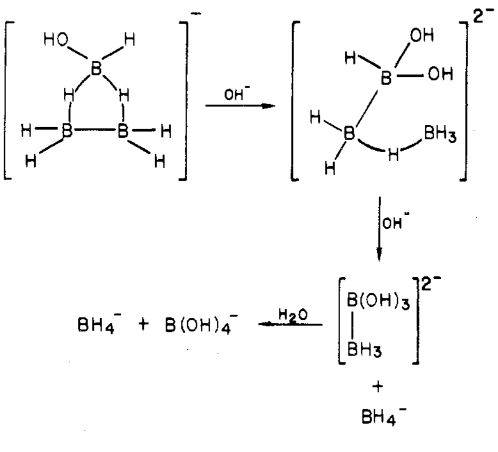
Scheme I



It is tempting to speculate on the mechanism of the decomposition of $B_3H_7OH^-$. A mechanism based on successive attack of hydroxide ions on the most positive boron atom in the group, as shown in Scheme I, seems reasonable.

Acknowledgment. This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy. We wish to thank Mr. Rudi Nunlist for his help in obtaining the NMR spectra.

Registry No. $B_3H_8^-$, 12429-74-2; $B_3H_7OH_2$, 60718-92-5; $B_3H_7OH^-$, 68438-59-5.

References and Notes

(1) G. Kodama and R. W. Parry, *J. Am. Chem. Soc.*, **82**, 6250 (1960).
(2) R. Schaeffer and F. N. Tebbe, *J. Am. Chem. Soc.*, **84**, 3974 (1962).
(3) B. B. Spielvogel, Ph.D. Dissertation, University of Michigan, 1963.
(4) G. E. Ryschkewitsch and V. H. Miller, *J. Am. Chem. Soc.*, **97**, 6258 (1975).
(5) P. J. Dolan, J. H. Kindsvater, and D. G. Peters, *Inorg. Chem.*, **15**, 2170 (1976).
(6) W. V. Hough, L. J. Edwards, and A. D. McElroy, *J. Am. Chem. Soc.*, **80**, 1828 (1958).
(7) W. L. Jolly and T. Schmitt, *J. Am. Chem. Soc.*, **88**, 4282 (1966).
(8) W. L. Jolly and T. Schmitt, *Inorg. Chem.*, **6**, 344 (1967).
(9) F. T. Wang and W. L. Jolly, *Inorg. Chem.*, **11**, 1933 (1972).
(10) H. C. Miller and E. L. Muetterties, *Inorg. Synth.*, **10**, 81 (1967).
(11) K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Nucl. Chem. Lett.*, **6**, 767 (1970).
(12) The apparatus was similar to that illustrated in ref 9.
(13) G. Kodama, *Inorg. Chem.*, **14**, 452 (1975).
(14) Other structures can be derived from either of these structures by interchanging the hydroxyl group with any one of the terminal hydrogen atoms. Even though some of the derived structures would have three different boron atoms, they are consistent with the ^{11}B NMR spectrum if we assume that the ion is rapidly fluxional with respect to the nonhydroxyl hydrogen atoms.
(15) B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 2669 (1961).
(16) R. Schaeffer in "Progress in Boron Chemistry", Vol. 1, H. Steinberg and A. L. McCloskey, Eds., Pergamon Press, Oxford, 1964, pp 417–62.

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Studies of the Interactions between Boron Trihalides and Tris(ethylthio)borane with Hydrogen Sulfide and Their Reactions with Tetraalkylammonium Hydrosulfides

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Received June 2, 1978

Thiohydrolysis in the $BX_3/H_2S/NR_4SH$ system, where X = Cl, Br, or SC_2H_5 and R = CH_3 or C_2H_5, has been investigated; the BX_3/H_2S system was considered as a comparative standard. At 195 K the $BCl_3/H_2S/NR_4SH$ and $BBr_3/H_2S/NR_4SH$ systems always lead to the formation of the thioloborates $NR_4[BCl_3SH]$ and $NR_4[BBr_3SH]$, respectively. No thiohydrolysis occurred in these systems, which is in contrast to the $B(SC_2H_5)_3/H_2S/NR_4SH$ system. At 195 K in liquid H_2S, $B(SC_2H_5)_3$ and NR_4SH in up to 2:1 molar ratio reacted to yield the thioborates $(NR_4)_{2-x}[B_3S_3(SH)_{4-y}(SR)_{y+1-x}]$, where $x = 0$ or 1 and $y = 0$, 1, or 2. The Raman spectrum of the adduct $H_2S{\cdot}BCl_3$ at 195 K was recorded. BBr_3 reacts in liquid H_2S at 195 K to yield $BBr(SH)_2$ which, at elevated temperatures, is converted to $(-BBr-S-)_3$ with the evolution of H_2S.

Introduction

Interactions in the system $BX_3/H_2S/NR_4SH$ (X = Cl, Br, or SC_2H_5; R = CH_3 or C_2H_5) have been studied in order to elucidate whether or not it is possible for BX_3 to react under displacement of X^- by HS^- or S^{2-} ions and formation of thioborates. So far, compounds of the latter type have been prepared either by solid-state or solid/gas reactions at high temperatures, e.g., by reaction of B_2S_3 with metal sulfides,[2] by reaction of elemental boron with an alkali metal sulfide and a mixture of H_2S and H_2,[3] or by reaction of $LiBH_4$ with elemental sulfur. By carrying out the last reaction in ether, the addition product, the thioloborate $Li[BH_3SH]$, was obtained.[4] In contrast to thioborates, thioloborates are accessible from liquid H_2S at 195 K according to the equation $NR_4SH + BX_3 \rightleftarrows NR_4[BX_3SH]$.[5]

Tris(alkylthio)boranes have been prepared by the reaction of boron trihalides with an excess of alkanethiol.[6] Experiments failed, however, to produce thioborates by reacting the former with H_2S and an alkali metal thiolate in either methyl- or ethylthiol in a high-vacuum apparatus.

An important factor for the understanding of the chemistry of $BX_3/H_2S/NR_4SH$ systems is the knowledge of the corresponding BX_3/H_2S system. There is indeed much known about these systems;[6-9] however, it is not clear, what products of BBr_3 or $B(SR)_3$ are present in H_2S at 195 K.

Experimental Section

Apparatus. The utilized high-vacuum apparatus consisted of three major segments: the pump stand, the vacuum line, and the assembly for cleaning the N_2. The pump stand essentially consisted of a Hg diffusion pump, connected in series with a turning slide pump, and a shortened McLeod manometer, which was situated between two cooling traps.

The main vacuum line was connected to the pump stand by a stopcock with a 12-mm bore. To this were attached 3-L or 6-L gas containers and the assembly for cleaning the N_2 and a small modified Stock-type apparatus with a Hg manometer for the distillation of gases and—when needed—reaction bulbs and Schlenk tubes and similar reaction vessels connected by four separate entry or exit ports. The main vacuum line and the gas containers were protected against

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Table I. Experiments in the $BX_3/H_2S/NR_4SH$ Systems

X	R	system	*T*, K	molar ratio N:B	weights, mg NR_4-SH	weights, mg BX_3	vol of H_2S, mL	reacn time, h	wt of $NR_4[BX_3SH]$, mg exptl	wt of $NR_4[BX_3SH]$, mg theor	dev exptl/theor, %
Cl	CH_3	soln, open	195	1:1	54	58	20	1	107	112	−4.5
Cl	CH_3			1:1	65	72	25	1	130	137	−5
Cl	C_2H_5			1:1	69	50	20	1	118	119	−1
Cl	CH_3	suspension, open	195	1:1	325	351	15	1	602	676	−12[a]
Cl	CH_3			1:1	317	348	20	48	610	665	−9[b]
Cl	CH_3			1:2	338	750	15	1	711	708	+0.5
Cl	CH_3			1:2	192	425	15	72	398	406	−2
Cl	CH_3			2:1	320	175	15	48	503	495	+1.5
Cl	CH_3			2:1	296	140	15	3	340	336	+1
Cl	C_2H_5			1:2	297	348	15	20	485	479	+1.5
Cl	CH_3	soln, closed tube	293	1:1	19	21	0.1	24	37	40	−7
Cl	CH_3			2:1	28	14	0.1	720	43	42	−2
Cl	CH_3			3:1	24	8	0.06	24	35	32	+10
Cl	CH_3			1:2	10	21	0.1	72	28	31	−10
Br	CH_3	soln, open	195	1:1	40	100	20	1	130	133	−2
Br	C_2H_5			1:1	54	90	25	1	126	136	−7.5
Br	CH_3	suspension, open	195	1:1	205	490	25	24	655	685	−4
Br	CH_3			2:1	250	295	15	1	551	545	+1
Br	CH_3			2:1	175	200	15	72	370	372	−0.5
Br	CH_3			3:1	199	152	15	4	355	351	+1

[a] Salt^{+}. [b] Salt^{2+}.

overpressure by Hg safety valves which were simultaneously utilized for a rough reading of the pressure.

Starting Materials. Gaseous H_2S (commercial product) was successively passed through towers filled with $CaCl_2$ and P_4O_{10} and then liquefied in a graduated Schlenk tube cooled at 195 K (CO_2/C_3H_6O). The tube was filled with known quantities of H_2S and was connected to the vacuum line. The distilled (77–178 K) H_2S was then stored over Hg in a 6-L gas container of the high-vacuum apparatus.

BCl_3, commercial grade, was pure after condensing it into a cooling trap at 178 K (solid and liquid acetone) of the Stock apparatus, degassing it at 77 K (liquid nitrogen) under high vacuum for 1 h and trap-to-trap distilling it at least twice. The gas, bp 285.65 K, was stored in a 3-L gas container of the high-vacuum line with 50 torr.

BBr_3 was purified by placing of 25 g of commercial grade BBr_3 (Merck) into a 50-mL storage bulb connected with an evacuation and tap tube, removing HBr by degassing under high vacuum at 195 K and distilling off from H_3BO_3 at room temperature; it was stored under dry N_2. For dosage of the purified BBr_3, bp 364 K, vapor pressure 55 torr at 293 K, the storage bulb was weighed, was cooled to 76 K, was connected with the vacuum line in a N_2-countercurrent technique, and was degassed at 195 K under high vacuum. After removal of the cooling bath the gas expanded into a known volume. As soon as the desired pressure (10–15 torr) was reached, the storage bulb was separated by turning off the tap.

$B(SC_2H_5)_3$, bp 356–358 K at 2 torr, was prepared by reaction of BCl_3 with C_2H_5SH in the presence of triethylamine in benzene for 2 h at 293 K and subsequent distillation between 346 K at 1 torr and 369 K at 2 torr. $B(SCH_3)_3$ was prepared in an analogous fashion.[10]

$N(CH_3)_4SH$ was produced after modification of the literature method[11] in the following way: by degassing at least 30 mL of a 0.1 M solution of tetramethylammonium hydroxide in 2-propanol/methanol at 195 K, saturating with H_2S for 1 h at 195 K, and distilling off solvents and excess H_2S at 293 K as soon and as completely as possible. The remaining colorless crystals (containing methyl alcohol) are extremely hygroscopic and oxygen sensitive.

$N(C_2H_5)_4SH$ was prepared by generating tetraethylammonium hydroxide in alcoholic solution via anion exchange (ESB 274 of Permutit AG) of a 0.25 M solution of the bromide in absolute methyl alcohol—analogous to a published preparation for tetrabutylammonium hydroxide[12]—degassing, saturating with H_2S, and stripping of solvent to yield colorless crystals, which lose the alcohol of crystallization under vacuum at 348 K.

Raman spectral data were recorded on a Cary Model 82 instrument.

Results and Discussions

In the BX_3/H_2S systems (X = Cl, Br, or SC_2H_5) the reactions at 195 K were reinvestigated. BCl_3 is soluble in liquid H_2S only up to 0.3 M; it exists in such a solution in the form of the soluble adduct $H_2S{\cdot}BCl_3$; at higher concentrations the colorless adduct precipitates. However, at just about the melting temperature of 238 K the adduct decomposes into H_2S and BCl_3, as was shown by a vapor pressure diagram over the range 195–293 K.[1]

The Raman spectrum of a suspension of the adduct $H_2S{\cdot}BCl_3$ in liquid H_2S at 195 K exhibits the following lines: 2571 (vs), 2430 (w), 1167 (vs), 1123 (s), 832 (w), 800 (sh), 664 (w), 577 (m), 459 (w), 395 (vs), 257 (s), 254 (s), 210 (vw), 182 (vs), and 163 (m, sh) cm^{-1}. It cannot be assigned with exception of the bands at 2571 and 1167 cm^{-1} (H_2S) as well as 459 and 254 cm^{-1} (BCl_3).

The reactions between BCl_3 and H_2S in a closed tube under high H_2S pressure give, on warming from 195 to 293 K, detectable amounts of BCl_2SH, as was illustrated by Raman spectral data.

BBr_3, in concentrated solutions up to 1 M in liquid H_2S at 195 K, forms essentially $BBr(SH)_2$ besides small amounts of BBr_2SH; some unchanged BBr_3 remains in the equilibrium mixture, as was shown by the comparison of the Raman spectra of the cited compounds. In contrast to the BCl_3 system, displacement of Br by SH occurs even at low temperature; there is no evidence for the formation of the adduct $H_2S{\cdot}BBr_3$. At room temperature $BBr(SH)_2$ cyclizes to yield $(-BBr-S-)_3$ with the elimination of H_2S, as was demonstrated by Raman spectral data.[1]

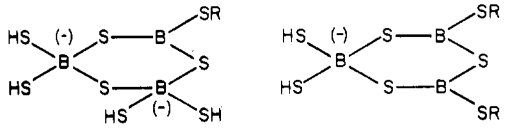
In a closed tube at 293 K, a concentration-dependent substitution of BBr_3 to yield BBr_2SH and $BBr(SH)_2$ occurs, determined once again by Raman spectral data. By heating to ca. 333 K, three new weak Raman lines develop, which probably arise from a cyclization to yield $(-BBr-S-)_3$.

$B(SC_2H_5)_3$ is soluble in liquid H_2S at 195 K up to a 3 M homogeneous solution. Stepwise vacuum distillation of such a solution at 195 K provides an indication about the prevailing species. In a sealed tube under high H_2S pressure at room temperature, the thioborane reacts only to a small extent with H_2S within a range of a 1:1 to 1:12 molar ratio, as was shown by Raman spectra. Only a few weak bands of a thiohydrolysis product were observed.

If the known properties of the BF_3/H_2S system[13] are taken into consideration, it is apparent that for boron trihalides the ability to add H_2S followed by HX elimination increases in

Table II. Chemical Analysis (mol %) Related to N = 1

	N	C	H	S	Cl
salt$^+$	1	4.2	14.1	0.90	3.2
salt^{2+}	1	4.5	13.5	0.84	3.1
$[N(CH_3)_4][BCl_3(SH)]$	1	4	13	1	3



I
B:N = 3:2
B:SC_2H_5 = 3:1

II
B:N = 3:1
B:SC_2H_5 = 3:2

Figure 1. Possible structural formulas for alkylated thioborates.

the order $BF_3 < BCl_3 < BBr_3$.

In the case of $B(SC_2H_5)_3$ an addition of H_2S is unlikely to occur due to the bulkiness of the ligand; furthermore, the trigonal boron is stabilized by π contribution to the B–S bonding.[14,15]

In the $BCl_3/H_2S/NR_4SH$ (R = CH_3, C_2H_5) and $BBr_3/H_2S/NR_4SH$ systems the 1:1 adducts $NR_4[BX_3SH]$ (= thioloborates) are formed at 195 K, independent of molar ratio and concentration of the reactants and/or the reaction times. The thioloborate was also observed in the case of BCl_3 in a closed tube at room temperature (*attention*! from 323 to 333 K an explosion occurred), whereas in the pure BCl_3/H_2S system—as indicated by Raman spectra—detectable amounts of BCl_2SH are formed. This observation illustrates that the base NR_4SH hinders thiohydrolysis (Tables I and II).

In contrast to these systems, $B(SC_2H_5)_3$ reacts with the base $N(CH_3)_4SH$ in a great excess of liquid H_2S at 195 K up to a B:N ratio of 2:1 with thiohydrolysis, as was shown by chemical analysis and weight analysis (Table III). In this conjunction weight analysis means that all the gaseous compounds were distilled off; residues were weighed and related to the weighed amounts of the reactants. $B(SC_2H_5)_3$ does not react beyond the B:N ratio of 2:1, and the excess may be distilled off.

The colorless powdery and foul-smelling products discolor to yellow to reddish brown in air by hydrolysis. The hygroscopic products react violently with water. On slow warming in a sealed tube under nitrogen cover, the powders melt with decomposition between 399 and 453 K. The Raman spectra show strong fluorescence, and only weak bands may be recorded between 2900 and 3200 cm^{-1}.

As shown in Table III, the sum of the contents of the chemical analysis of the thioborate ranges from 86 to 93% by weight; the missing 7–14% is due to partial hydrolysis. For correction of the sulfur contents, the mole number of oxide or hydroxide was calculated and added to the analytically determined mole number of sulfur. Beyond the relative weight increase the molar ratio B:SC_2H_5 is introduced for the degree of the thiohydrolysis. Assuming that N is present only as $[N(CH_3)_4]^+$, we calculated SC_2H_5 by the formula (C – 4N):2, relative to B = 1 (Table IV). The ratio (B:SC_2H_5 may vary between 1:3 (if no thiohydrolysis occurs) and 1:0 (complete thiohydrolysis). In the alkylated thioborates the molar ratios of B:SC_2H_5 are 0.15 to 0.65 or 6:1 to 3:2 instead of 3:9 (if no thiohydrolysis had occurred). The ratio in the thioborate depends on the ratio and the quantities of the reactants.

The illustrated structural formulas (Figure 1) for alkylated thioborates are in accordance with these results. Some experiments produced the pure compound I; others, a mixture of I and II. Species II alone cannot be formed since the ratio B:N never was higher than 2:1.

It is surprising that thiohydrolysis of BCl_3 and BBr_3 is hindered in the presence of the base, whereas in the case of

Table III. Experiments in the $B(SC_2H_5)_3/H_2S/N(CH_3)_4SH$ System

molar ratios N:B	reacn time, h	weights, mg		reacted mass of $B(SR)_3$, mg	wt of thioborate, mg	chemical analysis of the thioborate											fp (dec), K
						% by weight					sum of % by weight	mol % (N = 1)					
		NR_4SH	$B(SR)_3$			N	C	H	S	B		N	C	H	S	B	
1:0.98	1	176	310	294	302	6.8	30.6	7.6	40	4.9	90	1	5.3	16	2.6	0.93	443–453
1:1.0	3	168	301	301	285	7.5	32.0	7.8	39	6.0	92	1	5.0	14	2.3	1.02	445–452
1:1.27	2	243	552	552	376	7.5	30.0	7.7	40	7.1	86	1	4.7	14	2.3	1.3	399–403
1:3.02	2	68	369	196	170	6.0	23.1	6.1	48	7.6	91	1	4.3	14	3.5	1.6	
1:2.85	2	122	625	393	232	5.1	25.0	6.5	45	7.3	90	1	5.8	18	3.9	1.8	425–428
1:8.3	2	53	790	191	154	4.4	24.4	6.2	51	6.9	93	1	6.5	20	5.2	2.0	

Table IV. Chemical Analysis (mol %) Related to B = 1

calcd for	molar ratios N:B	N	C	H	S	B	C_2H_5
	1:0.98	1.01	5.7	17	4.2	1	0.65
	1:1.0	0.98	4.9	14	3.1	1	0.5
	1:1.27	0.8	3.6	11	3.0	1	0.2
	1:3.02	0.6	2.7	9	3.0	1	0.15
	1:2.85	0.6	3.2	10	3.1	1	0.4
	1:8.3	0.5	3.3	10	3.3	1	0.65
I		0.67	3.0	11	2.67	1	0.33
II		0.33	2.67	8	2.33	1	0.67

$B(SC_2H_5)_3$ it is facilitated. This different behavior can only be explained by the bulkiness of the SC_2H_5 ligand.

In B–S chemistry, the formation of six-membered rings comprised of three alternating B and three S atoms is more common than for B–O compounds. For example, thioboric acid is a cyclic trimer,[16] while orthoboric acid is a monomer with strong hydrogen bonds. Among the borates, only the less common triborates have six-membered ring structures analogous to the known alkali metal thioborates; for example, $NaBS_2$ is better represented by the formula $Na_3B_3S_6$.[17]

More highly condensed S-containing ring systems similar to the spiranlike pentaborates are not formed despite the utilization of an up to eightfold excess of $B(SC_2H_5)_3$. This result can be explained by the fact that, as in the case of thioboric acid,[16] the endocyclic B–S bonding distances are smaller than the endocyclic ones. Since the sulfur atoms are larger than the oxygen atoms, the formation of two spiranlike rings at one boron atom as in the pentaborates is unlikely in the B–S chemistry.

Acknowledgment. We are grateful to the "Fonds der Chemischen Industrie" for financial support of this work. The authors also express thanks to Dr. habil. R. Minkwitz for recording and interpreting the low-temperature Raman spectra, to Mrs. B. Suttkus for assistance in chemical analyses, and to Dr. B. Horvath for helpful reading of the English manuscript.

Registry No. I·2[$N(CH_3)_4$], 68550-24-3; II·[$N(CH_3)_4$], 68474-91-9; $H_2S·BCl_3$, 68474-69-1; BCl_2SH, 39130-80-8; BBr_3, 10294-33-4; BBr_2SH, 39130-81-9; $BBr(SH)_2$, 40679-99-0; $(-BBr-S-)_3$, 18495-45-9; $B(SC_2H_5)_3$, 998-26-5; $N(CH_3)_4SH$, 10408-32-9; $N(C_2H_5)_4SH$, 10408-33-0; $N(CH_3)_4[BCl_3SH]$, 15820-64-1; $N(CH_3)_4[BBr_3SH]$, 68474-92-0; $N(C_2H_5)_4[BCl_3SH]$, 15649-93-1; $N(C_2H_5)_4[BBr_3SH]$, 68474-93-1; BCl_3, 10294-34-5; H_2S, 7783-06-4.

References and Notes

(1) Abstracted from the Ph.D. dissertation of W. E., Department of Chemistry, Freie Universität Berlin, Berlin, 1977.
(2) D. Thomas and G. Tridot, *C. R. Hebd. Seances Acad. Sci.*, **258**, 2587 (1964).
(3) F. Chopin and P. Hagenmuller, *C. R. Hebd. Seances Acad. Sci.*, **256**, 5578 (1963); **261**, 142 (1965); *C. R. Hebd. Seances Acad. Sci., Ser. C*, **262**, 418 (1966).
(4) H. Nöth and G. Mikulaschek, *Z. Anorg. Allg. Chem.*, **311**, 241 (1962).
(5) J. D. Cotton and T. C. Waddington, *J. Chem. Soc. A*, 789 (1966).
(6) J. Bouix and R. Hillel, *Can. J. Chem.*, **51**, 292 (1973).
(7) M. Fouassier, M. T. Forel, J. Bouix, and R. Hillel, *J. Chim. Phys. Phys.-Chim. Biol.*, **70**, 1519 (1973).
(8) J. Bouix, M. Foussier, and M. T. Forel, *J. Mol. Struct.*, **15**, 103 (1973).
(9) R. Hillel, J. Bouix, and M. T. Forel, *Bull. Soc. Chim. Fr.*, 83 (1974).
(10) B. M. Mikhailov and Yu. N. Bubnov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1378 (1962).
(11) J. D. Cotton and T. C. Waddington, *J. Chem. Soc. A*, 785 (1966).
(12) G. A. Harlow, C. M. Noble, and G. E. A. Wyld, *Anal. Chem.*, **28**, 737 (1956).
(13) A. Germann and H. S. Booth, *J. Phys. Chem.*, **30**, 369 (1926).
(14) J. Kroner, D. Nölle, and H. Nöth, *Z. Naturforsch., B*, **28**, 416 (1973).
(15) M. F. Lappert, M. R. Litzow, J. B. Pedley, P. N. K. Riley, T. R. Spalting, and A. Tweedale, *J. Chem. Soc. A*, 2320 (1970).
(16) W. Schwarz, H. D. Hausen, H. Hess, J. Mandt, W. Schmelzer, and B. Krebs, *Acta Crystallogr., Sect. B*, **29**, 2029 (1973).
(17) J. C. Rosso and M. Dubusc, *Chim. Ind., Genie Chim.*, **102**, 409 (1969).

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Reactions of Tetrasulfur Tetranitride with Bromine. Reaction in Carbon Disulfide Solution To Give $CS_3N_2Br_2$

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Received June 9, 1978

The products of the reaction of tetrasulfur tetranitride depend strongly on the reaction conditions. Recently it has been shown that gas-phase bromination of solid S_4N_4 causes polymerization to conducting $(SNBr_{0.4})_x$ while reaction with liquid bromine leads to a stable tribromide $S_4N_3Br_3$.[4] In contrast the reaction of S_4N_4 with bromine in carbon disulfide solution results in a mixture of $S_4N_3Br_3$, S_4N_3Br, and a novel ionic compound $CS_3N_2Br_2$.

As part of a continuing study of the bromination of S_4N_4,[2,4] the products of bromination in solution have been investigated. We previously reported the reaction of bromine vapor with solid S_4N_4 which gives $(SNBr_{0.4})_x$,[2,3] a highly conducting solid, very similar in its physical properties to brominated $(SN)_x$. The reaction of S_4N_4 with liquid bromine gives the ionic compound $S_4N_3^+Br_3^-$,[4,5] which contains stacks of alternating planar $S_4N_3^+$ rings and asymmetric Br_3^- cations. The bromination of S_4N_4 in CS_2 was first reported by Clever and Muthman in 1896.[6] These authors describe their reaction product as bronze crystals which they assumed to be $S_4N_4Br_4$, similar to the known chlorination product $S_3N_3Cl_3$. Later Becke-Goehring[7] formulated the compound as a polymer $(SNBr)_x$, largely on the basis of its insolubility in nonpolar organic solvents. Heal[8] repeated the synthesis and analyzed the product to be $S_3N_2Br_2$ analogous to the known compound $S_3N_2Cl_2$.[9] In another study Zborilova et al.[10] concluded the bronze crystals were actually a mixture of S_4N_3Br and $S_3N_2Br_2$. In this paper data will be presented which show that the bronze crystals are indeed a mixture, but of $S_4N_3^+Br^-$, its corresponding tribromide, and $CS_3N_2Br_2$ rather than $S_3N_2Br_2$.

Experimental Section. Reaction of Bromine with S_4N_4 in CS_2

All manipulations were carried out under vacuum or in a dry argon atmosphere with purified reagents and dried solvents. A total of 2.5 mL of bromine was added to 1.75 g (9.5 mmol) of S_4N_4 dissolved in 200 mL of CS_2. After 24 h olive brown crystals were collected on a frit and thoroughly washed with CS_2 until the washings were only slightly yellow. The product was then dried under vacuum to give a yield of 3.75 g. This product was then further extracted with liquid SO_2 for 7 days until the washings were almost colorless. The yield of the SO_2-insoluble fraction was 1.03 g. Anal. Calcd for $CS_3N_2Br_2$: C, 4.06; S, 32.48; N, 9.46; Br, 53.99. Found: C, 4.24; S, 31.80; N, 9.94; Br, 53.35.

0020-1669/79/1318-0383$01.00/0