

SHORT COMMUNICATIONS

A Coordination Compound between Vanadium Oxytrichloride and Triphenyl Phosphine

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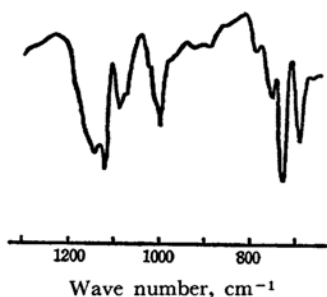
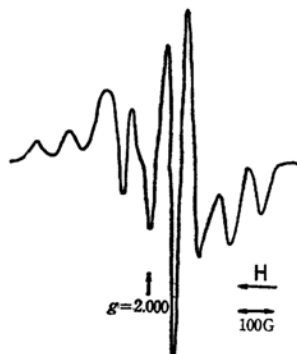
While various kinds of coordination compounds of vanadium oxytrichloride (VOCl_3) have been reported,¹⁾ any compound between VOCl_3 and triphenyl phosphine (PPh_3) has not been synthesised. The authors found the formation of this compound in the course of a study on the catalytic action of VOCl_3 .²⁾ When VOCl_3 was added to petroleum ether solution of PPh_3 , red brown powders precipitated at room temperature. The elemental analysis of this precipitate after purification showed that the composition of this compound was $\text{VOCl}_3\text{PPh}_3$ (Found: V, 11.81; Cl, 23.66; C, 49.75; H, 4.24%. Calcd: V, 11.91; Cl, 24.43; C, 49.52; H, 3.45%).

This compound melts with partial decomposition at a temperature higher than 210°C . At room temperature it is decomposed by moisture, but is stable in dry oxygen. It is soluble in tetrahydrofuran, but is insoluble in carbon tetrachloride and *n*-hexane.

Infrared spectrum of VOCl_3 has a sharp absorption at 1035 cm^{-1} due to the stretching vibration of $(\text{V}=\text{O})^{3+}$ ³⁾ and the center of this peak shifts to 1000 cm^{-1} in the case of $\text{VOCl}_3\text{PPh}_3$ as shown in Fig. 1. This red shift reveals that an increase of electron density on vanadium ion is caused by coordination of PPh_3 . This increase of electron density on vanadium ion is ascertained also by the ESR

measurement.

Vanadium oxytrichloride does not show any ESR signal, but $\text{VOCl}_3\text{PPh}_3$ shows an ESR spectrum with h.f.s. similar to that of $(\text{V}=\text{O})^{2+}$ in vanadium oxy-sulfate supported on γ -alumina⁴⁾ (Fig. 2). When triphenylphosphine was added to $\text{VOCl}_3\text{PPh}_3$ suspended in carbon tetrachloride at 10 – 25°C , oxygen was rapidly absorbed and triphenyl phosphine oxide was catalytically produced. Further kinetic studies for this oxidation reaction are in progress.

Fig. 1. Infrared spectrum of $\text{VOCl}_3\text{PPh}_3$ (Nujol).Fig. 2. ESR spectrum of $\text{VOCl}_3\text{PPh}_3$ at room temperature.

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