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Infrared Spectroscopic Studies on Vaska Complex using Heavy Oxygen

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Recently several transition metal complexes coordinated with molecular oxygen have been described.[1-5] With respect to iridium metal in particular, the reaction of the species having the general formula $[Ir(p\text{-}p)_2]Cl$ and $IrXCO(PPh_3)_2$ (p-p: $Ph_2PCH_2CH_2PPh_2$, X: halide) with molecular oxygen has been studied in detail.[6,7] The structures of these iridium complexes have been made clear by X-ray analysis.[8,9]

In Vaska iridium oxygen complex, ($IrClCO(PPh_3)_2O_2$), the strong IR absorption spectrum at 856 cm^{-1} is ascribed to the peroxy-vibration,[1] but no definite assignment has been made. Hirota and his coworkers[10] studied the spectra of the peroxy-complexes, $Ni(Bu^tNC)_2O_2$ and $Pd(Bu^tNC)_2O_2$ and observed three bounds due to ^{16}O–^{16}O, ^{16}O–^{18}O and ^{18}O–^{18}O.[10]

In order to investigate the nature of chemical bonds of the iridium complexes, we have studied the IR and FIR (far infrared) spectra of Vaska oxygen complex containing heavy oxygen molecule.

The iridium oxygen complex containing heavy oxygen was prepared by the reaction of $IrClCO(PPh_3)_2$ complex and heavy oxygen (25.5% as $^{18}O_2$) at 170 mmHg for 45 hr. The IR spectrum of the complex in Nujol mulls is shown in Fig. 1. The IR band at 856 cm^{-1} splites into three strong absorption bands at 856, 832 and 808 cm^{-1}. Since the iridium oxygen complex contains three molecular species such as ^{16}O–^{16}O, ^{16}O–^{18}O and ^{18}O–^{18}O, the calculation on the assumption of free diatomic molecules gives wave numbers to be 856, 832 and 807 cm^{-1}. A good agreement between the observed wave numbers and those calculated shows that the band at 856 cm^{-1} which has been reported by Vaska[1] is clearly assignable to the stretching vibration of the O–O bond.

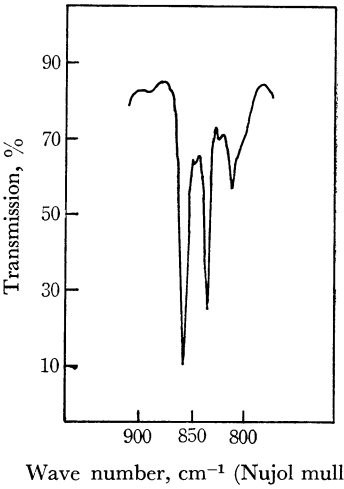

Fig. 1. Infrared spectrum of the iridium oxygen complex.

By measuring the relative intensity of the three bands at 856, 832 and 808 cm^{-1}, these bands are ascribed to such molecular species as ^{16}O–^{16}O, ^{16}O–^{18}O and ^{18}O–^{18}O, respectively. The shoulders at 843 cm^{-1} and 820 cm^{-1} are assignable to the stretching vibration of ^{16}O–^{17}O and ^{17}O–^{18}O, respectively, in comparison with the calculated.

The FIR spectra of Vaska complexes were reported already by Bennett *et al.*,[11] but those of Vaska oxygen complexes are not known and were measured accordingly.

The FIR spectrum of this oxygen adduct shown in Fig. 2 indicates that the very strong band assignable to the stretching vibration of Ir–Cl bond[11] shifts from 318 to 314 cm^{-1} and that a band at 184

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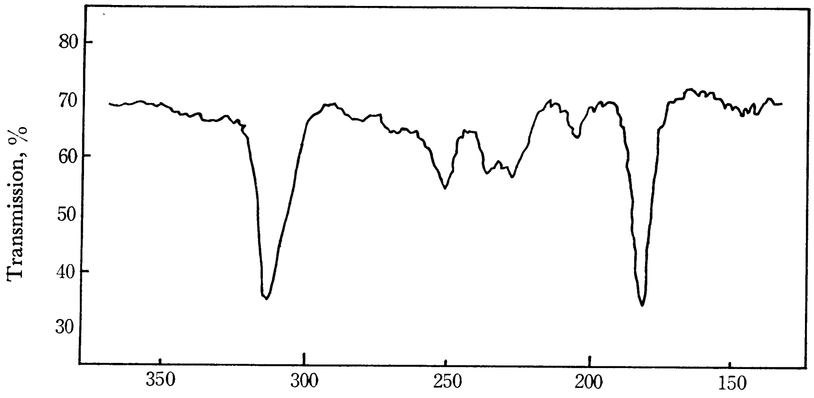

Wave number, cm^{-1} (Nujol mulls)

Fig. 2. Far infrared spectrum of the iridium oxygen complex.

cm^{-1} shifts to 182 cm^{-1} when heavy oxygen was used.

The stretching band of Ir–O bond which is expected in the region of 450—600 cm^{-1} can not be detected due to overlapping of the strong bands of triphenylphosphine ligand.

In addition, we have found that the oxygen complexes can easily cause the oxidation reaction of olefins under mild condition.[12)]

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