The Triphenylphosphine–Sulphur Trioxide Complex: Confirmation of Structure

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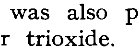
Summary The structure of the triphenylphosphine–sulphur trioxide complex has been established by *X*-ray crystallography which shows that the complex contains a phosphorus–sulphur bond and demonstrates the way in which the sulphur atom is shielded by the three aromatic rings.

Sulphur trioxide readily forms complexes with various nucleophiles, *e.g.* pyridine[1] and *NN*-dimethylformamide.[2] These complexes are valuable reagents, acting as sources of 'moderated' sulphur trioxide,[3] and may be used for the sulphonation of reactive heterocycles and the activation of amino-acid carboxy-groups in peptide synthesis.[4]

Our attention was focussed on the previously described complex formed between sulphur trioxide and triphenylphosphine.[5] The complex was prepared both by the original method and by reaction of triphenylphosphine with chlorosulphonic acid in dioxan.[4] The new method of preparation gave a product of slightly higher melting point (196 °C) than that observed previously (191 °C).[5] As has been described elsewhere the complex has been used for carboxyl activation,[4] through the mixed carboxylic sulphuric anhydride, to prepare methionine enkephalin and the C-terminal tetrapeptide of gastrin.

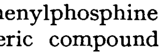
Recently we have found that the reagent may also be effectively used for the sulphonation of indole and pyrrole giving indole-3-sulphonic acid (71% yield) when using pyridine as solvent and pyrrole-2-sulphonic acid (42%; isolated as the barium salt). Dichloromethane was unsuitable as a solvent since it could not form an intermediate SO_3 complex and our work with carboxyl activation has shown that intermediate complex formation is important if good yields are to be obtained.

The two structures (**1**) and (**2**) are both feasible for the $Ph_3P.SO_3$ complex, the former being that originally assigned by Becke-Goehring and Thielmann.[5] Our present work immediately ruled out the possibility of two species being present as the ^{31}P n.m.r. spectrum showed only one signal at δ $-19{\cdot}6$ p.p.m. (downfield of H_3PO_4 external standard) in CD_2Cl_2.



$Ph_3\overset{+}{P}{-}SO_3^-$

(**1**)



$Ph_3\overset{+}{P}{-}O{-}SO_2^-$

(**2**)

The complex is unexpectedly resistant to hydrolysis, requiring a 3-day reflux in aqueous acetonitrile to effect complete hydrolysis. The hydrolysis gives almost exclusively triphenylphosphine with traces of the corresponding oxide. This behaviour is in marked contrast to that of a closely related compound of identical empirical formula which was also prepared from triphenylphosphine and sulphur trioxide. This second, isomeric compound was stable only at low temperatures (−78 °C) and decomposed immediately on warming to 0 °C.[6]

On heating the complex *in vacuo* to 170 °C, sulphur dioxide and triphenylphosphine oxide are the sole products. Also, the electron impact mass spectrum shows only peaks associated with sulphur dioxide and triphenylphosphine oxide[7] (*m/e* 278, $C_{18}H_{15}OP$; 277, $C_{18}H_{14}OP$; 262, $C_{18}H_{15}P$; 261, $C_{18}H_{14}P$; 64, SO_2).

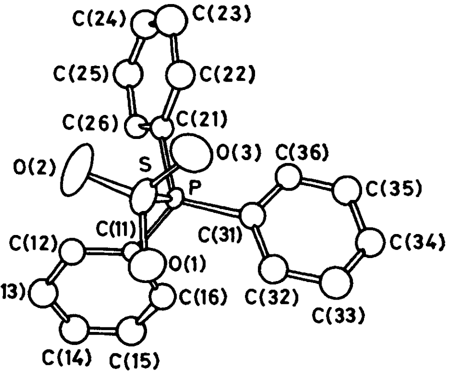


FIGURE. X-ray crystal structure of $\mathrm{Ph_3\overset{+}{P}{-}SO_3^-}$.

Crystal data: $C_{18}H_{15}O_3PS$, M^+ 342, monoclinic, space group $P2_1/c$, a = 11·024, b = 9·205, c = 19·181 Å, β = 124·44°, U = 1605 Å^3, Z = 4, D_c = 1·41 g cm^{-3}. Intensity data were recorded on a Hilger and Watts Y290 computer-controlled four-circle diffractometer.†

The hydrolysis evidence was therefore ambiguous and the other experimental observations supported structure (**2**) for the complex. We therefore resorted to an X-ray crystallographic study[8] to solve the structural problem.

The result shown in the Figure leaves no doubt that the complex has structure (**1**) and that a P–S bond is present.

The structure shows a 'propeller-like' arrangement of aromatic rings with the sulphur–oxygen bonds staggered with respect to the bonds between the phosphorus and the phenyl rings. Thus the unstable compound of similar formulation mentioned above[6] may well have the alternative P–O–S bonding arrangement shown in structure (**2**). The complex (**1**) clearly owes much of its stability to the fact that the sulphur trioxide is shielded on one side from the majority of nucleophiles, and it is therefore particularly useful as a source of 'moderated' sulphur trioxide.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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