$(CDCl_3)$ δ 1.22 (t, $J = 7.5$ Hz, 2 H, CH_2Mn), 2.68 (t, $J = 7.5$ Hz, 2 H, $CH_2C{=}O$), 3.68 (s, 3 H, OCH_3); ir (hexane) ν_{CO} 2110 (w), 2046 (w), 2014 (s), 1996 (s) cm^{-1}; C=O of ester at 1744 cm^{-1}; exact mass for P − 2CO peak 225.9677 (calcd for $C_7H_7O_5Mn$ 225.9674).

Compound **6** was obtained as a colorless oil: NMR $(CDCl_3)$ δ 1.58 (d, $J = 7.5$ Hz, 3 H, CH_3), 2.31 (quartet, $J = 7.5$ Hz, 1 H, CH–Mn), 3.65 (s, 3 H, OCH_3); ir (hexane) ν_{CO} 2115 (w), 2054 (w), 2027 (s), 1999 (s) cm^{-1}; C=O of ester at 1711 cm^{-1}; exact mass of P − 1CO peak 253.9613 (calcd for $C_8H_7O_6Mn$ 253.9623).

Registry No. **4**, 21910-29-2; **5**, 59301-76-7; **6**, 59301-77-8.

References and Notes

(1) C. P. Casey and C. A. Bunnell, *Inorg. Chem.*, **14**, 796 (1975).
(2) R. McKinney, G. Firestein, and H. D. Kaesz, *J. Am. Chem. Soc.*, **95**, 7910 (1973).
(3) C. P. Casey, R. A. Boggs, D. F. Marten, and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, 243 (1973).
(4) B. L. Booth and R. G. Hargreaves, *J. Chem. Soc. A*, 2766 (1969).
(5) A. Schoenberg and R. F. Heck, *J. Am. Chem. Soc.*, **96**, 7761 (1974).
(6) H. W. Sternberg and I. Wender, "International Conference on Coordination Chemistry, 1959", Chemical Society, London, 1959, p 35.
(7) C. S. Kraihanzel and L. G. Herman, *J. Organomet. Chem.*, **15**, 397 (1968).
(8) B. L. Booth, M. Gardner, and R. N. Haszeldine, *J. Chem. Soc., Dalton Trans.*, 1863 (1975).
(9) M. P. Cooke, Jr., and R. M. Parlman, *J. Am. Chem. Soc.*, **97**, 6863 (1975).

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Matrix Isolation Study of the Products of Volatilization of Polymeric Sulfur Nitride

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Received January 16, 1976 AIC60045I

Polymeric sulfur nitride has recently become a subject of great interest because of the demonstration of its metallic and superconducting properties.[1-6] Among the chemical and structural features of this material,[7,8] an unusual property for a polymeric substance is that it can be sublimed and in fact high-quality films of $(SN)_x$ have been prepared by sublimation of the polymer.[4] In an effort to shed some light on the depolymerization and repolymerization processes which occur in the sublimation, we have explored the matrix isolation technique as a means of characterizing, perhaps identifying, the molecular species in the vapor phase. This is a first report of that study.

Samples of the $(SN)_x$ polymer, prepared by Professor A. G. MacDiarmid and his co-workers,[8] were introduced into a Pyrex Knudsen cell which had been incorporated into an Air Products Displex refrigeration system. The polymer was heated to about 160 °C and the effluent from the cell orifice directed at a cold (10 K) window or surface about 1 in. away. At the same time a stream of argon gas was also directed at the cold surface, and during the matrix deposition process, the pressure in the refrigerator system was kept by pumping at about 10^{-4} Torr. The concentrations of our matrices are expressed by the M/A ratio where M is the number of moles of argon admitted to the cell and A is the amount of sulfur nitride arbitrarily expressed as the equivalent moles of $(SN)_4$. For purposes of reference, the infrared and uv–visible absorption spectra were determined for argon matrix isolated samples of pure S_2N_2 and of pure S_4N_4, two well-characterized sulfur nitride molecules.[9] The matrices containing either S_2N_2 or S_4N_4 molecules were all colorless.

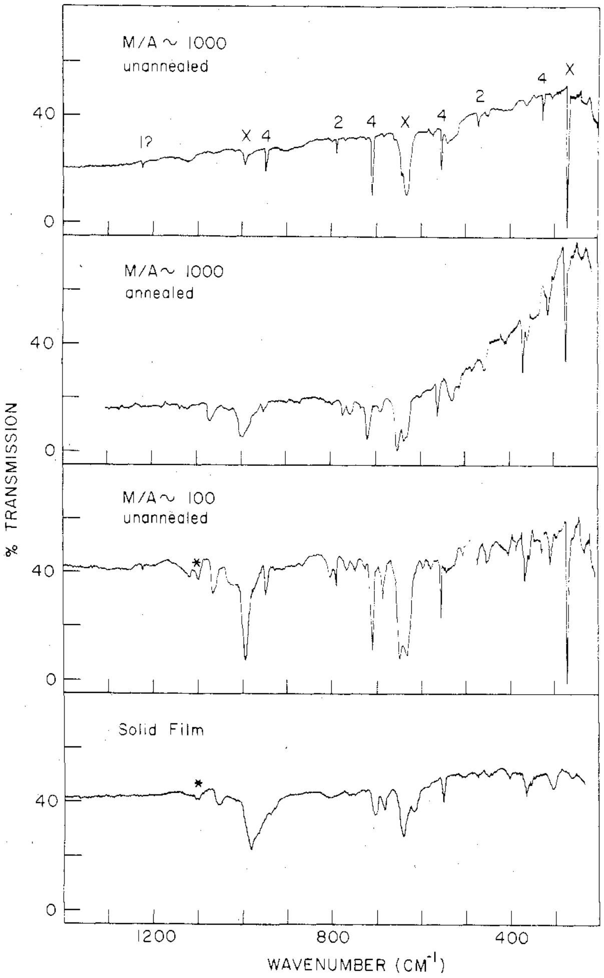

Figure 1. Infrared absorption spectra recorded at 10 K of condensed vapor species obtained by heating $(SN)_x$ to about 160 °C. The top three panels are argon matrices with the M/A ratios as indicated, each matrix deposited at the rate of about 0.01 mol of argon/h: top panel, freshly deposited matrix with $A = 10^{-5}$ molar equiv of $(SN)_4$; second panel, same matrix as above after being heated to 40 K for $^1/_2$ h; third panel, freshly deposited matrix with $A = 2 \times 10^{-5}$ molar equiv of $(SN)_4$; bottom panel, 20 μ thick solid film of condensed vapor species. Asterisk indicates impurity on window. The 1, 2, 4, and X signify SN, S_2N_2, S_4N_4, and unknowns.

Figure 1 shows the infrared spectrum of the vapor species obtained by heating $(SN)_x$ and then trapped in an argon matrix at an M/A ratio of about 1000. At this concentration the matrix is light orange. The infrared spectrum has a number of sharp absorption features and several broad ones. It is clear from the frequency coincidences and the relative intensities that most of the bands belong to S_2N_2 and S_4N_4. The very weak band at 1225 cm^{-1} suggests the presence also of a little SN (the vibrational frequency of the gaseous SN molecule[10] is given as 1204.1 cm^{-1}). Besides several weak features in the spectrum, the broader absorption maximum at 996 cm^{-1}, the one at 634 cm^{-1} with its two sharp shoulder peaks at 646.4 and 644.7 cm^{-1}, and the relatively sharp band at 273.2 cm^{-1} and its shoulders at 274.3 and 272.0 cm^{-1} are assigned to some unidentified species X, which is probably also responsible for the color of the matrix. Essentially the same spectrum is obtained even if M/A is increased to 10 000. When the matrix just described was annealed it acquired a rusty orange color and exhibited the infrared spectrum shown in Figure 1. The spectrum is now richer and the bands attributed to the X species are more intense relative to the S_2N_2 and S_4N_4 absorptions. From the intensity changes it is clear

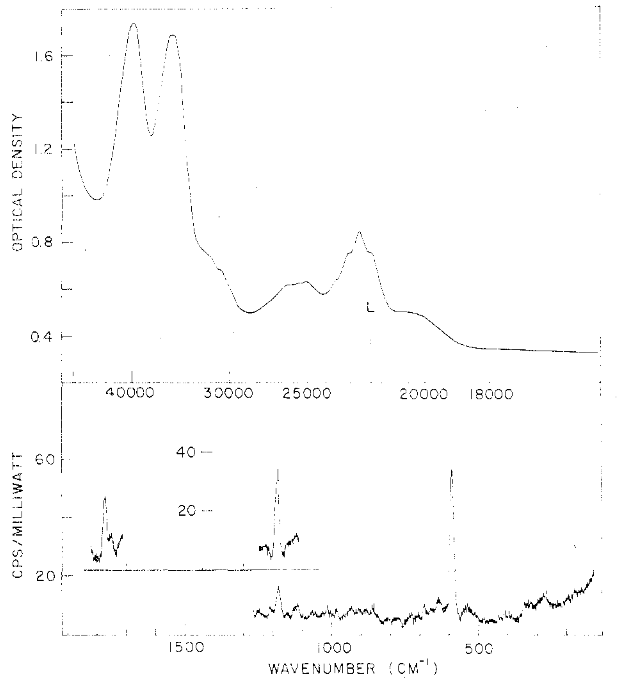

Figure 2. Top panel: absorption spectrum of argon matrix at 10 K deposited at rate of 0.01 mol/h of argon and containing an equivalent of about 10^{-6} mol of $(SN)_x$ of vapor species formed by heating $(SN)_x$ to 140 °C; $M/A \approx 3000$. Bottom panel: Raman spectrum at 10 K of argon matrix deposited at rate of 0.01 mol/h of argon and with $M/A \approx 1000$ and $A \approx 10^{-5}$ molar equiv of $(SN)_x$. Spectrum excited by 10-mW power in 22 000-cm^{-1} laser line (L in top panel) and recorded at scan rate of 100 cm^{-1}/min, 10 cm^{-1} spectral slit width, and 1-s rise time.

moreover that there is more than one unknown "X", i.e., more than one molecular entity or more than one kind of matrix trapping site. A possibility is that diffusion of molecules in the matrix at 40 K produces more X species at the expense of S_2N_2 and S_4N_4 molecules. Similar annealing of matrices containing only S_2N_2 and/or S_4N_4 molecules does not produce any of the "X" absorptions but only new absorptions which we attribute to weakly bound "aggregates" of these molecules, i.e., $(S_2N_2)_2$, $(S_2N_2)_3$, etc.

Qualitatively the same spectral changes resulting from annealing a dilute matrix can be achieved by depositing a more concentrated matrix. This is illustrated in Figure 1 by the spectrum of the dark orange matrix with an M/A of about 100. Finally, Figure 1 also contains the spectrum of a bright red solid film of the condensed vapors from $(SN)_x$. The dominant infrared absorptions of the film are in the frequency ranges of the X bands of the matrices.

In the uv–visible spectrum of a dilute matrix (Figure 2) the absorption maximizing at about 40 000 cm^{-1} is due to S_2N_2 and S_4N_4. The strong band at 35 000 cm^{-1} and the broad absorption from 28 000 to 19 000 cm^{-1} belong to the "X" substances. When the matrix is irradiated with a low-power level of the 22 000-cm^{-1} laser line (near the absorption maximum at about 22 500 cm^{-1}), a resonance Raman effect is observed with the appearance of a vibrational fundamental at 593 cm^{-1} and the first and second overtones at 1185 and 1773 cm^{-1} (Figure 2). However exposure of the matrix to higher power or prolonged irradiation by this blue line causes the resonance Raman effect to vanish and the matrix to turn grayish. (The red laser line at 15 454 cm^{-1} on the other hand does not degrade the matrix even at a power of 200 mW and yields a Raman line at 593 cm^{-1}, one due to S_2N_2 at 503 cm^{-1}, and a very broad feature centered at 950 cm^{-1}.) The 593- and 503-cm^{-1} lines have half-widths of less than 10 cm^{-1}, whereas the 950-cm^{-1} band is about 60 cm^{-1} wide.

Silver wool exposed to S_4N_4 vapor and presumably thus acquiring a coating of Ag_2S provides an effective surface for converting S_4N_4 to S_2N_2.[8] An experiment of passing the vapors from $(SN)_x$ through such silver wool plugs markedly increased the S_2N_2 absorptions, decreased the S_4N_4 bands, and completely eliminated the absorption by the unknown species X.

Our preliminary results show that under our conditions the volatilization of $(SN)_x$ at 140–160 °C produces some S_2N_2 molecules and possibly a trace of SN but mostly the well-known cyclic S_4N_4 molecule and more than one unidentified species. The unknowns are completely converted to S_2N_2 by the silver wool treatment. One or more of them are highly colored and give rise to broad bands in both the infrared and Raman spectra of the argon matrices. We might speculate that nonrigid, noncyclic biradical isomers of S_2N_2, S_4N_4, and possibly S_6N_6 could have these properties. When the blood red film of condensed vapor is warmed from 10 K, the infrared spectrum shows some slight continuous changes in band intensities, but quite suddenly at about 200 K the film becomes blue to transmission and its infrared spectrum is then characteristic of polymeric films. This all suggests that one or more of the unknown materials play a key role in the polymerization process. Further efforts in identifying the unknowns will be pursued.

Acknowledgment. This work was supported by the National Science Foundation under Grant DMR-7203025.

Registry No. S_2N_2, 25474-92-4; S_4N_4, 28950-34-7; SN, 12033-56-6; $(SN)_x$, 55892-53-0.

References and Notes

(1) V. V. Walatka, M. M. Labes, and J. H. Perlstein, *Phys. Rev. Lett.*, **31**, 1139 (1973).
(2) C. Hsu and M. M. Labes, *J. Chem. Phys.*, **61**, 4640 (1974).
(3) R. L. Greene, P. M. Grant, and G. B. Street, *Phys. Rev. Lett.*, **34**, 89 (1975).
(4) A. A. Bright, M. J. Cohen, A. F. Garito, A. J. Heeger, C. M. Mikulski, P. J. Russo, and A. G. MacDiarmid, *Phys. Rev. Lett.*, **34**, 206 (1975).
(5) A. A. Bright, M. J. Cohen, A. F. Garito, A. J. Heeger, C. M. Mikulski, and A. G. MacDiarmid, *Appl. Phys. Lett.*, **26**, 612 (1975).
(6) R. L. Greene, G. B. Street, and L. J. Suter, *Phys. Rev. Lett.*, **34**, 577 (1975).
(7) A. G. MacDiarmid, C. M. Mikulski, P. J. Russo, M. S. Saran, A. F. Garito, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 476 (1975).
(8) C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito, and A. J. Heeger, *J. Am. Chem. Soc.*, **97**, 6358 (1975).
(9) For infrared spectra in solution or gas phase see J. R. Warn and D. Chapman, *Spectrochim. Acta*, **22**, 1371 (1966); J. Bragin and M. V. Evans, *J. Chem. Phys.*, **51**, 268 (1969).
(10) R. F. Barrow, G. Drummond, and P. B. Zeeman, *Proc. Phys. Soc. London, Sect. A*, **67**, 365 (1954).

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Direct Synthesis of Mono- and Disubstituted Phosphorus Ligand Derivatives of Dodecacarbonyltetrairidium

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Received January 15, 1976 AIC60043Y

Substitution of carbonyl ligands in $Ir_4(CO)_{12}$ by phosphine and phosphite ligands requires elevated temperatures (ca. 110 °C).[1-6] The only complexes observed are the final substitution products $Ir_4(CO)_8L_4$ or $Ir_4(CO)_9L_3$, depending on the bulk of the entering ligand. Drakesmith and Whyman[3] observed