Thermal Isomerisation of Sulphur Dicyanide $S(CN)_2$ to Cyanogen Isothiocyanate, NCNCS

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Summary During flow pyrolysis experiments involving sulphur dicyanide vapour, $S(CN)_2$, a new microwave spectrum was detected, analysis of which indicates that $S(CN)_2$ isomerises to cyanogen isothiocyanate, NCNCS, at 850 °C.

RECENT microwave and photoelectron experiments have shown that the sulphido boron species, XB=S (with X=F, Cl, and Br) can be produced by passing sulphur halides such as X_2S_2 over crystalline boron at 1000 °C.[1,2] In subsequent experiments using sulphur dicyanide $S(CN)_2$ a new strong microwave spectrum was observed. The rotational constants of the new species and the spectral pattern have been assigned to cyanogen isothiocyanate, NCNCS, an isomer of the parent species. This species appears to have been made previously by Neidlein and Reuter[3] by the reaction of $COCl_2$ with K_2S_2CNCN in dichloromethane, and confirmed by condensing the product with phenylhydrazine to form 3-mercapto-5-amino-1-phenyl-1*H*-1,2,4-triazole.

The spectrum is obtained by flowing the $S(CN)_2$ vapour at *ca.* 30 μm pressure *via* a quartz tube (0·8 mm internal diameter) filled with broken quartz chips and heated to 850 °C for *ca.* 15 cm of its length, through the cell of the microwave spectrometer. The rotational constants $B_0 = 1628{\cdot}09 \pm 0{\cdot}03$ and $C_0 = 1599{\cdot}37 \pm 0{\cdot}03$ MHz have been obtained from the low K_A lines of the $J = 8,9,10$, and 11 R-branch transitions. The higher K_A lines show complex patterns which do not readily fit the standard transition frequency relations. This may well be because the molecule is quasi-linear, as are many other isocyanates and isothiocyanates, and analysis will require the flexibility to be treated in detail. The vibrational satellite structure is also anomalous as expected. Similar problems have been encountered in MeNCO, MeNCS,[4] HNCO,[5] SiH_3NCO,[6] HC≡CNCO,[7] and $SiMe_3NCO$.[8]

A *preliminary* fit to the rotational constants of N≡C–N=C=S was made by assuming the structural parameters $r(N{\equiv}C) = 1{\cdot}164$,[9] $r(C{-}N) = 1{\cdot}283$,[10] $r(N{=}C) = 1{\cdot}207$,[11] and $r(C{=}S) = 1{\cdot}566$ Å.[11] The angles $\angle(NCN)$ and $\angle(NCS)$ were assumed to be 180° and the angle $\angle(CNC)$ was varied to give a fitting. The optimum angle was 149·4° which yielded (in MHz) $A = 94188{\cdot}46$, $B = 1627{\cdot}28$, and $C = 1599{\cdot}65$ which can be compared with the above observed rotational constants. Centrifugal distortion has been included but as the higher K lines are not well fitted meaningful values await a detailed understanding of this unusual spectrum now under way. This angle may be compared with that obtained by Hocking and Gerry[10] in NCNCO of $\angle(CNC) = 140°$.

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