

Sulphur Dioxide Complexes of Platinum Metals

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SULPHUR DIOXIDE complexes of ruthenium have been known for many years;¹ more recently similar complexes of rhodium and iridium have been reported.² Structural studies³ establish that metal-sulphur dioxide co-ordination occurs through the sulphur atom in these compounds. Although it has been postulated that catalytic oxidation of sulphur dioxide at platinum surfaces involves chemisorption of the gas on the metal,⁴ no complexes containing sulphur dioxide co-ordinated to platinum or palladium have been isolated.

We now report the preparation of sulphur dioxide complexes of platinum and palladium and their ready oxidation to sulphato-complexes by molecular oxygen.

Oxygen-free benzene solutions of tetrakis(triphenylphosphine)platinum(0) react instantly with sulphur dioxide at 25° to give red-brown solutions from which the complex $\text{Pt}(\text{SO}_2)(\text{PPh}_3)_3 \cdot x\text{C}_6\text{H}_6$, ($x \simeq 1.5$) (A) rapidly crystallises in excellent yield, as dark purple, air-sensitive needles. The infrared spectrum of (A) shows bands assigned to co-ordinated sulphur dioxide² (1195 and 1045 cm^{-1}) and triphenylphosphine together with a strong band at 677 cm^{-1} attributed to benzene. Other bands due to benzene are masked by the spectrum of the triphenylphosphine ligands. (A) retains benzene after prolonged pumping (10^{-4} mm., 25°), but loses it readily on washing with diethyl ether. The resultant red-brown, benzene-free, complex $\text{Pt}(\text{SO}_2)(\text{PPh}_3)_3$ (B), in marked contrast to (A),

oxidises only slowly in air at 25°. The infrared spectrum of (B) contains no band at 677 cm^{-1} but is otherwise identical with that of (A).

On heating *in vacuo* at 100–120°, (A) rapidly loses benzene then, more slowly, sulphur dioxide to yield tris(triphenylphosphine)platinum(0). (A), on exposure to air for 24 hr. at 25°, or 1 hr. at 100°, is oxidised to the sulphato-complex $\text{Pt}(\text{SO}_4)(\text{PPh}_3)_2$ (C), (m.p. 265° with decomp.) identical with an authentic specimen.⁵ The infrared spectrum of (C) shows strong broad bands at 1280, 1155, 885, and 655 cm^{-1} attributable to the sulphate ligand. Oxygen-saturated solutions of tetrakis(triphenylphosphine)platinum(0) react immediately with sulphur dioxide to give pale yellow solutions from which the sulphato-complex (C) crystallises directly.

Solutions of tetrakis(triphenylphosphine)palladium(0) in oxygen-free benzene react with sulphur dioxide to yield the air-stable, purple-red complex

$\text{Pd}(\text{SO}_2)(\text{PPh}_3)_3$. In presence of excess of oxygen this reaction yields the known yellow sulphato-complex $\text{Pd}(\text{SO}_4)(\text{PPh}_3)_2$.⁶ The infrared spectra of these palladium complexes are similar to those of their platinum analogues.

The sulphur dioxide complexes dissolve in oxygen-free chloroform to give yellow solutions; osmometric molecular weight data for these solutions indicate that extensive dissociation has occurred. (*e.g.*, calc. for $\text{Pt}(\text{SO}_2)(\text{PPh}_3)_3$, 1046; found, 568.) Similar dissociation has been reported⁷ for tris(triphenylphosphine)platinum(0). Satisfactory analytical data have been obtained for all compounds mentioned.

Further work is in progress on the reactivity of these sulphur dioxide complexes and on the reactions of sulphur dioxide and related ligands with other complexes of nickel, palladium, and platinum.

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