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The Reactions of Group V Metal Amide with Sulfur Dioxide

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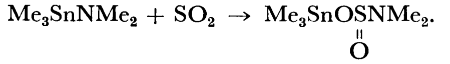
Tris(dialkylamino)-arsines (I), -stibines (II), and -bismuthines (III) react with sulfur dioxide to give the corresponding tetraalkylsulfurous diamides and the corresponding metal oxides or polymers containing the metals. The reactivity of these metal amides in view of the fastness of the initial reactions follows the order III>II>I, however, the yields decrease in the order I>II>III. Tris(dialkylamino)phosphines, on the other hand, give hexaalkylphosphoric triamides and hexaalkylphosphorothioic triamides in a ratio of 2 : 1. The reactivity of the various phosphorus compounds toward sulfur dioxide increases with increasing nucleophilicity of the phosphorus atom; $P(NEt_2)_3 > Ph_2PNEt_2 > Ph_2POEt > PhP(OEt)_2 > P(OEt)_3$. The reaction mechanism of compounds (I), (II), and (III) with sulfur dioxide is different from that of the phosphorus amides.

Sulfur dioxide is unique in the point that it exhibits both nucleophilic and electrophilic behavior.[1] Many studies of the reaction of sulfur dioxide with organometallic compounds have been reported.[2,3] Lappert *et al.* have found that the reaction of sulfur dioxide with (dimethylamino)trimethyltin affords the insertion product,[4]



$$Me_3SnNMe_2 + SO_2 \rightarrow Me_3SnO\underset{\underset{O}{\|}}{S}NMe_2. \qquad (1)$$

The reaction of tris(dialkylamino)boron with sulfur dioxide yields tetraalkylsulfurous diamides and tris(dimethylamino)boroxin,[5]

$$3B(NR_2)_3 + 3SO_2 \rightarrow 3(R_2N)_2SO + (R_2NBO)_3. \qquad (2)$$

The group V metal amides; $P(NR_2)_3$, $As(NR_2)_3$, $Sb(NR_2)_3$, and $Bi(NR_2)_3$ are very reactive compounds and thus are valuable as synthetic intermediates. They are known to react with ketones,[6-8] acetic anhydride,[7,9] and heterocumulenes,[7,9] but there is no report concerning their chemistry with sulfur dioxide. This paper describes the reactions of the group V metal amides with sulfur dioxide, and a reaction mechanism is proposed based on relative reactivities.

Results and Discussion

Tris(dimethylamino)-, tris(diethylamino)-, and tris(dipropylamino)-arsine reacted with sulfur dioxide at −30 °C to give the corresponding tetraalkylsulfurous diamides and As_2O_3 which was identified by X-ray powder diffraction.

$$2As(NR_2)_3 + 3SO_2 \rightarrow 3(R_2N)_2SO + As_2O_3. \qquad (3)$$

The sulfurous diamides were identified by comparison of their IR and NMR spectra with those of authentic samples obtained by the reaction of thionyl chloride with the corresponding secondary amines.[10,11] The identity of the sulfurous diamides was confirmed by the fact that their reaction with acetic anhydride gave the appropriate *N*,*N*-dialkylacetamides accompanied by the evolution of sulfur dioxide.[12]

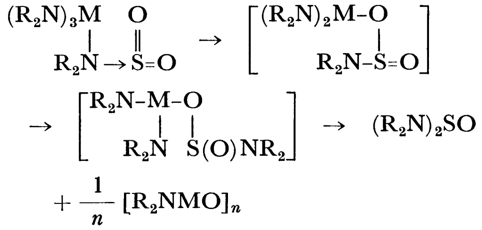
The reaction of tris(dialkylamino)-stibines and -bismuthines with sulfur dioxide proceeded more vigorously, but the yield of sulfurous diamides was lower than the case of tris(dialkylamino)arsine. In addition to sulfurous diamides, in both cases polymeric residues, which were formulated on the basis of elemental analyses as $(R_2NSbO)_n$ or $(R_2NBiO)_n$, are formed. IR spectra of the residues showed a stretching mode for Sb–O–Sb at 750—715 cm^{-1} and for Bi–O–Bi at 630—620 cm^{-1}.[13]

$$M(NR_2)_3 + SO_2 \rightarrow (R_2N)_2SO + \frac{1}{n}(R_2NMO)_n. \qquad (4)$$

$M = Sb$ and Bi

These residues are hydrolyzed in the presence of hot water to afford Sb_2O_3 or Bi_2O_3 which was identified by X-ray powder diffraction.

There is a similarity between the reactions described here and the amination reactions of carbonyl compounds with group V metal amides.[8] Bismuth amides react with sulfur dioxide most vigorously. The reactivity order in view of the fastness of the initial reaction is Bi>Sb>As, whereas, the yields of sulfurous diamides decrease as follows As>Sb>Bi (Table 1). A mechanism for the reaction can be discussed in terms of the nucleophilicity of nitrogen atom and the affinity of the metal atom for oxygen. The first step involves the nucleophilic attack by the nitrogen atom of the metal amide on the sulfur atom of sulfur dioxide thus forming an insertion product.



$$\begin{array}{c}(R_2N)_3M\ \ O\\ |\ \ \ \|\\ R_2N\rightarrow S{=}O\end{array} \rightarrow \left[\begin{array}{l}(R_2N)_2M\text{-}O\\ \qquad\quad |\\ \quad R_2N\text{-}S{=}O\end{array}\right] \rightarrow \left[\begin{array}{l}R_2N\text{-}M\text{-}O\\ \qquad |\ \ |\\ \quad R_2N\ \ S(O)NR_2\end{array}\right] \rightarrow (R_2N)_2SO + \frac{1}{n}[R_2NMO]_n \qquad (5)$$

The degree of ionic character of metal–nitrogen bonds increases with decreasing electronegativity of the central metal. The rates of the initial addition step are found to be parallel with the ionic degree of the metal–nitrogen bonds. On the other hand, the affinity of metal atoms

Table 1. Yields(%) of tetraalkylsulfurous diamide in the reaction of $M(NR_2)_3$ with SO_2

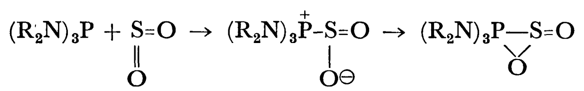
M	R: Me	R: Et	R: Pr
As	76	75	88
Sb	62	48	49
Bi	46	45	46

for oxygen decreases in the order; As>Sb>Bi.[8,14] Therefore, bismuth amides are the most reactive in the initial step, but their poor affinities for oxygen result in decreased yields of the sulfurous diamides as the result of the formation of the polymeric residues which contain the dialkylamino moieties instead of the metal oxides.

When tris(dialkylamino)phosphines were treated with sulfur dioxide, hexaalkylphosphoric triamides and hexaalkylphosphorothioic triamides were obtained in the ratio of 2:1.

$$3(R_2N)_3P + SO_2 \rightarrow 2(R_2N)_3P{=}O + (R_2N)_3P{=}S \qquad (6)$$

Similarly, (diethylamino)diphenylphosphine, ethyl diphenylphosphinite and ethyl diphenylphosphinothioite gave the corresponding P=O and P=S compounds in the ratio of 2:1. The reactivity of the various trivalent phosphorus compounds toward sulfur dioxide was compared by means of GLC analysis. The order of the reactivity, $P(NEt_2)_3 > Ph_2PNEt_2 > Ph_2POEt > PhP(OEt)_2 > P(OEt)_3$, is parallel with the order of electron density on the phosphorus atom.[15,16] Tris(diethylamino)phosphine has the highest electron density on the phosphorus atom because of the (p-d)π interaction between the nitrogen atom and the phosphorus atom. In the case of phosphites, although there may be some degree of oxygen to phosphorus (p-d)π bonding, the inductive effect of oxygen atoms provide a greater influence on the reactivity. Thus it would appear most reasonable to expect that the reactive site on the aminophosphine is the phosphorus atom instead of the nitrogen atom. On this basis a tentative mechanism for the reaction is as follows.



$$(R_2N)_3P + \underset{\underset{O}{\|}}{S}{=}O \rightarrow (R_2N)_3\overset{+}{P}{-}\underset{\underset{O^{\ominus}}{|}}{S}{=}O \rightarrow (R_2N)_3P{-}S{=}O$$

$$\rightarrow (R_2N)_3PO + [SO]$$

$$[SO] \rightarrow \frac{1}{2}(S) + \frac{1}{2}SO_2$$

Nucleophilic attack by the phosphorus atom on the sulfur atom of sulfur dioxide occurs as the first step of the reaction, and follows the formation of the P–O bond, generating the products. This mechanism is principally the same as that proposed by Smith *et al.* for the reaction of phosphines with sulfur dioxide.[17,18] Aminophosphines exhibit an ambident nature in their reactions with various kinds of electrophilic reagents, such as phenyl cyanate, and β-propiolactone.[19,20] In the reaction with cyclic carbonates, the nitrogen atom of the aminophosphine acts as the nucleophilic site whereas in the reaction with alkyl benzenesulfonate, the phosphorus atom attacks the electrophilic reagent forming the phosphonium salt.[21,22] Although it is very difficult to predict which atom of the aminophosphines acts as a nucleophilic site, the HSAB concept may prove helpful. Since the phosphorus atom of the aminophosphine is softer than the nitrogen atom, a soft electrophile would be expected to prefer to interact with the phosphorus atom. The striking difference in mechanism of the reaction of sulfur dioxide with aminophosphines and with aminoarsines, aminostibines and aminobismuthines is not explainable on the basis of HSAB theory. The fact that the metal sulfides of the type, $(R_2N)_3M{=}S$ where M=As, Sb, and Bi were not formed suggests that the poorer stability of the M=S bond relative to P=S may be a factor of significant importance.

Experimental

All the reactions were carried out under an argon atmosphere. The IR, NMR, and mass spectra were recorded on a Shimadzu IR-430 spectrometer, a JEOL-C60 HL spectrometer, and a JMS-D300 spectrometer, respectively. GLC analyses were carried out on a Simadzu GC 6A apparatus, using PEG 6000 (10%)-Shimalite W 301 (1 m) column with helium as the carrier gas.

Materials. Tris(dialkylamino)arsines, -stibines, and -bismuthines were prepared by the methods priviously reported[9,23]: $As(NMe_2)_3$; bp 68—72 °C/18 mmHg, $As(NEt_2)_3$; bp 62—65 °C/0.3 mmHg, $As(NPr_2)_3$; bp 82—86 °C/0.08 mmHg, $Sb(NMe_2)_3$; bp 55—61 °C/5 mmHg, $Sb(NEt_2)_3$; bp 59—62 °C/0.02 mmHg, $Sb(NPr_2)_3$; bp 107—111 °C/0.1 mmHg, $Bi(NMe_2)_3$; bp 34—36 °C/0.2 mmHg, $Bi(NEt_2)_3$; bp 75—77 °C/0.12 mmHg, $Bi(NPr_2)_3$; bp 73—77 °C/0.05 mmHg. All the phosphorus compounds used in this experiment are synthesized according to the methods described in the literature.[24] Sulfur dioxide, obtained from a commercial source, was dried by passage through concentrated sulfuric acid. Organic solvents were dried by conventional methods.[25]

Reaction of Tris(dialkylamino)arsines with Sulfur Dioxide. Dry sulfur dioxide was bubbled through tris(dimethylamino)arsine (2.67 g, 12.9 mmol) in diethyl ether (5 ml) at −30 °C. An exothermic reaction took place to give a white precipitate. After removal of the precipitate, the solvent and excess SO_2, tetramethylsulfurous diamide (2.00 g, 76%) was obtained by distillation under reduced pressure; bp 70—73 °C/16 mmHg, mp 30—30.5 °C, IR (neat) ν(S=O) 1150, $\nu(NC_2)$ 930, 908, ν(S–N) 670, 656, 646 cm^{-1}, NMR ($CHCl_3$) δ 2.62, MS *m/e* 136 (M$^+$).

Similar treatment of tris(diethylamino)arsine (5.09 g, 17.5 mmol) with sulfur dioxide resulted in the formation of tetraethylsulfurous diamide (3.77 g, 75%); bp 82—84 °C/3 mmHg, n_D^{20} 1.4635, IR(neat), ν(S=O) 1110 cm^{-1}, $\nu(NC_2)$ 924, 894, 876 cm^{-1}, ν(S–N) 652 cm^{-1}, NMR ($CHCl_3$) δ 1.10 (3H, t), 3.06 (2H, q), MS *m/e* 192 (M$^+$). Reaction of tris(dipropylamino)arsine (4.16 g, 11.1 mmol) with sulfur dioxide gave tetrapropylsulfurous diamide (3.63 g, 88%); bp 66—68 °C/0.03 mmHg, n_D^{20} 1.4667, IR (neat) ν(S=O) 1110 cm^{-1}, $\nu(CN_2)$ 692 cm^{-1}, NMR ($CHCl_3$); δ 0.89 (3H, t), 1.53 (2H, m), 2.94 (2H, t), MS *m/e* 248 (M$^+$).

Reaction of Tris(diethylamino)stibine with Sulfur Dioxide. When sulfur dioxide was passed through an ethereal solution of tris(diethylamino)stibine (1.93 g, 5.71 mmol) at −30 °C, a violent reaction took place to give a yellowish white precipitate, which was filtered and washed twice with ether. The filtrate was distilled to give tetraethylsulfurous diamide (0.79 g, 48%), bp 44—46 °C/0.02 mmHg. The polymeric residue exhibited Sb–O–Sb bands at 750, 616 cm^{-1} and several absorptions ascribed to the diethylamino moiety. (Found: C, 23.6%, H, 4.98%. Calcd for $C_4H_{10}NOSb$; C, 22.90%, H, 4.80%.)

Reaction of Tris(diethylamino)bismuthine with Sulfur Dioxide. Tris(diethylamino)bismuthine (2.85 g, 6.70 mmol) reacted readily with sulfur dioxide to give hexaethylsulfurous diamide (0.88 g, 45%) and a yellowish white precipitate; IR (KBr) 618 cm^{-1} (Bi–O–Bi). (Found: C, 16.4%, H, 3.66%, Calcd for $C_4H_{10}NOBi$; C, 16.17%, H, 3.39%)

TABLE 2. SPECTROSCOPIC DATA OF THE PRODUCTS OF THE REACTION BETWEEN SEVERAL PHOSPHORUS COMPOUNDS AND SO_2

Compound	NMR δ (TMS)	IR ν(P=O or P=S) cm^{-1}
$Ph_2P(O)NEt_2$	1.07(6H, t), 3.07(4H, m, $J_{PNCH}=11.4$ Hz), 7.51, 7.90(10H, m)	1180
$Ph_2P(S)NEt_2$	1.07(6H, t), 3.07(4H, m, $J_{PNCH}=11.2$ Hz), 7.50, 7.90(10H, m)	753, 578
$Ph_2P(O)OEt$	1.35(3H, t), 4.30(2H, m, $J_{POCH}=7.1$ Hz)	1225
$Ph_2P(S)OEt$	1.31(3H, t), 4.10(2H, m, $J_{POCH}=8.8$ Hz)	782, 610
$Ph_2P(O)SEt$	1.29(3H, t), 2.84(2H, m, $J_{PSCH}=11.6$ Hz), 7.51, 7.87(10H, m)	1200
$Ph_2P(S)SEt$	1.25(3H, m, $J_{PSCH}=2.1$ Hz),	785
	2.84(2H, m, $J_{PSCH}=7.3$ Hz), 7.46, 7.85(10H, m)	630

Reaction of Tris(dialkylamino)phosphines with Sulfur Dioxide. Sulfur dioxide was bubbled through tris(dimethylamino)phosphine (1.65 g, 10.1 mmol) in diethyl ether (5 ml) at −30 °C. After removal of the volatile materials, the reaction mixture was distilled to give a fraction having a boiling point of 53—72 °C/0.6 mmHg. The distillate showed two spots on thin layer chromatograph at $R_f=0.87$ and 0.19. Separation of the distillate by a column chromatograph (silica gel-chloroform) gave hexamethylphosphorothioic triamide (0.53 g, 27%) as a first eluate and hexamethylphosphoric triamide (0.87 g, 48%) as a second eluate, as identified by the comparison of their IR and NMR spectra with those of authentic materials.[24] Similarly, sulfur dioxide was passed through an ethereal solution of tris(diethylamino)phosphine (1.83 g, 7.40 mmol) at −30 °C, and the reaction mixture was distilled. The fraction of the bp range 36—86 °C/0.1 mmHg was collected, and column chromatograph of this fraction gave hexaethylphosphorothioic triamide (0.56 g, 27%) $R_f=0.70$, NMR ($CHCl_3$) δ 1.11 (3H, t), 3.14 (2H, m, $J_{PNCH}=11.6$ Hz). IR ν(P=S) 798, 696 cm^{-1}, and hexaethylphosphoric triamide (0.98 g, 50%), NMR ($CHCl_3$) δ 1.22 (3H, t), 3.31 (2H, m, $J_{PNCH}=16.5$ Hz), IR ν(P=O) 1205 cm^{-1}. Reaction of tris(dipropylamino)phosphine with sulfur dioxide gave hexapropylphosphorothioic triamide (0.37 g, 20%), NMR ($CHCl_3$) δ 0.86 (3H, t), 1.56 (2H, m), 2.96 (2H, m), IR ν(P=S) 796, 736 cm^{-1}, and hexapropylphosphoric triamide (0.82 g, 45%), NMR ($CHCl_3$) δ 0.91 (3H, t), 1.63 (2H, m), 3.01 (2H, m), IR ν(P=O) 1242 cm^{-1}.

The similar treatment of (diethylamino)diphenylphosphine, ethyl diphenylphosphinite and ethyl diphenylphosphinothioite with sulfur dioxide gave the corresponding P=O and P=S compounds in the ratio of 2:1. And the spectral data of these products are shown in Table 2.

Effect of Substituent on the Reactivity. A reaction of a phosphorus (III) compound (0.1 mol/l) with a large excess sulfur dioxide was initiated at −55 °C by mixing THF solutions of each reagent containing an internal standard. Aliquots of the reaction mixture were withdrawn at appropriate times, and the remaining amount of the phosphorus (III) compound was determined by GLC analysis (Table 3).

Reaction of Tetraalkylsulfurous Diamide with Acetic Anhydride. Acetic anhydride (1.3 g, 11.1 mmol) was added to an ice-cooled ethereal solution of tetramethylsulfurous diamide (1.51 g, 11.1 mmol) with stirring. An exothermic reaction took place accompanied by the evolution of a gas. After removal of the solvent, *N,N*-dimethylacetamide (17.4 g, 90%) was obtained by distillation, bp 67—70 °C/20 mmHg. Similarly an equimolar reaction of tetraethylsulfurous diamide (1.56 g, 8.13 mmol) with acetic anhydride gave *N,N*-diethylacetamide (1.63 g, 87%), bp 101—104 °C/55 mmHg.

TABLE 3. REMAINING AMOUNT OF TRIVALENT PHOSPHORUS COMPOUNDS AFTER 40 min

Compound	Concentration (mmol/l)
$P(NEt_2)_3$	0
Ph_2PNEt_2	14.2
Ph_2POEt	21.8
$PhP(OEt)_2$	51.6
$P(OEt)_3$	98.6

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