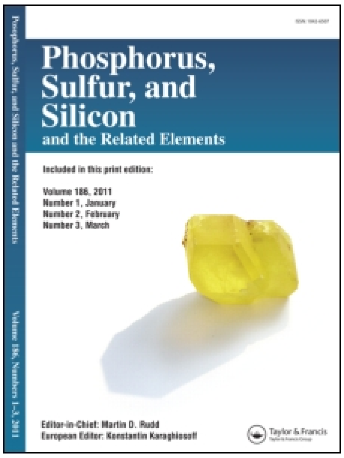


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REACTIONS BETWEEN SULFUR DIOXIDE AND PHOSPHINES

Selwyn Chan[a]; Harold Goldwhite[a]
[a] Department of Chemistry, California State University, Los Angleles, California

To cite this Article Chan, Selwyn and Goldwhite, Harold(1978) 'REACTIONS BETWEEN SULFUR DIOXIDE AND PHOSPHINES', Phosphorus, Sulfur, and Silicon and the Related Elements, 4: 1, 33 — 34

To link to this Article: DOI: 10.1080/03086647808079960

URL: http://dx.doi.org/10.1080/03086647808079960

Phosphorus and Sulfur
1978, Vol. 4, pp. 33-34

REACTIONS BETWEEN SULFUR DIOXIDE AND PHOSPHINES

SELWYN CHAN and HAROLD GOLDWHITE

Department of Chemistry, California State University,
Los Angleles, California 90032

(Received April 19, 1977)

Reaction between sulfur dioxide and trimethyl phosphine yields both phosphine oxide and sulfide. Reactions between sulfur dioxide and phosphines containing P-H bonds generally give rise to the most fully oxidized acid containing phosphorus that can be formed without cleaving P-C bonds. Thus, diphenylphosphine gives diphenylphosphinic acid (and some tetraphenyldiphosphine disulfide) and phenylphosphine gives phenylphosphonic acid.

INTRODUCTION

Reactions between sulfur dioxide and phosphines might be expected to fall into two categories: (i) Lewis-acid-base adduct formation; (ii) reduction of the sulfur dioxide by the phosphine, with concomitant production of four-coordinate phosphorus products. Both modes of reaction have been briefly reported. A 1:1 complex of tris(*o*-tolyl) phosphine and sulfur dioxide has been described;[1] and two sets of workers have noted the reduction of sulfur dioxide by tertiary phosphines.[2,3]

We became interested in this topic while exploring the chemistry of phosphiran,[4] a heterocyclic secondary phosphine. Since there appeared to be no previous work on reactions of sulfur dioxide with phosphines containing a P-H bond, we decided to examine a number of systems of this type.

RESULTS AND DISCUSSION

Previous workers[1,2] have observed, in reactions between triaryl phosphines and sulfur dioxide, conversion of the phosphines to mixtures of phosphine oxide and phosphine sulfide. However, it was reported that trimethylphosphine yielded only the phosphine oxide in reaction with sulfur dioxide.[3] In our hands this reaction followed a stoichiometry of 3 moles of phosphine: 1 mole of SO_2 and yielded a 2:1 molar ratio of phosphine oxide: phosphine sulfide:

$$3(CH_3)_3P + SO_2 \rightarrow 2(CH_3)_3PO + (CH_3)_3PS$$

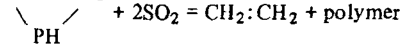
This reaction proceeded rapidly, even at the melting point of sulfur dioxide (–75°C) and it was not possible to find any evidence for prior complex formation.

The stoichiometric results of the reactions studied with compounds containing P-H bonds are summarized in the following equations:

$$4(C_6H_5)_2PH + 2SO_2 = 2(C_6H_5)_2P(O)OH + (C_6H_5)_4P_2S_2$$

$$2C_6H_5PH_2 + 3SO_2 = 2C_6H_5P(O)(OH)_2 + 3S$$

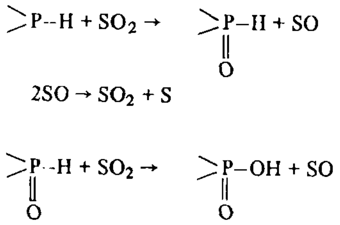
$PH_3 + 2SO_2 = ?(H_3PO_4 + 2S)$ (intractable to work-up).



$$2\,\underset{PH}{CH_2{-}CH_2} + 2SO_2 = CH_2{:}CH_2 + \text{polymer}$$

Apart from the phosphiran reaction, which is difficult to interpret because of the known high reactivity of phosphiran towards polymerization and ethylene elimination with a wide variety of Lewis acids[4,12] the reactions fit into a pattern. The predominant product is the most fully oxidized phosphorus–containing acid that can be derived from the starting material without cleaving carbon-phosphorus bonds. The oxygen of the sulfur dioxide is fully utilized in forming phosphorus-oxygen bonds, while the sulfur may be reduced to the elemental state, or be utilized in forming phosphorus-sulfur bonds.

It is certainly premature to speculate extensively on the mechanisms of these reactions, but one interesting possibility is indicated in the following scheme:



$$>P{-}H + SO_2 \rightarrow\ >\underset{\underset{O}{\|}}{P}{-}H + SO$$

$$2SO \rightarrow SO_2 + S$$

$$>\underset{\underset{O}{\|}}{P}{-}H + SO_2 \rightarrow\ >\underset{\underset{O}{\|}}{P}{-}OH + SO$$

The reactive sulfur monoxide, which is known to undergo disproportionation to sulfur and oxides of sulfur,[13] may be involved as an intermediate in these reactions, and we are currently beginning some electron spin resonance experiments to see if it can be detected.

EXPERIMENTAL

Volatile materials were handled in a conventional vacuum line. Non-volatile compounds were handled in dry nitrogen. Nmr spectra were determined on a Varian A-60 spectrometer; infrared spectra were recorded on Beckman IR-5 and IR-12 spectrometers.

Trimethylphosphine,[5] diphenylphosphine,[6] phenylphosphine[7] and phosphiran[4] were prepared by published procedures.

Trimethylphosphine and sulfur dioxide

A mixture of trimethylphosphine (0.270 g, 3.54 mmole) and sulfur dioxide (3.87 mmole) was held at room temperature for 16 hr in a 20 ml sealed thick-walled tube. The tube was then opened and unreacted sulfur dioxide (2.61 mmole) was separated from the white, solid residue. The ^1H nmr spectrum of a $CDCl_3$ solution of the residue showed only two doublets, the first at chemical shift $\delta = 1.53, J_{HCP} = 13.1$ Hz (relative intensity 2) assigned to trimethylphosphine oxide (literature values[7] for a D_2O solution, $\delta = 1.93, J = 13.4$ Hz); and the second at $\delta = 1.78, J = 13.2$ Hz (relative intensity 1) assigned to trimethylphosphine sulfide (literature values[7] for $CDCl_3$ solution, $\delta = 1.74, J = 13.0$ Hz). The infrared spectrum of the product confirmed its formulation as a mixture of these two compounds.[8]

Diphenylphosphine and sulfur dioxide

Diphenylphosphine (0.513 g, 2.76 mmole) and sulfur dioxide (5.77 mmole) were held at room temperature for 20 hr in a sealed tube. Then unreacted sulfur dioxide (4.45 mmole) was separated from the white, solid product. The bulk of the product was soluble in isopropanol. Evaporation of the isopropanol solution yielded a white solid which was identified by its infrared spectrum ($\bar{\nu}$ at 2600, 2200, and 1660 cm^{-1}) as diphenylphosphinic acid[9] (0.230 g, 1.05 mmole). An authentic sample of the acid was prepared for comparison by treatment of diphenylphosphinous chloride with hydrogen peroxide solution.

The residual solid, insoluble in isopropanol, was identified as tetraphenyldiphosphine disulfide (0.26 g, 0.60 mmole) and had mp 168–170° (from ethanol) (lit.[10] mp 170–172°). This compound was further characterized by its ir spectrum and by elemental analysis. Found: C, 66.1; H, 5.08%. Calc. for $(C_6H_5)_4P_2S_2$, C, 66.4; H, 4.60%.

Phenylphosphine and sulfur dioxide

Phenylphosphine (0.390 g, 3.55 mmole) and sulfur dioxide (7.80 mmole) were warmed to room temperature in a sealed Pyrex tube. Reaction occurred before room temperature was reached: a yellow powder and a white solid were produced. The tube was left at room temperature for 16 hr and was then opened, and unreacted sulfur dioxide (2.66 mmole) was recovered. The product mixture was extracted with boiling carbon disulfide. The solid residue (0.540 g, 3.42 mmole) was identified by its infrared spectrum as phenylphosphonic acid.[11] Evaporation of the carbon disulfide solution yielded elemental sulfur (0.15 g, 4.7 mmole).

Phosphine and sulfur dioxide

Phosphine (17.73 mmole) and sulfur dioxide (16.99 mmole) were held at room temperature in a sealed heavywall tube for 16 hrs. The formation of a large amount of a yellow solid and some orange-colored solid was observed. On opening the tube, 8.85 mmole of unreacted phosphine was recovered. The non-volatile products proved intractable.

Phosphiran and sulfur dioxide

Phosphiran (1.66 mmole) and sulfur dioxide (1.68 mmole) were warmed to 0° in a sealed Pyrex tube. Soon after reaching 0°, the mixture formed a yellow solution, then started to bubble and foam, and finally the yellow color disappeared and a white foamy substance was produced. After 20 hr at 0°, the tube was opened, and unreacted sulfur dioxide (0.04 mmole) was found. Ethylene (0.88 mmole) was also found. After removing all the volatiles, a white foamy polymer was left behind, which could not be characterized.

ACKNOWLEDGEMENTS

This work was supported by Public Health Service Grant No. CA-07182 from the National Cancer Institute.

REFERENCES AND NOTES

1. S. I. A. El Sheikh, B. C. Smith and M. E. Sobier, *Angew. Chem. Internat. Ed.* 9, 308 (1970).
2. E. Fluck and H. Binder, *Angew. Chem.* **77**, 381 (1965).
3. B. C. Smith and G. H. Smith, *J. Chem. Soc.* 5516 (1965).
4. R. I. Wagner, L. D. Freeman, H. Goldwhite and D. G. Rowsell, *J. Am. Chem. Soc.* **89**, 1102 (1967).
5. F. G. Mann and A. F. Wells, *J. Chem. Soc.* 702 (1938).
6. K. Sasse, Methoden der Organischen Chemie (Houben-Weyl), Vol. XXI/1, Georg Thieme, Stuttgart, 1963.
7. J. B. Hendrickson, M. L. Maddox, J. J. Sims and H. D. Kaesz, *Tetrahedron* **20**, 449 (1964).
8. D. E. C. Corbridge, *Topics in Phosphorus Chemistry*, eds. M. Grayson, E. J. Griffith (Wiley-Interscience N.Y., 1969). Vol. 6, p. 235.
9. J. T. Braunholtz, G. E. Hall, F. G. Mann and N. Sheppard, *J. Chem. Soc.* 868 (1959).
10. K. A. Pollart and H. Y. Harwood, *J. Org. Chem.* **27**, 4444 (1962).
11. L. W. Daasch and D. C. Smith, *Anal. Chem.* **23**, 853 (1951).
12. S. Chan and H. Goldwhite, unpublished observations.
13. P. W. Schenk, *Z. Anorg. Chem.* **233**, 385 (1937).