BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1433—1434 (1971)

The X-Ray Powder Diffraction Pattern of Tetrasulfur Tetranitride

Shuichi HAMADA, Akira TAKANASHI, and Toshiaki SHIRAI

Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo

(Received December 11, 1970)

Tetrasulfur tetranitride, S_4N_4, is an eight-membered ring molecule, one which involves four coplanar nitrogen atoms. The molecular symmetry and the crystal system of tetrasulfur tetranitride have been reported to be $\bar{4}2\,m(D_{2d})$[1] and monoclinic[2-4] respectively. On the basis of an X-ray analysis on the single crystal, Clark[5] verified the unit cell dimensions and the space group reported by Buerger[4] to be as follows: $a_0=8.75$, $b_0=7.16$, $c_0=8.65$ Å, $\beta=92.5°$, and space group, $P2_1/n(C_{2h}^5)$. However, studies of X-ray powder diffractometry on tetrasulfur tetranitride have been reported only by Garcia-Fernandez,[6,7] and the Miller indices were not assigned in his reports.

In this work, a reexamination and an assignment of the Miller indices on the X-ray powder diffraction peaks will be attempted.

Experimental

Materials. The tetrasulfur tetranitride was prepared by the method reported by Villena-Blanco and Jolly.[8] A crude product was extracted with dry dioxane. When the dioxane solution was cooled to room temperature, tetrasulfur tetranitride crystallized out as orange-yellow crystals. These crystals were filtered off and dried in a paper-box contained silica-gel, and so a sample for tetrasulfur tetranitride was obtained without further purification.

Procedure. An infrared spectrophotometer, Model DS-403G, from the Japan Spectroscopic Company was used to obtain the infrared spectra of a carbon disulfide solution of the sample at wave numbers ranging from 2400 to 3600 cm^{-1}, and from 600 to 1000 cm^{-1}.

An Olympus reflecting microscope, Model STS, was used to determine the melting point of the sample in a heating block at the heating rate of 0.5°C/min. The temperatures of the heating block were calibrated by using materials with known melting points.

The thermal gravimetric analysis and the differential thermal analysis of the sample were carried out at a heating rate of 5°C/min in a nitrogen atmosphere using a Thermoflex, Model 8002, from the Rigaku Denki Company.

An X-ray diffractometer, Model JDX-5P, from the Japan Electron Optics Laboratory was used to obtain X-ray powder diffraction intensity diagrams; a goniometer and Cu$K\alpha$ radiation were also used. The diffraction angles were calibrated by using silicon.

Results and Discussion

The IR Spectra of the Sample. Only the characteristic absorption bands[9,10] of tetrasulfur tetranitride at 938 and 700 cm^{-1} were observed in the spectra of the carbon disulfide solution of the sample.

The Melting Point of the Sample. The melting point of the sample was estimated to be 182.0°C. The melting points for tetrasulfur tetranitride have been reported to range from 176°C to 187.5°C.[11-19] The value of the melting point for tetrasulfur tetranitride, which was prepared by the Jolly method,[8] was found to be 178—179°C.[20] However, by repeated recrystallization from benzene, or by purification on an alumina chromatographic column, tetrasulfur tetranitride with a melting point as high as 187—187.5°C has been obtained.[19] Therefore, the sample obtained in this work was considered to be pure enough for us to obtain a good diffraction pattern for tetrasulfur tetranitride from the results of the IR spectra and the melting point of the sample.

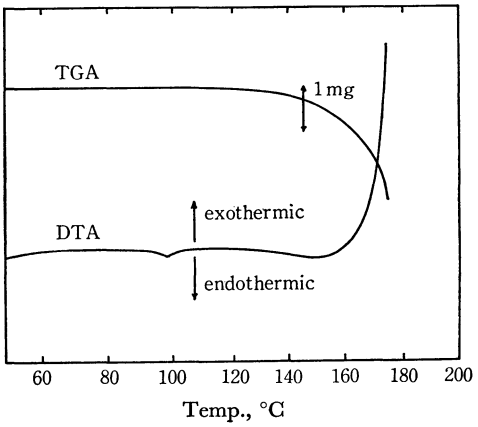

Fig. 1. TGA and DTA curves of sample.

1) C. S. Lu and J. D. Donohue, *J. Amer. Chem. Soc.*, **66**, 818 (1944).
2) E. Artini, *Z. Krist.*, **42**, 68 (1907).
3) G. F. H. Smith, *Miner. Mag.*, **16**, 97 (1911).
4) J. M. Buerger, *Amer. Min.*, **21**, 575 (1936).
5) D. Clark, *J. Chem. Soc.*, **1952**, 1615.
6) H. Garcia-Fernadez, *Compt. Rend.*, **250**, 3181 (1960).
7) H. Garcia-Fernandez, *Bull. Soc. Chim. Fr.*, **1961**, 1021.
8) M. Villena-Blanco and W. L. Jolly, "Inorganic Syntheses," Vol. IX, ed. by S. Y. Tyree, Jr., *et al.*, McGraw-Hill, New York (1967), p. 98.
9) H. Garcia-Fernandez, *Compt. Rend.*, **260**, 6107 (1965).
10) H. G. Heal, "Inorganic Sulfur Chemistry," ed. by G. Nickless, Elsevier, Amsterdam (1968), p. 464.
11) A. G. McDiarmid, *J. Amer. Chem. Soc.*, **78**, 3871 (1956).
12) C. G. R. Nair and A. R. V. Murthy, *J. Inorg. Nucl. Chem.*, **25**, 453 (1963).
13) O. Glemser, A. Haas, and H. Reinke, *Z. Natruforsch.*, **20b**, 809 (1965).
14) Y. Sasaki and F. P. Olsen, *Inorg. Nucl. Chem.*, **3**, 351 (1967).
15) O. Ruff and E. Geisel, *Ber.*, **38**, 2659 (1905).
16) M. Goehring, *Quart. Rev.*, **10**, 437 (1956).
17) P. S. Braterman, *J. Chem. Soc.*, **1965**, 2297.
18) M. H. M. Arnold, J. A. C. Hugill, and J. M. Hutson, *ibid.*, **1936**, 1645.
19) M. Villena-Blanco, *U. S. Atom. Energy Commun.*, **1963**, UCRL 11081.
20) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds," Prentice-Hall, Englewood Cliffs, N. J. (1970), p. 502.

However, there is some doubt whether or not the observed melting point shows the proper melting point of tetrasulfur tetranitride. Figure 1 shows the results of the thermal gravimetric analysis and the differential thermal analysis of the sample. An abrupt weight loss near the melting point was found to be due to exothermic change in the sample. Moreover, an explosive decomposition occurred just after the measurements stopped. Judging from the standard heat of formation, ΔH^0, of tetrasulfur tetranitride (110±2 kcal/mol),[21] the thermal decomposition was considered to dominate the sublimation near the melting point. Therefore, the fusion of tetrasulfur tetranitride must accompany the thermal decomposition. Goehring and Voigt[22] have reported that tetrasulfur tetranitride decomposed into its elements at approximately 130°C.

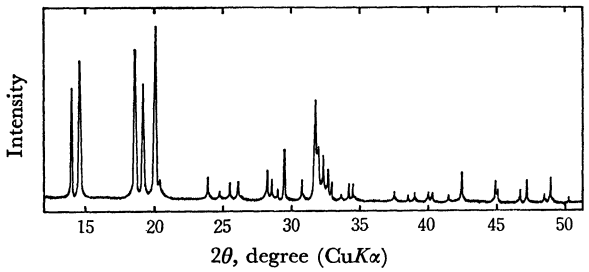

Fig. 2. X-Ray powder diffraction pattern of tetrasulfur tetranitride.

The X-Ray Powder Diffraction Pattern of Tetrasulfur Tetranitride. The X-ray powder diffraction pattern was obtained over the 2θ range from 13° to 50°, as is shown in Fig. 2. The observations in the 2θ range over 50° were omitted. The diffraction peak, d=5.06 Å, reported by Garcia-Fernandez was not observed in the sample, but this peak was observed in a residue of the dioxane solution. Therefore, the peak was considered to be due to a by-product, although the by-product was not identified.

The Miller indices were assigned to the corresponding observed d values as is shown in Table 1, since the observed d values agreed well with those calculated from the lattice constants reported by Clark.[5]

The observed relative intensities of diffraction peaks did not agree with the intensities which were calculated by using the structure factors reported by Sharma and Donohue.[23] The relative intensities were apt to change with the conditions of the sample in spite of a good agreement in the d values. The crystallization rate from the dioxane solution affected the relative intensities; decreases in the intensities of the ($\bar{1}11$), (111), and (200) peaks, and increases in the intensities of the (101) and (202) peaks were observed at a rapid crystallization, for example, while the pulverizing condition scarcely affected the intensities of the same sample at all.

Table 1. The d values and the relative intensities of tetrasulfur tetranitride

$h\,k\,l$	Calcd		This work		Garcia-Fernandez	
	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0
$\bar{1}\,0\,1$	6.29	40.4	6.28	64	6.32	33—80
1 0 1	6.01	42.6	6.02	81	6.06	33—80
					5.06	15—33
$\bar{1}\,1\,1$	4.72	100	4.73	88	4.76	80—100
1 1 1	4.61	80.9	4.61	69	4.61	80—100
2 0 0	4.37	67.7	4.38	100	4.39	33—80
0 0 2	4.32	12.7	4.34	11		
0 1 2	3.70	15.8	3.71	11	3.70	15—33
0 2 0	3.58	15.3	3.58	5	3.61	15—33
$\bar{2}\,1\,1$	3.47	7.5	3.48	9		
2 1 1	3.38	6.8	3.39	10		
$\bar{2}\,0\,2$	3.14	8.4	3.15	17		
$\bar{1}\,2\,1$	3.11	20.6	3.11	12		
1 2 1	3.08	8.9	3.08	5		
2 0 2	3.01	15.2	3.02	29	3.02	1—15
$\bar{2}\,1\,2$	2.88	12.0	2.89	11	2.88	15—33
$\bar{3}\,0\,1$	2.80	47.4	2.81	58		
2 1 2	2.77	22.2	2.78	31	2.77	80—100
$\bar{1}\,0\,3$	2.77	12.6				
2 2 0	2.77	5.8				
0 2 2	2.76	43.7	2.76	26		
3 0 1	2.73	22.4	2.73	18		
1 0 3	2.70	17.3	2.71	10		
$\bar{2}\,2\,1$	2.66	3.9	2.66[a]	3		
$\bar{1}\,2\,2$	2.65	3.1				
1 2 2	2.61	8.8	2.61	9	2.61	33—80
$\bar{3}\,1\,1$	2.61	2.5				
$\bar{1}\,1\,3$	2.59	5.3	2.59	8		
$\bar{2}\,2\,2$	2.36	7.9	2.37	6	2.36	15—33
$\bar{3}\,1\,2$	2.33	0.8	2.33[a]	4		
$\bar{2}\,1\,3$	2.32	2.5				
2 2 2	2.30	3.7	2.31	6		
0 2 3	2.24	27.2	2.25	6	2.24	15—33
2 1 3	2.24	3.9				
$\bar{1}\,3\,1$	2.23	7.0	2.23[a]	6		
1 3 1	2.22	5.0				
$\bar{3}\,2\,1$	2.20	4.3				
3 2 1	2.17	4.2	2.17	4		
$\bar{3}\,0\,3$	2.09	12.1	2.10	16	2.10	15—33
0 3 2	2.09	2.7				
0 1 4	2.07	4.3	2.08	2		
$\bar{3}\,1\,3$	2.01	4.5	2.01	12	2.02	15—33
$\bar{4}\,0\,2$	1.99	2.8	2.00	4		
3 1 3	1.93	6.9	1.94	7		
4 0 2	1.92	4.8	1.92[a]	13	1.92	15—33
$\bar{4}\,1\,2$	1.91	9.7				
2 0 4	1.90	4.0				
4 2 0	1.87	4.1	1.87	5	1.87	15—33
4 1 2	1.85	3.9	1.86	13		
0 2 4	1.85	2.5				
$\bar{1}\,3\,3$	1.81	6.9	1.82	2	1.81	15—33

a) assignments are uncertain

21) C. K. Baker, A. W. Cordes, and J. L. Margrave, *J. Phys. Chem.*, **69**, 334 (1965).

22) M. Goehring and D. Voigt, *Z. Anorg. Allgem. Chem.*, **285**, 181 (1956).

23) B. D. Sharma and J. Donohue, *Acta Crystallogr*, **16**, 891 (1963).