requirements, on differences with variation in thermal activation temperatures, and on what other types of molecules interact.

Acknowledgment. The generous support of the Department of Energy (Contract ERDA-FE, E(49-18)-2211) is gratefully acknowledged. Helpful discussions with Professors K. Tanabe, V. I. Stenberg, N. F. Woolsey, and R. J. Baltisberger are greatly appreciated. The National Science Foundation provided a traineeship for R.M., which is greatly appreciated.

Registry No. MgO, 1309-48-4; CaO, 1305-78-8; SrO, 1314-11-0; BaO, 1304-28-5; ThO_2, 1314-20-1; $C_6H_5NO_2^{-}\cdot$, 15753-78-3; CO·, 630-08-0.

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Reactions of Tetrasulfur Tetranitride with Liquid Bromine and Iodine Monochloride

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Received March 17, 1978

The reactions of tetrasulfur tetranitride with halogens have been the subject of numerous investigations.[1-3] Though the fluorination[4] and chlorination[5] are well understood, leading to such products as NSF, NSF_3, or $(NSF)_4$ and NSCl or $(NSCl)_3$, respectively, the bromination does not proceed analogously and has been reported to give a variety of products including $S_4N_4Br_6$[1] and $(NSBr)_x$.[2,3] Recently the reaction of sulfur–nitrogen compounds with bromine and also iodine monochloride has become a topic of renewed interest because of their influence on the electrical properties of $(SN)_x$ and their ability to cause spontaneous polymerization of S_4N_4.[6,7] Bromine increases the conductivity[8] of $(SN)_x$ by an order of magnitude and also increases the superconducting transition temperature by ~25%[9] whereas ICl only doubles the conductivity. Long exposure of $(SN)_x$ to ICl leads to decomposition and shorter exposure leads only to surface reaction. Electron diffraction[10] and Raman studies[11] indicate the presence of ICl. In contrast it has been shown from Raman[11,12] and far-IR studies[13] that brominated $(SN)_x$ contains the tribromide ion Br_3^-. The influence of the resulting charge transfer on the band structure of $(SN)_x$ has been invoked to explain the increase in the normal-state conductivity as well as the superconducting transition temperature.[14] Both Br_2 and ICl vapors also react with S_4N_4 to give conducting solids.[6,7,15] In the case of bromine vapor the reaction with solid S_4N_4 leads to spontaneous polymerization to $(SNBr_{0.4})_x$, identical with the product of bromination of $(SN)_x$. ICl vapor and solid S_4N_4 lead to a more complicated reaction. Although compositions such as $(SN(ICl)_{0.4})_x$ have been isolated, the iodine–chlorine ratio is usually less than unity. Previously Clever and Muthmann[1] reported that bromine vapor reacted with solid S_4N_4 to give garnet red crystals of $S_4N_4Br_6$. We have observed that if S_4N_4 was brominated with liquid bromine instead of bromine vapor, the major product was an insulating yellow solid. A similar compound was formed upon reaction of S_4N_4 with liquid ICl. Motivated by these anomalies, we have investigated the reaction of S_4N_4 with Br_2 and ICl, under a variety of conditions. In this note we report on the reaction of S_4N_4 with liquid bromine and iodine monochloride.

Table I.

Observed Infrared Frequencies (cm^{-1})			
$S_4N_3Br_3$ in Br_2 Solution	Solid $S_4N_3Br_3$ (Nujol)	Solid $S_4N_3ICl_2$ (Nujol)	Solid S_4N_3Cl[13] (Nujol)
1185,vs	1165,vs	1176,s	1163,s
1145,m	1125,m		1125,w
			1102,vw
1030,vs	1010,vs	1017,vs	998,vs
970,vw			
942,vw	940,vw	902,vw	
		849,w	
742,w	722,w	720,w	
680,vs	675,s	675,s	678,s
	632,w		
618,m	605,w		606,w
572,s	575,w		
560,s	565,s	566,m	561,s
	535,m		
472,s	475,vs	477,vs	466,s
430,m	435,m	440,w	451,s
341,m	320,s	322,s	317,m

Experimental Section

General Procedures. S_4N_4 was prepared according to the literature[16] and fractionally sublimed before use. All solvents and bromine were dried and distilled and the reactions were carried out in the absence of moisture, either under vacuum or in a dry nitrogen or argon atmosphere. The IR spectra were recorded in NaCl, KBr, and polyethylene cells using a Perkin-Elmer IR grating spectrophotometer, Model 283. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out using glass, platinum, or gold sample containers. Elemental analysis was performed by the University of California, Analytical Services, Berkeley, Calif.

Preparation of $S_4N_3Br_3$. S_4N_4, 456 mg (2.47 mmol), was heated with 0.8 mL of bromine at ~70 °C in a sealed evacuated glass tube. After 2 days the tube (which now contained a pressure of gas even at liquid nitrogen temperatures due to the liberation of N_2) was carefully opened, and the excess bromine was removed by pumping for at least 4 h at room temperature, leaving an orange-yellow solid—$S_4N_3Br_3$(I). In order to obtain crystals of I the bromine must be removed very slowly (several days) until no bromine atmosphere develops over a period of 2 h after the pumping is interrupted. The yield of I was 1020 mg (100%). Anal. Calcd for $S_4N_3Br_3$: Br, 58.47; N, 10.25; S, 31.27. Found: Br, 58.8; N, 10.3; S, 30.5.

Determination of Liberated Nitrogen. S_4N_4, 368 mg (2 mmol), and 1 mL of bromine were placed in a flask connected via a reflux condenser to a gas buret. All joints were lubricated with halogen-resistant grease. After 24 h of refluxing, the nitrogen evolved was measured to be 22.7 mL at STP or 0.5 mol/mol of S_4N_4.

Preparation of $S_4N_3ICl_2$. S_4N_4, 500 mg (2.71 mmol), was heated with 1.5 mL of ICl at ~100 °C for 48 h in the same experimental setup used for $S_4N_3Br_3$. After the tube was opened the excess ICl and the I_2 which was also formed were removed by pumping for 24 h at ~50 °C. The yield of yellow-orange polycrystalline material

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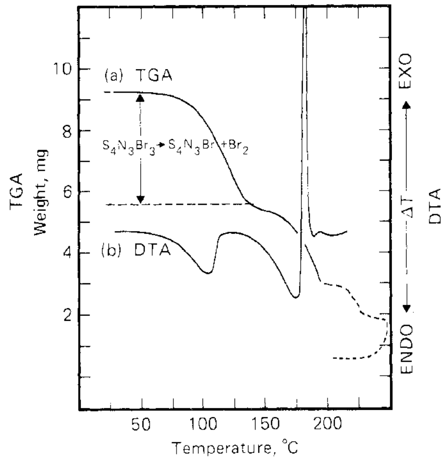

Figure 1. Thermal analysis of $S_4N_3Br_3$ in helium atmosphere: (a) thermogravimetric analysis—heating rate 10°/min; (b) differential thermal analysis—heating rate 10°/min.

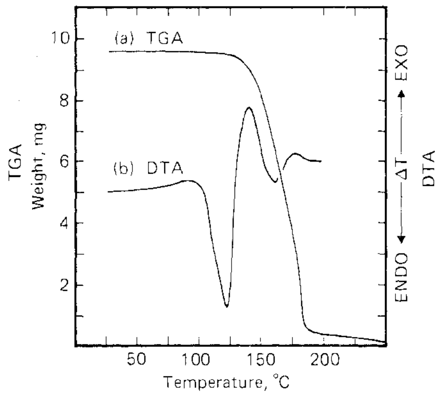

Figure 2. Thermal analysis of $S_4N_3ICl_2$ in helium atmosphere: (a) thermogravimetric analysis—heating rate 10°/min; (b) differential thermal analysis—heating rate 10°/min.

was 995 mg (100%), and analysis was in good agreement with $S_4N_3ICl_2$. Anal. Calcd: Cl, 19.26; I, 34.48; N, 11.42; S, 34.84. Found: Cl, 19.6; I, 34.7; N, 11.3; S, 34.9.

Discussion

When S_4N_4 is reacted with an excess of bromine either by heating in a sealed glass tube or by refluxing under an inert atmosphere, it dissolves completely and 0.5 mol of N_2/mol of S_4N_4 is evolved. Slow cooling of the bromine solution leads to deep red transparent crystals which become opaque and yellow when the adhering bromine is removed by pumping. Analysis of these yellow crystals showed them to be $S_4N_3Br_3$. The reaction proceeds in 100% yield as shown in eq 1.

$$S_4N_4 + {}^3/_2Br_2 \rightarrow {}^1/_2N_2 + S_4N_3Br_3 \qquad (1)$$

We believe that the deep red crystals are identical with those reported by Clever and Muthmann.[1] These authors assumed them to be $S_4N_4Br_6$ despite their analysis which indicated $S_4N_{3.4}Br_{5.7}$. From our own experience it appears that these red crystals are really $S_4N_3Br_3$. The higher bromine content reported by Clever and Muthmann probably results from occluded bromine or perhaps Br_5^-. The high nitrogen content is most likely explained by the presence of NH_4Br which we have also observed if moisture is not rigorously excluded.

Comparison of the IR data for $S_4N_3Br_3$ (I) dissolved in bromine and as Nujol mull with that of S_4N_3Cl[17] in Table I confirms the presence of a cyclic $S_4N_3^+$ cation. This suggests that the bromine is not attached to the ring but must be present as a Br_3^- ion. This is consistent with the ready conversion to S_4N_3Br (identical with the sample prepared by treating S_4N_3Cl with KBr)[18] either on recrystallization from formic acid or on heating to ~70 °C as shown in the TGA data in Figure 1(a). This is also consistent with the DTA data in Figure 1(b) which show a broad endotherm at ~100 °C due to loss of 1 mol of bromine followed at higher temperatures by decomposition of S_4N_3Br. X-ray studies have now confirmed these findings showing that the compound consists of stacks of alternating $S_4N_3^+$ ions and linear asymmetric Br_3^- ions.[19]

Though we have not investigated it in such detail, the reaction of liquid ICl with S_4N_4 appears to give a similar product. $S_4N_3ICl_2$ (II) is formed according to eq 2.

$$S_4N_4 + 2ICl \rightarrow {}^1/_2N_2 + S_4N_3ICl_2 + {}^1/_2I_2 \qquad (2)$$

Compound II can also be precipitated by adding ICl to a solution of S_4N_3Cl in formic acid. Evidence for the presence of the $S_4N_3^+$ cation is given by the IR data (Table I). The yellow-orange crystals (II) are even more thermally stable than $S_4N_3Br_3$ (I). Unlike the tribromide it does not seem to decompose in two stages as shown in the DTA/TGA data in Figure 2. ICl is not eliminated before decomposition of the $S_4N_3^+$ cation takes place.

The ready formation and stability of ionic sulfur–nitrogen compounds is of particular significance in view of the apparent role of Br_3^- ions[12] in enhancing the conductivity[8] and superconductivity of $(SN)_x$.[9] In the case of brominated $(SN)_x$ the tribromide ion is even more stable.[20]

We believe reaction 1 proceeds at least in part by a volatile intermediate NSBr. This is evidenced by a small amount of thiotrithiazyl bromide which forms when the volatile species evolved during the reaction are passed via a reflux condenser through CCl_4. Neither S_4N_4 nor S_4N_3Br are volatile enough to pass the condenser suggesting that this volatile intermediate is NSBr. Further evidence for the presence of NSBr is obtained by following reaction 1 in the IR region using an NaCl cell. A band at 1319 cm^{-1} appears in the region expected for sulfur–nitrogen stretching frequency corresponding to a bond order between 2 and 3 (cf. 1372 cm^{-1} for NSF[21] and 1325 cm^{-1} for NSCl).[22] This 1319-cm^{-1} band increases in intensity as the S_4N_4 slowly dissolves eventually reaching an equilibrium value. The $S_4N_3^+$ bands continue to rise and eventually the 1319-cm^{-1} peak disappears as the NSBr is all used up. Nelson and Heal[23] previously reported that NSBr is possibly involved in the reaction of S_4N_4 with bromine in CS_2 solution. NSBr has also been identified mass spectrometrically[15,24] as an important species in the vapor phase above $(NSBr_{0.4})_x$—the product of bromination of $(SN)_x$ and S_4N_4. It is the only example of a SN compound with bromine directly attached to sulfur. MacDiarmid[25] has suggested that in the preparation of S_4N_3Cl by reaction of S_4N_4 with such chlorinating agents as S_2Cl_2, CH_3COCl, or $SOCl_2$, trace amounts of HCl present in these materials are responsible for reaction. In this investigation the dry bromine was freed from HBr by treatment with $CuSO_4$ and so we have no reason to believe that HBr plays any role in the formation of I.

Acknowledgment. We wish to thank the Office of Naval Research for partial support of this work by ONR Contract 318-042. G.W. wishes to express his gratitude to IBM for an IBM World Trade Fellowship from West Germany.

Registry No. I, 67145-67-9; $S_4N_3ICl_2$, 59369-15-2; S_4N_4, 28950-34-7; Br_2, 7726-95-6; ICl, 7790-99-0.

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Relationship between Porphyrin Basicity and Thiocyanate Anation Rates of Cobalt(III) Porphyrins in Neutral Detergent Solutions

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Received March 20, 1978

Mechanistic kinetic studies on porphyrin and metalloporphyrin systems are usually done in aqueous solution using synthetic porphyrins made water soluble by virtue of *N*-methylpyridinium, sulfonic acid, or carboxylic acid functions.[1] While these peripheral charge-type variations modify porphyrin reactivity, such charge effects can never be clearly separated from the basicity effects of the central porphyrin nitrogen atoms, since charge and basicity often parallel one another. Uncharged water-insoluble disubstituted deuteroporphyrin esters and related natural porphyrins offer a wide range of nitrogen basicities and can be conveniently studied in aqueous detergent solutions.[2,3] We report (a) a comparison of equilibrium and kinetic parameters for the complexation of thiocyanate by synthetic water-soluble cobalt(III) porphyrins both in the presence and in the absence of a neutral detergent and (b) anation studies of water-insoluble cobalt(III) porphyrins of varying basicity in the same detergent media.

Experimental Section

The cobalt(II) porphyrins were purified chromatographically and air-oxidized to their Co(III) forms. The Co(II) disubstituted deuteroporphyrin esters have their Soret bands at ca. 412 nm, while those of Co(III) are at ca. 427 nm. Cobalt(III) uroporphyrin I, prepared either by air-oxidation under acidic conditions in detergent, in aqueous basic solution, or with DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) in benzene, gave identical kinetic results.

Spectroscopic grade Triton X-100, a neutral detergent, was added (2%) in some kinetic runs but not in others. All experiments were maintained at 25 °C, pH 1.5, and ionic strength 0.5 ($HClO_4/NaClO_4$). The basicity parameters, pK_3, for the monocation–free base porphyrin equilibrium $(H_3\text{-}P)^+/(H_2\text{-}P)$ were measured in 2.5% sodium dodecyl sulfate and obtained from the literature.[2,4]

Table I. Effect of the Neutral Detergent Triton X-100 on the Cobalt(III)–Porphyrin–SCN Formation Constant and Anation Rate[a]

	k_f, M^{-1} s^{-1}		$10^{-3}K$, M^{-1}	
porphyrin[b]	H_2O	detergent	H_2O	detergent
TMpyP(4)	2.1[c]	3.0	6.4[c]	7.8
TMpyP(3)	2.8[d]	3.7	3.4[d]	28.0
$TPPS_4$	157[e]	200	11.0[e]	24.3

[a] 25 °C, pH 1.5, $\mu = 0.5$ $NaClO_4/HClO_4$, H_2O or 2% Triton X-100. [b] TMpyP is tetrakis(4(or 3)-*N*-methylpyridyl)porphyrin; $TPPS_4$ is tetrakis(4-sulfonatophenyl)porphyrins. [c] Pasternack, R.; Cobb, M. *J. Inorg. Nucl. Chem.*, **1973**, 35, 4327; Ashley, K.; Berggren, M; Cheng, M. *J. Am. Chem. Soc.*, 1975, 97, 1422. [d] Williams, G. N; Hambright, P. *Bioinorg. Chem.*, 1977, 7, 267. [e] Our data on Co^{III}-$TPPS_4$ in water is in reasonable agreement with that of Ashley, K; Au-Young, S. *Inorg. Chem.*, **1976**, 15, 1937.

Table II. Thiocyanate Formation Constants and Anation Rates of Cobalt(III) Porphyrins in 2% Triton X-100[a]

porphyrin[b]	pK_3	k_f, M^{-1} s^{-1}	$10^{-3}K$, M^{-1}	peripheral charge
$TPPCOO^-$	6.1	450[c]	3	−4
MPDME	5.9	333	114	0
DPDME	5.6	238	36	0
$TPPS_4$	4.9	200	24	−4
Uro I	3.4	26.4	16	0
Br_2DPDME	3.0	22.7	114	0
TPPCOOH	2.9	20.1	143	0
TMpyP(3)	2.0	3.7	28	+4
TMpyP(4)	1.6	3.0	8	+4

[a] 25 °C, pH 1.5, $\mu = 0.5$ $NaClO_4/HClO_4$. [b] TPPCOOH, tetrakis-(4-carboxyphenyl)porphyrin; MPDME, mesoporphyrin IX dimethyl ester (DME); DPDME, deuteroporphyrin IX DME; $TPPS_4$, tetrakis(4-sulfonatophenyl)porphyrin; Uro I, uroporphyrin I; Br_2DPDME, 2,4-dibromodeuteroporphyrin IX DME; TMpyP(X), tetrakis(4(or 3)-*N*-methylpyridyl)porphyrin. [c] k_f and K in H_2O; data from Pasternack, R; Parr, G. *Inorg. Chem.*, **1976**, 15, 3087.

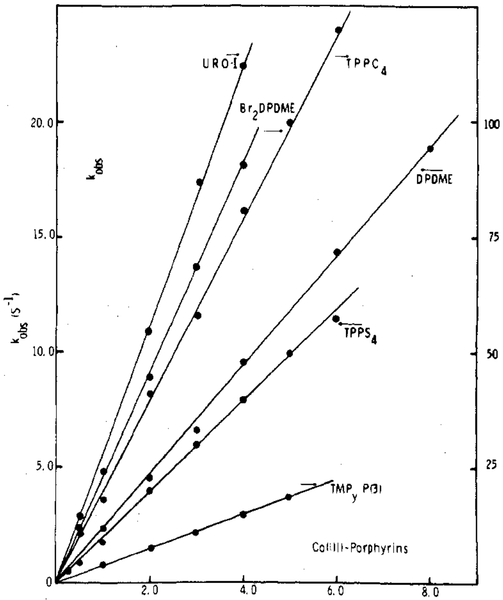

Figure 1. Plots of k_{obsd} vs. $[SCN^-]_0$ for the anation of cobalt(III) porphyrins in 2% Triton X-100 at 25 °C, pH 1.5, $\mu = 0.5$ ($HClO_4/NaClO_4$). The porphyrin abbreviations are listed in Table II.

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