure 2. MNDO heats of formation ΔH_f^{MNDO} (kJ/mol) for F_2HCN_3, F_2HCN, FHC=NF, F_2C=NH, and FCN + HF (shown in boxes) as well as for the connecting saddle points of lower (open arrows) and higher (dashed open arrows) energy as determined by gradient norm minimization (see text).

Judging from the ΔH_f^{MNDO} values (Figure 2), an intermediate formation of the difluoro-stabilized methylnitrene should be more favorable than N_2 extrusion accompanied by synchronous H or F migrations. For the consecutive 1,2-hydrogen shift a low barrier of only ~15 kJ/mol is predicted. On the other hand, any resulting F_2C=NH should be rather stable with respect to HF elimination unless this splitoff is heterogeneously catalyzed[15] e.g. by the surface of the molybdenum reaction tube on heat transfer from its wall. Otherwise, the nonobservability of F_2C=NH must be due to some process not covered by the limited semiempirical approach (Figure 2), e.g. to nonconcerted processes such as a radical chain decomposition of the intermediate nitrene F_2HCN or the neglect of nonequilibrium effects and molecular dynamics along the individual reactive trajectories.

Similar fragmentations have been observed in the gas-phase pyrolysis of other azides, e.g.[2]

$$\begin{aligned} &NC\text{-}CH_2\text{-}N_3 \xrightarrow{670K} 2\ HCN + N_2 \\ &Cl\text{-}CH_2\text{-}CH_2\text{-}N_3 \xrightarrow{620K} H_3C\text{-}CN + HCl + N_2 \end{aligned} \qquad (3)$$

Obviously, whenever a good leaving molecule such as a cyanogen derivative can be split off from the expected primary extrusion product, partial or complete fragmentation results, since the accompanying highly exothermic reaction enthalpy (to which the considerable activation enthalpy for the gas-phase azide decomposition must be added, cf. Figure 2) cannot be effectively dissipated under the nearly unimolecular pyrolysis conditions. Another example is provided by the thermolysis of methyl azide at temperatures above 850 K (cf. eq 1), which yields HCN and hydrogen as byproducts: on heating of pure methanimine, H_2C=NH, under otherwise identical conditions, HCN is observed only at temperatures above 1100 K.[2]

With the boiling points of FCN and HF differing by more than 60 °C, the selective thermal decomposition of difluoromethyl azide (eq 2) offers advantages for the preparation of pure FCN.[16]

Acknowledgment. Research on thermal decomposition of azides is supported by Land Hessen, Deutsche Forschungsgemeinschaft, and Fonds der Chemischen Industrie.

Registry No. F_2HCN_3, 41796-84-3; F_2HCCl, 75-45-6; NaN_3, 26628-22-8; FCN, 1495-50-7; F_2C=NH, 2712-98-3; HF, 7664-39-3; N_2, 7727-37-9.

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(14) Cf. e.g.: Bieri, G.; Åsbrink, L.; von Niessen, W. *J. Electron Spectrosc. Relat. Phenom.* **1981**, *23*, 281. Wittel, K.; Bock, H. In "The Chemistry of the Carbon-Halogen Bond"; Patai, S., Ed.; Wiley: Chichester, England, 1983; pp 1517, 1523, and literature cited therein.

(15) Makarov, S. P.; Yakubovich, A. Y.; Ginsburg, V. A.; Filatov, A. S.; Englin, M. A.; Privezentseva, N. F.; Nikoforova, T. Y. *Dokl. Akad. Nauk. SSSR* **1961**, *141*, 357. In this paper, the authors report to have generated F_2C=NH by reaction of 1-phenyl-3-(trifluoromethyl)-1-triazine with phenol and pyrolyzed it under vacuum over NaF at 690–720 K to FCN and HF. Attempts to generate F_2C=NH by repeating the reaction under PE spectroscopic gas analysis yielded, however, no evidence for its formation.

(16) Mixtures of FCN and HF should be handled with care; cf. e.g.: "Comprehensive Inorganic Chemistry"; Pergamon Press: Oxford, England, 1973; Vol. 1, p 1246.

Inorg. Chem. **1985**, *24*, 4429–4430

Supplementary Material Available: Listings of MNDO geometry optimized structures of all molecules and transition states shown in Figure 2 (8 pages). Ordering information is given on any current masthead page.

Notes

Contribution from the Department of Chemistry,
Auburn University, Auburn, Alabama 36849,
and Department of Natural Science,
Eastern Montana College, Billings, Montana 59101

Interaction of Complexes $Mn(PPhMe_2)Br_2$ and $Mn(PEt_3)Br_2$ with Sulfur Dioxide

W. E. Hill,*[†] S. D. Worley,*[†] D. K. Paul,[†] and V. F. Newberry[‡]

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There has been considerable recent interest in complexes of the form $MnLX_2$ (L = tertiary phosphine, X = anion) and their interaction with dioxygen.[1,2] Infrared work in these laboratories concerning films of the complexes has shown that the complexes do exist and that some do interact reversibly with dioxygen, the extent of which is markedly dependent upon the nature of the tertiary phosphine ligand.[3,4] All of the complexes studied here, however, exhibit competing irreversible decay channels at room temperature to the corresponding phosphine oxide complexes.[3,4] The purpose of this note is to report infrared data concerning the interaction of the complex films with sulfur dioxide.

The complex films studied here were prepared by sublimation of $MnBr_2$ onto a KBr infrared window followed by heating to ca. 473 K in a specially designed infrared cell[3,4] at 10^{-6} torr to remove all water. Then the dry $MnBr_2$ films were exposed to either $PPhMe_2$ or PEt_3 in situ to form the $MnLX_2$ complex films. Extensive evacuation at 10^{-6} torr was employed to remove all traces of excess phosphine. The films thus prepared were exposed to SO_2/evacuation cycles with infrared spectra (Perkin-Elmer Model 580 or 983 instrument with data station) being monitored at appropriate intervals. Since $SO_2(g)$ exhibits infrared bands near 520, 1150, and 1360 cm^{-1}, which might have interfered with resolution of the complex bands, the cell was always briefly evacuated following SO_2 exposure immediately before infrared analysis.

Figure 1 shows the infrared spectra corresponding to the $Mn(PPhMe_2)Br_2$ complex film interacting with SO_2. A comparison of Figure 1, parts b and a, reveals that new infrared bands at (SO_2 ($S^{18}O_2$)) 412 (410), 445 (440), 525 (515), 785 (780), 995 (950), 1002 (968), and 1075 (1028) cm^{-1} appear that can be attributed to a new complex(es) formed from the reaction of SO_2 with $Mn(PPhMe_2)Br_2$. The intense band at 1115 cm^{-1} in Figure 1b, which does not shift appreciably upon $S^{18}O_2$ exposure, can be assigned to a ligand vibrational mode ($\nu_{PC\text{-}aryl}$), which is accentuated due to the presence of SO_2; this band was also observed to be enhanced by the presence of dioxygen.[4] All of the bands mentioned above declined markedly upon evacuation at 10^{-6} torr for 12 h (Figure 1c). We have been able to observe cycling of the intensities of these bands upon reexposure/evacuation for up to three cycles; ca. 12-h evacuation is required to essentially remove the SO_2. However, upon lengthy exposure (72 h) at high pressure (120 torr) the spectrum shown in Figure 1d resulted, which could not be reversed by lengthy evacuation. The bands at 995, 1002, and 1075 cm^{-1} for the complex shift substantially when $S^{18}O_2$ is used and obviously correspond to S–O stretching vibrational modes; the fact that three such bands were present indicates that more than one type of complex is probably being formed. On the other hand, the bands at 412 and 445 cm^{-1} shifted little upon isotopic substitution; these bands could correspond to Mn–S modes. The bands at 525 cm^{-1} in Figure 1b and 625 cm^{-1} in Figure 1d did shift appreciably when $S^{18}O_2$ was employed and probably correspond to Mn–O modes.

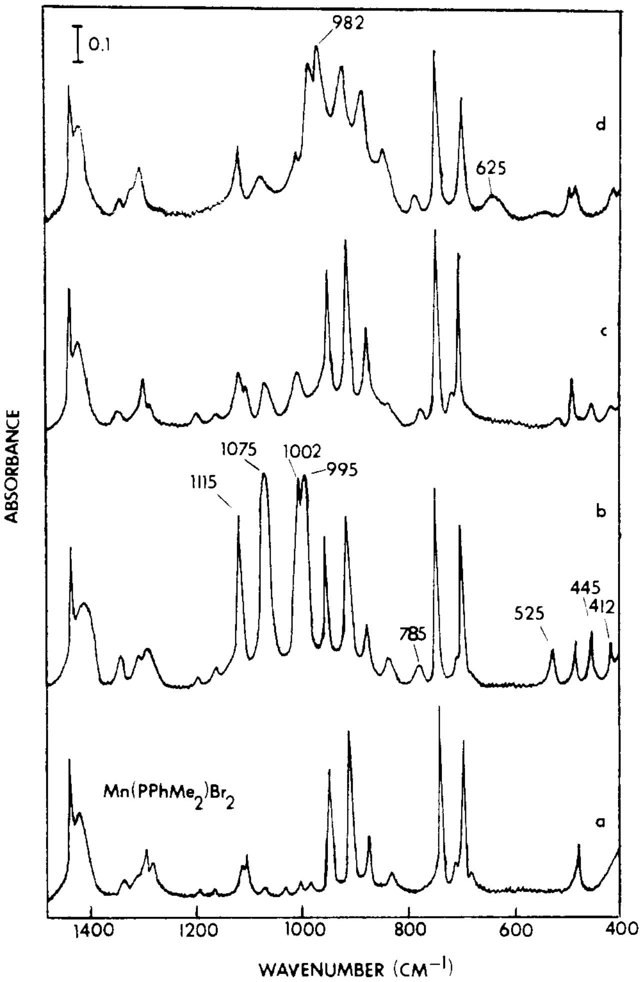

Figure 1. Infrared spectra of a $Mn(PPhMe_2)Br_2$ film: (a) following initial preparation; (b) following exposure to 50 torr of SO_2 for 24 h at 298 K and then brief evacuation; (c) following an evacuation cycle for 12 h at 10^{-6} torr at 298 K; (d) following exposure to 120 torr of SO_2 for 72 h at 298 K and lengthy evacuation.

Figure 2 shows a similar series of experiments for $Mn(PEt_3)Br_2$ interaction with SO_2. Band positions for $S^{18}O_2$ complex spectra

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[†] Auburn University.
[‡] Eastern Montana College.

[1] McAuliffe, C. A. *J. Organomet. Chem.* **1982**, *228*, 255 and numerous references quoted therein.
[2] Brown R. M.; Bull, R. E.; Green, M. L. H.; Grebenik, P. D.; Martin-Polo, J. J.; Mingos, D. M. P. *J. Organomet. Chem.* **1980**, *201*, 437.
[3] Burkett, H. D.; Newberry, V. F.; Hill, W. E.; Worley, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 4097.
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