The Reaction of Group V Metal Alkoxides with Sulfur Dioxide and Selenium Dioxide

Fumio Ando, Jugo Koketsu,* and Yoshio Ishii

Department of Industrial Chemistry, Chubu Institute of Technology, 1200 Matsumoto, Kasugai 487

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Trialkoxyarsines (I) and -stibines (II) react with sulfur dioxide to give the corresponding dialkyl sulfites and arsenic trioxide or polymeric residues containing antimony. The reactivity of the compounds (I) is very low, and the yield is poor. Reactions of I and II with selenium dioxide afford dialkyl selenites together with arsenic trioxide or the same polymeric residues containing antimony as in the case of the reaction with sulfur dioxide. The reaction followed a stoichiometry of three moles of trialkyl phosphites (III) and one mole of selenium dioxide yields a 2 : 1 molar ratio of the phosphates : the phosphoroselenoates. A similar reaction of the phosphites with selenium dioxide in a 2 : 1 stoichiometry gives the phosphates and red selenium quantitatively. The rate of oxidation of the phosphorus compounds by selenium dioxide decreases in the order $Bu_3P > BuP(OEt)_2 > P(OEt)_3$. Based on these results, the possible mechanisms have been discussed.

In a previous paper,[1] the reaction of group V metal amides with sulfur dioxide was reported. In the reaction of phosphorus amide, the phosphorus atom is oxidized giving P=O, and P=S compounds. Tris-(dialkylamino)arsine and stibine, however, add across the S=O bond of sulfur dioxide and deoxygenation by the metal atom occurs giving the tetraalkylsulfurous diamides.

Selenium dioxide, a white crystalline solid, has been used as a selective oxidizing agent of organic compounds.[2] There are, however, few reports concerning the reaction of selenium dioxide with the group V metal compounds. Triaryl phosphines, arsines, and stibines react with selenium dioxide to give the corresponding oxides and selenides.[3,4] Esters of arsinous acids $R_2As(OR')$[5] and arsonous acids $RAs(OR')_2$[6] are also oxidized with selenium dioxide to arsinic acid esters $R_2As(O)OR'$ and arsonic acid esters $RAs(O)(OR')_2$, respectively. The oxidation of the cyclic esters of arsonous acid with selenium dioxide however, yields the spirocyclic esters of orthoarsonic acids instead of the normal arsonic acid esters.[7]

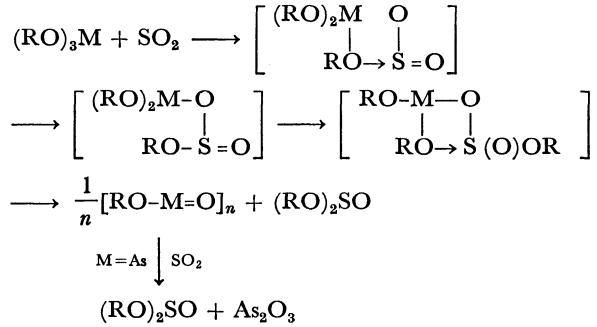
Trialkoxyarsines and -stibines are very reactive compounds and react with acetic anhydride[8] and heterocumulenes such as phenylisocyanate[9] and ketene.[10] However no study concerning the reaction between group V metal alkoxides and selenium dioxide has been found except for Dubrovia's report[11] concerning the reaction between triethoxystibine with selenium dioxide. Equally there are no reports of the reactions between group V metal alkoxides and sulfur dioxide. In this paper, the reactions between group V metal alkoxides and sulfur dioxide and selenium dioxide will be reported and discussed.

Results and Discussion

Trialkoxyarsines react very slowly with sulfur dioxide to give a precipitate of arsenic trioxide and dialkyl sulfites in low yields. The reaction was incomplete and large amounts of the starting materials were recovered, even on heating at 100 °C for several months.

The reaction of trialkoxystibines with sulfur dioxide proceeded more readily than that of the arsines to give the corresponding dialkyl sulfites and polymeric residues in place of antimony trioxide. The polymeric residues, which were formulated as $(ROSbO)_n$ on the basis of the elemental analysis showed infrared absorption bands assignable to the Sb–O–Sb[12–14] group (745, 618, and 540 cm^{-1} for $R=Pr^n$) and alkoxyl group. The residues were insoluble in many organic solvents and hydrolyzed in hot water to give antimony trioxide (identified by X-ray powder diffraction). It is interesting to note that the As–O bond is less reactive to sulfur dioxide than Sb–O, and this may be due to improved matching of the sizes of the reaction centers and also to the ionic properties of metal oxygen bonds. As the degree of ionic character in the metal oxygen bond increases when the central metal changes from arsenic to antimony, it appears that the nucleophilic property of the oxygen atom of antimony alkoxide is much greater than that of arsenic alkoxide.

The affinity of the metal atom for oxygen decreases in the order : As>Sb>Bi,[1] and therefore trialkoxystibine is more reactive than trialkoxyarsine, but the poor affinity for the oxygen atom results in the failure of Sb_2O_3 formation. Based on these considerations, one of the possible mechanisms consists of the nucleophilic attack by a alkoxyl group on the sulfur atom rather than the electrophilic attack by the metal on the oxygen atom of sulfur dioxide, to form an insertion product, and the reaction proceeds as follows :



Trialkoxyarsines reacted completely with selenium dioxide in boiling benzene to give arsenic trioxide and the corresponding selenites in poor yield due to the thermal decomposition of the selenites.[15] The reaction of the trialkoxystibines with selenium dioxide also gave the selenites and the polymers, which showed the same physical and spectral properties as those observed in the reaction with sulfur dioxide. An

Table 1. Products of the reaction of trialkoxystibine with sulfur dioxide

$(RO)_2S{=}O$	Bp (°C/mmHg)	Yield (%)	n_D^{20}	IR ν(S=O)cm^{-1} a)	NMR (δ) ppm b)
R=Et	53—55/16	45	1.4142	1205	1.34 (3H, t) 4.05 (2H, q)
n-Pr	78—79/13	41	1.4236	1208	0.98 (3H, t) 1.70 (2H, m) 3.95 (2H, m)
i-Pr	60.5—62/15	44	1.4150	1200	1.34 (6H, d) 4.78 (H, m)
n-Bu	87—90/5	56	1.4290	1208	0.94 (3H, t) 1.56 (4H, m) 3.97 (2H, m)

a) Coated on KBr plate. b) In CCl_4.

Table 2. Oxidation products of trialkyl phosphites with selenium dioxide in the ratio of 3 : 1

$(RO)_3P$	$(RO)_3P{=}O$ compound		$(RO)_3P{=}Se$ compound		
	Yield (%)	IR ν(P=O) cm^{-1}	Yield (%)	IR ν(P=Se) cm^{-1}	NMR (δ) ppm a)
$(MeO)_3P$	49	1275	27	557, 502	3.90 (d, J=14.6)
$(EtO)_3P$	62	1270	18	568, 525	1.35 (t, 3H) 4.20 (dq, 2H, J=10.0)
$(i\text{-}PrO)_3P$	47	1274	21	570, 534	1.34 (d, 6H) 4.83 (m, 1H, J=10.5)
$(n\text{-}BuO)_3P$	50	1277	26	585, 548	0.95 (t, 3H) 1.10—1.88 (m, 4H) 4.20 (dt, 2H, J=9.8)
$(i\text{-}BuO)_3P$	39	1284	12	572, 545	0.97 (d, 6H) 2.00 (m, 1H) 3.88 (dt, 2H, J=8.8)

a) In $CHCl_3$, the J value is J_{POCH} (Hz).

analytical pure sample $(ROSbO)_n$ could not be obtained since it was impossible to completely remove the unreacted selenium dioxide. The structure was however shown to be the same as the product in the reaction of trialkoxystibine with sulfur dioxide. The stoichiometric results of the reactions studied with selenium dioxide are shown in the following equations :

$$2As(OR)_3 + 3SeO_2 \longrightarrow 3(RO)_2SeO + As_2O_3,$$

$$Sb(OR)_3 + SeO_2 \longrightarrow (RO)_2SeO + \frac{1}{n}(ROSbO)_n.$$

The reaction of trialkoxyarsines and -stibines with selenium dioxide may proceed *via* an identical pathway to that of sulfur dioxide.

The reaction of trialkyl phosphites with excess sulfur dioxide was performed at room temperature to yield trialkyl phosphates and trialkyl phosphorothioates in the ratio of 2 : 1, the results of which agree with those reported by Fluck and Binder.[16] The reaction of trialkyl phosphites with selenium dioxide, however, gave different products, depending on the proportions of the reagents used.

The reaction followed a stoichiometry of 3 mol of trialkyl phosphite and 1 mol of selenium dioxide yields a 2 : 1 molar ratio of trialkyl phosphate : trialkyl phosphoroselenoate. The phosphoroselenoates were identified by comparing the spectral data with those of authentic samples[17-19] prepared by the reaction between phosphite and selenium. Ethyl dibutylphosphinite was also oxidized with selenium dioxide to give ethyl dibutylphosphinate and ethyl dibutylphosphinoselenoate. The products from the oxidation in the 3 : 1 stoichiometric ratio are listed in Table 2.

Similar reactions of the phosphites with selenium dioxide in a 2 : 1 stoichiometry gave the phosphates and selenium in quantitative yields.

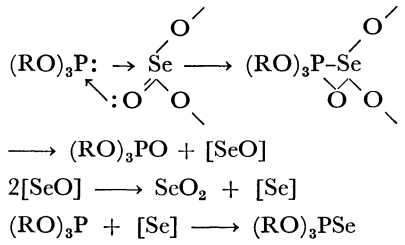
Trialkyl phosphoroselenoates reacted readily with selenium dioxide to yield the corresponding phosphites and selenium in good yields, the reactions of which are summarized in the following equations :

$$3(RO)_3P + SeO_2 \longrightarrow 2(RO)_3PO + (RO)_3PSe$$

$$2(RO)_3P + SeO_2 \longrightarrow 2(RO)_3PO + Se,$$

$$2(RO)_3PSe + SeO_2 \longrightarrow 2(RO)_3PO + 3Se.$$

The reactivity of trivalent phosphorus compounds toward selenium dioxide has been compared by means of GLC analysis by the same method used in a previous paper[1] and found to decrease in the order, $Bu_3P > BuP(OEt)_2 > P(OEt)_3$. This order is parallel with the order of electron density on the phosphorus atom, and consistents with the order found in the reaction of phosphorus compounds with sulfur dioxide.[1] It may be reasonable to consider the nucleophilic attack by the phosphorus atom on selenium occurs as the first step in the formation of cyclic intermediates followed by the formation of phosphoryl bonds to give trialkyl phosphates and selenium monoxide, which disproportionates into selenium and selenium dioxide. The selenium reacts with unreacted phosphites to provide phosphoroselenoates.



$$(RO)_3PO + [SeO]$$

$$2[SeO] \longrightarrow SeO_2 + [Se]$$

$$(RO)_3P + [Se] \longrightarrow (RO)_3PSe$$

Experimental

All the reactions as well as preparations of trialkoxyarsines and stibines were conducted under an atmosphere of argon or nitrogen. The IR spectra were taken with a Shimadzu IR-430 spectrometer. The NMR spectra were run on a JEOL-C60 HL spectrometer in CCl_4 or $CHCl_3$ using TMS as internal standard. The analytical GLC was conducted with a Shimadzu GC 6A gas chromatograph using a 3 m glass column packed with 10% PEG 6000.

Materials. Trialkoxyarsines were prepared according to the method described by Brill and Campbell;[20] $As(OMe)_3$; bp 90—96 °C/35 mmHg, $As(OEt)_3$; bp 120—126 °C/18 mmHg, $As(OPr^n)_3$; bp 107—108 °C/43 mmHg, $As(OPr^i)_3$; bp 92—94 °C/12 mmHg, $As(OBu^n)_3$; bp 60—72 °C/0.05 mmHg. The preparation of the trialkoxystibines was conducted by the reaction between antimony trichloride and 3 mol of lithium alkoxide. $Sb(OEt)_3$; bp 89—96 °C/0.08 mmHg, $Sb(OPr^n)_3$; bp 70—74 °C/0.05 mmHg, $Sb(OPr^i)_3$; bp 39—44 °C/0.03 mmHg, $Sb(OBu^n)_3$; bp 81—89 °C/0.15 mmHg.

Triisopropyl phosphite,[21] triisobutyl phosphite,[21] diethyl butylphosphonite,[22] ethyl dibutylphosphinite,[23] and tributyl phosphine[24] were prepared by the methods previously reported. The other phosphorus compounds were obtained commercially and distilled prior to use.

Reaction of Trialkoxyarsines with Sulfur Dioxide. The triisopropoxyarsine (1.56 g, 6.24 mmol) was dissolved in an excess of liquid SO_2 and heated in sealed tube at 100 °C for 4 months during which time white precipitates of arsenic trioxide (0.20 g, 33% yield) were formed. The liquid part of the reaction mixture gave the fraction (0.76 g, bp 40—52 °C/50 mmHg) by distillation under reduced pressure. GLC analysis showed the presence of diisopropyl sulfite together with the starting material. These two compounds were identified by comparing the GLC retention times with those of authentic samples.

Reaction of Trialkoxystibines with Sulfur Dioxide. A mixture of triethoxystibine (2.76 g, 10.7 mmol) and excess sulfur dioxide was heated at 100 °C for 3 d in a sealed tube. After removal of the white precipitates and the excess sulfur dioxide, diethyl sulfite (1.00 g, 45%) was obtained by distillation under reduced pressure; bp 53—55 °C/16 mmHg, IR ν(S=O) 1205 cm^{-1}, NMR (CCl_4) δ=1.34 (3H, t), 4.05 (2H, q). The precipitates had strong infrared bands assignable to the Sb–O–Sb group (745, 618, 585 cm^{-1}) and the alkoxyl group (2980, 2940, 2900, 1225, 1170, 1120, 1065. 1015, and 920 cm^{-1}). Found; C, 13.8; H, 2.65%. Calcd for $C_2H_5O_2Sb$; C, 13.14; H, 2.76%. The reactions of other trialkoxystibines with sulfur dioxide were performed in the same way, the results of which are shown in Table 1. The white precipitates in each reaction also showed the same IR spectra as reported above and identified to be $(ROSbO)_n$.

Reaction of Trialkoxyarsines with Selenium Dioxide. A mixture of trimethoxyarsine (1.2 g, 7.20 mmol) and selenium dioxide (1.20 g, 10.8 mmol) in benzene (10 ml) was heated in a sealed tube at 100 °C for 2 d. The As_2O_3 precipitate was then filtered and the solvent removed using a rotary evaporator. The remaining product was distilled under vacuum to yield dimethyl selenite (1.41 g, 83%); bp 64—65 °C/15 mmHg, IR (neat) ν(Se=O) 926 cm^{-1}, ν(Se–O) 632 cm^{-1}; NMR (CCl_4) δ=3.70 (S).

Similar treatment of triethoxyarsine (1.45 g, 6.90 mmol) with selenium dioxide (1.15 g, 10.4 mmol) gave diethyl selenite (1.19 g, 62%); bp 76—76.5 °C/15 mmHg; IR (neat) ν(Se=O) 934 cm^{-1}, ν(Se–O) 632 cm^{-1}, NMR (CCl_4) δ=1.27 (3H, t), 4.03 (2H, m). The reaction of tri-*n*-propoxyarsine (1.90 g, 7.53 mmol) with selenium dioxide (1.26 g, 11.3 mmol) gave di-*n*-propyl selenite (1.58 g, 65%); bp 77—78 °C/2.5 mmHg; IR (neat) ν(Se=O) 930 cm^{-1}, ν(Se–O) 634 cm^{-1}; NMR (CCl_4) δ=0.98 (3H, t), 1.65 (2H, m), 3.94 (2H, m). The reaction of triisopropoxyarsine (1.76 g, 6.99 mmol) and tributoxyarsine (1.71 g, 5.80 mmol) with selenium dioxide gave the following products, respectively; diisopropyl selenite (1.08 g, 51%); bp 78—81 °C/14 mmHg; IR (neat) ν(Se=O) 940 cm^{-1}, ν(Se–O) 640 cm^{-1}; NMR (CCl_4) δ=1.30 (6H, m), 4.85 (1H, m), and dibutyl selenite (0.85 g, 41%); bp 127—129 °C/12 mmHg; IR (neat) ν(Se=O) 924 cm^{-1}, ν(Se–O) 635 cm^{-1}; NMR (CCl_4) δ=0.96 (t, 3H), 1.50 (m, 4H), 3.97 (m, 2H).

Reaction of Trialkoxystibines with Selenium Dioxide. A mixture of triethoxystibine (2.13 g, 8.29 mmol) and selenium dioxide (1.31 g, 11.8 mmol) was allowed to react at 100 °C for 3 d. After removal of the precipitates by filtration, the filtrate was distilled under vacuum to give diethyl selenite (0.76 g, 33%). Under similar conditions, tri-*n*-propoxystibine (2.09 g, 6.98 mmol) reacted with selenium dioxide and gave di-*n*-propyl selenite (0.76 g, 34%). Also diisopropyl selenite (0.88 g, 41%) and di-*n*-butyl selenite (0.52 g, 53%) were obtained by the reaction of selenium dioxide with triisopropoxystibine (1.99 g, 6.72 mmol) and tri-*n*-butoxystibine (1.15 g, 3.36 mmol), respectively.

The white precipitates obtained in each reaction exhibited the same IR absorptions as those obtained in the reaction of the corresponding trialkoxystibine with sulfur dioxide.

Reaction of Trialkyl Phosphites with Sulfur Dioxide. When an excess of dry sulfur dioxide was bubbled through trimethyl phosphite (2.20 g, 17.7 mmol) at −78 °C, an exothermic reaction took place which gave a colorless solution after standing for 30 min at room temperature. The reaction mixture was distilled to give a distillate (2.28 g) of boiling point range bp 71—78 °C/14 mmHg . From the mixture, trimethyl phosphate (1.35 g, 63%) and trimethyl phosphorothioate (0.75 g, 31%) were obtained by column chromatography (silica gel–chloroform). In a similar manner, triethyl phosphite (1.96 g, 11.8 mmol) reacted with sulfur dioxide to yield triethyl phosphite (1.14 g, 53%) and triethyl phosphorothioate (0.68 g, 29%). Triisopropyl phosphite (2.50 g, 11.7 mmol) also underwent a similar reaction to give triisopropyl phosphate (1.42 g, 54%) and triisopropyl phosphorothioate (0.76 g, 27%). These compounds were identified by comparing the physical (bp) and spectroscopic (IR and NMR) data with those of the authentic samples.[17]

Reaction of Trialkyl Phosphites with Selenium Dioxide in the Molar Ratio 3 : 1. Trimethyl phosphite (2.48 g, 20.0 mmol) was added slowly with stirring to selenium dioxide (0.74 g, 6.66 mmol) suspended in benzene (5 ml) at room temperature, and the solution stirred for 2 h. After removal of the solvent, the reaction mixture was distilled under reduced pressure. The distillate (3.04 g, bp 84—90 °C/15 mmHg) was subjected to column chromatography (silica gel–chloroform) to give trimethyl phosphate (1.39 g, 49%), and trimethyl phosphoroselenoate (1.10 g, 27%), IR (neat) ν(P=Se) 557, 502 cm^{-1}, NMR ($CHCl_3$) δ=3.74 (d, J_{POCH}=

14.4 Hz.

Further oxidations of phosphites with seleniium dioxide were conducted according to the same procedure as reported above, the results of which are shown in Table 2.

Reaction of Trialkyl Phosphites with Selenium Dioxide in the Molar Ratio 2 : 1. Trimethyl phosphite (1.77 g, 14.3 mmol) was added to selenium dioxide (0.79 g, 7.12 mmol) in benzene (5 ml) at room temperature. An exothermic reaction took place giving a red precipitate. The mixture was stirred overnight and the red selenium (0.47 g, 84%) was then filtered and the solvent removed from the filtrate using a rotary evaporator. The remaining product was distilled under reduced pressure to yield trimethyl phosphate (1.68 g, 84%); bp 77—78 °C/13 mmHg. Similar treatment of triethyl phosphite (1.94 g, 11.6 mmol) with selenium dioxide (0.65 g, 5.82 mmol) gave triethyl phosphate (1.89 g, 89%); bp 94—95 °C/12 mmHg and selenium (0.38 g, 82%).

Reaction of Trialkyl Phosphoroselenoates with Selenium Dioxide. The reaction of trimethyl phosphoroselenoate (0.87 g, 5.26 mmol) with selenium dioxide (0.24 g, 2.15 mmol) was conducted in benzene (5 ml) to produce trimethyl phosphate (0.46 g, 76%) and selenium (0.46 g, 91%). From triethyl phosphoroselenoate (1.29 g, 5.26 mmol) and selenium dioxide (0.29 g, 2.63 mmol) were obtained triethyl phosphate (0.92 g, 96%) and selenium (0.62 g, 100%).

Effect of Substituent on the Reactivity. A reactivity comparison of trivalent phosphorus compounds towards selenium dioxide was performed by mixing each reagent (0.05 mmol/l) in ethanol at −78 °C and determining by GLC analysis the remaining amount of trivalent phosphorus compound under the same conditions used in a previous paper.[1] The following figures show the remaining amounts of phosphorus compounds (mmol/l) after 30 min; Bu_3P : (0), $BuP(OEt)_2$: (0.0182), $P(OEt)_3$: (0.0485).

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