

**1028. Sulphur Dioxide. Part II.<sup>1</sup> Reactions of Tertiary Phosphines with Sulphur Dioxide**

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Sulphur dioxide reacts vigorously with trimethylphosphine to give trimethylphosphine oxide and sulphur. It reacts slowly with triphenylphosphine to give triphenylphosphine oxide and triphenylphosphine sulphide, but no reaction occurs with phosphorus trichloride under similar conditions. Possible mechanisms are discussed.

SULPHUR DIOXIDE is a well-known reducing agent, but its oxidising properties have received less attention. Some reactions in which tertiary phosphines are oxidised to the quinquivalent state are reported here.

When a mixture of trimethylphosphine and sulphur dioxide is allowed to warm from liquid-air temperature it is observed that immediate reaction occurs on melting. A transient orange brown coloration appears, and disappears completely on warming further to room temperature. This coloration is not reversibly temperature-dependent. The final reaction product consists of a mixture of trimethylphosphine oxide and sulphur. The coloration is almost certainly caused by the presence of disulphur monoxide, an orange solid, which is known to disproportionate into sulphur and sulphur dioxide on warming to room temperature.<sup>2</sup>

Initial reaction between triphenylphosphine and sulphur dioxide gives a bright yellow solid at low temperatures. The colour becomes less intense on warming to room temperature and more intense on cooling. The transient orange-brown colour of disulphur monoxide is not observed. The reaction product obtained after heating the mixture until the yellow thermochroism no longer occurs consists of triphenylphosphine oxide and triphenylphosphine sulphide. No trace of sulphur is found.

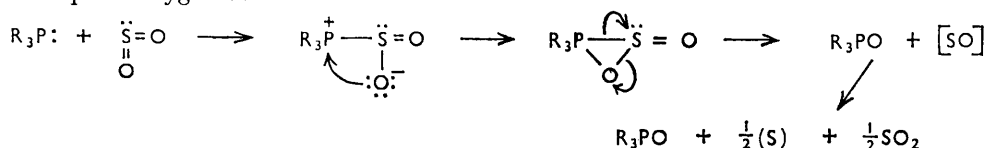
No reaction occurs between phosphorus trichloride and sulphur dioxide, even on heating in a sealed tube at 185° for 7 days.

There are similarities between the reactions described here and the oxidation of

<sup>1</sup> Part I, B. C. Smith and G. H. Smith, preceding Paper.

<sup>2</sup> D. J. Meschi and R. J. Myers, *J. Amer. Chem. Soc.*, 1956, **78**, 6220.

tervalent phosphorus compounds by dimethyl sulphoxide.<sup>3,4</sup> Possible mechanisms for this type of reaction are discussed at length elsewhere.<sup>4</sup> The rate of reaction with sulphur dioxide decreases in the order  $\text{Me}_3\text{P} > \text{Ph}_3\text{P} > \text{PCl}_3$ . This is the order of decreasing donor strength corresponding to decreasing electron supply to phosphorus from the substituents. The first stage of the reaction probably involves nucleophilic attack by phosphorus on sulphur, and this is followed by nucleophilic attack by oxygen on phosphorus. Reaction is completed by concurrent or successive rupture of the phosphorus-sulphur and sulphur-oxygen bonds.



The strong bond formed between trimethylphosphine and sulphur dioxide facilitates rapid nucleophilic attack by oxygen on phosphorus and the rapid formation of trimethylphosphine oxide and "sulphur monoxide" which decomposes further. Triphenylphosphine is a weaker donor which reacts slowly with sulphur dioxide to give triphenylphosphine oxide, and rapidly with the resulting sulphur<sup>5</sup> to give triphenylphosphine sulphide. A similar reaction with selenium dioxide gives a mixture of oxide and selenide.<sup>6</sup>

No reaction is observed with phosphorus trichloride, presumably because of its weak donor properties. It has been shown that thionyl chloride reacts slowly with phosphorus trichloride, and more rapidly with other trivalent phosphorus compounds to give phosphine oxides and phosphine sulphides.<sup>7</sup> Similarly, potassium fluorosulphinate reacts with chlorophosphines to give fluorophosphine oxides and fluorophosphine sulphides.<sup>8</sup>

#### EXPERIMENTAL

Equivalent quantities of phosphine and sulphur dioxide (*ca.* 0.7 mmole) were sealed under vacuum in 10 ml. Pyrex tubes using conventional vacuum-line techniques.

**Trimethylphosphine.**—Trimethylphosphine was generated by heating the complex  $(\text{AgI}, \text{PMe}_3)_4$  *in vacuo*,<sup>9</sup> and was purified by vacuum fractionation. To ensure complete reaction the mixture was heated at 185° (7 hr.). The solid off-white reaction product was separated into its components by vacuum sublimation. The colourless crystalline sublimate was identified as trimethylphosphine oxide, m. p. 136° (lit.,<sup>10</sup> 140–141°), by means of its infrared spectrum. A residue of sulphur was obtained.

**Triphenylphosphine.**—The reaction mixture was heated at 185° (3 days) until the yellow colour disappeared. The products dissolved completely in hot ethanol. Colourless needles of triphenylphosphine sulphide, m. p. 161.5–162.5° (lit.,<sup>11</sup> 161–162°), crystallised on cooling. Addition of water to the mother-liquor gave triphenylphosphine oxide, which recrystallised as colourless plates from aqueous ethanol. The infrared spectra of both compounds were identical to those of authentic samples.

**Phosphorus Trichloride.**—The mixture was heated at 185° (7 days). No reaction was observed and phosphorus trichloride remained unchanged. The infrared spectrum showed no absorption in the region of P=O or P=S stretching frequencies.

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<sup>3</sup> S. K. Ray, R. A. Shaw, and B. C. Smith, *Nature*, 1962, **196**, 372.

<sup>4</sup> E. H. Amonoo-Neizer, S. K. Ray, R. A. Shaw, and B. C. Smith, *J.*, 1965, 4296.

<sup>5</sup> J. I. G. Cadogan, *Quart. Rev.*, 1962, **16**, 208.

<sup>6</sup> N. N. Mel'nikov and M. S. Rokitskaya, *Zhur. obshchei Khim.*, 1933, **211**, 150.

<sup>7</sup> A. C. Poskus and J. E. Herweh, *J. Amer. Chem. Soc.*, 1957, **79**, 6127.

<sup>8</sup> F. Schmutzler, *J. Inorg. Nuclear Chem.*, 1963, **25**, 335.

<sup>9</sup> F. G. Mann, A. F. Wells, and D. Purdie, *J.*, 1937, 1828; E. J. Rosenbaum and C. R. Sandberg, *J. Amer. Chem. Soc.*, 1940, **62**, 1622.

<sup>10</sup> G. W. Fenton and C. K. Ingold, *J.*, 1929, 2342.

<sup>11</sup> W. Strecker and C. Grossman, *Ber.*, 1916, **49**, 63.