

## Oxidation of Phosphorus Trifluoride with Sulphur Trioxide

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Phosphorus trifluoride undergoes oxidation to phosphoryl fluoride with sulphur trioxide or freshly prepared oleum liberating equimolar amounts of sulphur dioxide.

During the course of an investigation on the chemical behaviour of phosphorus trifluoride it has been observed that sulphur trioxide or freshly prepared oleum oxidises phosphorus trifluoride to phosphoryl fluoride releasing an equimolar amount of sulphur dioxide.

Phosphorus trifluoride was prepared by the fluorination of phosphorus trichloride using sodium fluoride in boiling acetonitrile medium<sup>1</sup>. Sulphur trioxide was prepared by distillation of a commercial sample of oleum (25%) *in vacuo* and purified by repeated distillation over phosphorus pentoxide. A fresh sample of oleum was prepared by dissolving sulphur trioxide in sulphuric acid (AR). The "free" sulphur trioxide content of such a sample of oleum was found to be 18% as estimated by the titrimetric method<sup>2</sup>.

Known amounts of phosphorus trifluoride and sulphur trioxide were condensed into an evacuated reaction vessel fitted with vacuum stopcocks and connected to vacuum line. The container was allowed to attain room temperature (25°C). The IR spectrum of the vapour recorded after about 10 min exhibited peaks due to phosphoryl fluoride<sup>3</sup> [473(s), 483(ms), 873(ms), 990(vs), 1415(ms) cm<sup>-1</sup>] and sulphur dioxide<sup>4</sup> [520(s), 1150(s), 1360(s) cm<sup>-1</sup>] whereas the characteristic bands of phosphorus trifluoride<sup>5</sup> [487(m), 831(w), 860(vs), 890(vs) cm<sup>-1</sup>] were absent indicating completion of the reaction. The gaseous products were

Table 1—Oxidation of Phosphorus Trifluoride with Sulphur Trioxide and Oleum

PF <sub>3</sub> (mg) taken	SO <sub>3</sub> (mg) or Oleum (ml) taken	SO <sub>2</sub> (mg)		Oxidation %
		Calc.	Found	
Sulphur trioxide as oxidant				
358.0	325.4	260.4	259.1	99.50
357.0	324.5	259.6	258.3	99.49
359.8	337.0	245.0	244.1	99.60
Oleum as oxidant				
390.2	1.12	283.8	283.0	99.71
384.3	1.10	279.5	279.0	99.81
377.3	1.08	275.0	272.7	99.20

then swept in a current of dry nitrogen and absorbed in 2*N* sodium hydroxide solution. The sulphite content was estimated iodometrically. In a separate experiment the phosphoryl fluoride formed was hydrolysed with 2*N* sodium hydroxide solution and analysed for both phosphorus and fluorine contents. The purity was more than 99%.

The oxidation of phosphorus trifluoride with oleum is found to be rather sluggish at room temperature. However, on warming to 100°C for 30 min, the reaction goes to completion. The products have been analysed as indicated above.

The results of a few typical experiments, presented in Table 1, show that the overall oxidation of phosphorus trifluoride takes place according to Eq. (1).



### References

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