

## The (4+) Oxidation State in Simple Palladium Compounds

By C. C. ADDISON and B. G. WARD

(Department of Chemistry, The University, Nottingham)

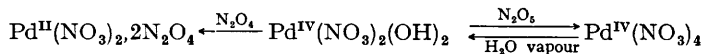
THE (4+) oxidation state in palladium is well known in complexes, but evidence for the Pd<sup>IV</sup> state in simple compounds is restricted to the unstable hydrated dioxide and chalconides in which the oxidation state is doubtful. We now report some reactions which suggest that the (4+) oxidation state may play a much more important part in palladium chemistry than has hitherto been assumed.

The product available commercially as palladium(II) nitrate was mixed with an excess of di-nitrogen pentoxide at -78°. On warming to room temperature, a brown viscous liquid was formed; within 24 hours brown plate-like crystals separated, the analysis of which corresponded precisely with the formula Pd(NO<sub>3</sub>)<sub>4</sub>. The compound is diamagnetic. This is the first simple salt of Pd<sup>IV</sup> to be prepared, and the first instance in which a metal has been found to form anhydrous nitrates in two oxidation states.

Formulation of the product as the adduct Pd(NO<sub>3</sub>)<sub>2</sub>·N<sub>2</sub>O<sub>5</sub> is dismissed by its inertness towards hydrocarbons, and the absence of NO<sub>2</sub><sup>+</sup>

bands in the infrared spectrum, which is nevertheless more complex than those of Sn(NO<sub>3</sub>)<sub>4</sub><sup>1</sup> and Ti(NO<sub>3</sub>)<sub>4</sub>.<sup>2</sup> No nitrate ions are present, and bridging nitrate groups no doubt account for the lack of volatility in the compound. The n.m.r. spectra of solutions in deuterated dimethyl sulphoxide confirm the absence of hydrogen in the product, and thus eliminate the formulation Pd(NO<sub>3</sub>)<sub>2</sub>·2HNO<sub>3</sub>. Palladium tetranitrate gives a yellow acid solution in water, which does not oxidise the ferrous ion but releases iodine from potassium iodide quantitatively according to the reaction Pd<sup>4+</sup> + 2I<sup>-</sup> → Pd<sup>2+</sup> + I<sub>2</sub>. On neutralisation with four equivalents of borax, a hydrated oxide is precipitated which also oxidises iodide.

Crystallisation from a solution obtained by dissolving palladium metal in nitric acid gives a product represented in most modern texts as Pd(NO<sub>3</sub>)<sub>2</sub>. However, the analysis, infrared and n.m.r. spectra, and oxidising properties indicate that this product is the Pd<sup>IV</sup> compound Pd(NO<sub>3</sub>)<sub>2</sub>·(OH)<sub>2</sub>. This is reduced by N<sub>2</sub>O<sub>4</sub> but not by N<sub>2</sub>O<sub>5</sub>, and the reaction can be represented as



(Received, February 15th, 1966; Com. 094.)

<sup>1</sup> C. C. Addison and W. B. Simpson, *J. Chem. Soc.*, 1965, 598.

<sup>2</sup> B. O. Field and C. J. Hardy, *J. Chem. Soc.*, 1963, 5278.