Tetramethyloxorhenium(VI), A Paramagnetic d^1 Alkyl

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Summary The interaction of oxotrichlorobis(triphenylphosphine)rhenium(V) or oxotetrachlororhenium (VI) with methyl-lithium gives an air-sensitive but thermally very stable red-purple crystalline solid whose spectroscopic and other properties show it to be $ReOMe_4$.

IN 1934, Druce claimed to have isolated a volatile trimethylrhenium by interaction of rhenium trichloride with methylmagnesium iodide,[1] but this work could not be repeated by Gilman *et al.*[2] In view of the stability of hexamethyltungsten[3] there was good reason to expect rhenium methyls and other elimination stabilized alkyls[4] to be isolatable. A number of such compounds have now been isolated[5] from halides or halide complexes of rhenium-(III), -(IV), -(V) and -(VI) but the most interesting is the rhenium(VI) methyl, $ReOMe_4$. This was initially obtained by interaction of methyl-lithium and $ReOCl_3(PPh_3)_2$ in diethyl ether at −35° in yields > 50% but it is best made from $ReOCl_4$.

The extremely air-sensitive red-purple crystalline compound, m.p. 44°, has been characterised by its mass spectrum which at 16 eV shows the parent ion for $[ReOMe_4]^+$ with the correct isotopic patterns for rhenium, and fragmentation ions $[ReOMe_n]^+$ ($n = 3,2,1$) resulting from loss of methyl groups. The i.r. spectrum in solution, or in an argon lattice at 20 K,[6] shows a strong band due to the Re=O stretch at 1016 cm^{-1}, while the characteristic C–H vibrations indicate a fairly high symmetry for the molecule; two bands at 529 and 553 cm^{-1} can be assigned as Re–C vibrations.

The compound is paramagnetic and the e.s.r. spectrum in frozen benzene at −175° shows hyperfine structure. There is one set of six lines with unequal spacing typical of interaction with one rhenium nucleus, but the spectrum is too complex to permit confident extraction of Hamiltonian parameters; it is however consistent with an $S = \frac{1}{2}$ system of near axial symmetry. Above −150° the spectrum loses the hyperfine structure, collapsing to one typical of $S = \frac{1}{2}$ with axial symmetry, $g_{\parallel} = 2{\cdot}25$ and $g_{\perp} = 1{\cdot}94$. At higher temperatures further collapse gives a weak, broad, structureless line, presumably due to fast relaxation through a low-lying excited state. These data are consistent with a square base pyramidal structure (C_{4v}) for $ReOMe_4$ at −175° which interconverts with probably a trigonal bypyramidal one (C_{3v}) at higher temperatures; fluxional behaviour is to be expected for a 5-co-ordinate species. The electronic absorption spectrum, which shows a strong band at 560 nm and an intense asymmetric band at 280 nm, as well as the photoelectron spectrum,[6] are consistent with the proposed structure.

The compound is thermally stable in the vapour to *ca.* 150 °C and is unreactive in solution at 25° being unaffected by water, alcohols, H_2, CO, SO_2, tetramethylthiuram disulphide, *etc.* Iodine yields methyl iodide quantitatively and both O_2 and NO react very rapidly.

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