

THE SOLID-STATE DEOXYGENATION OF DIOXYGENCARBONYLCHLOROBIS(TRIPHENYLPHOSPHINE)IRIDIUM(I)

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Summary

The thermal deoxygenation of solid $\text{IrO}_2\text{COCl}(\text{PPh}_3)_2$ in nitrogen has been studied, and the rate-controlling step between 379–397 K was found to be one of nucleation and growth of product, with an activation energy of 232 kJ mol^{-1} . There is then a change of mechanism and between 405 and 425 K a phase boundary mechanism is rate-controlling, with an activation energy of 180 kJ mol^{-1} . Some results obtained for the reaction under varying partial pressures of oxygen illustrate the balance between the known thermal and photochemical decompositions.

Introduction

Oxidative addition reactions of *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ have been widely studied. The formation and decomposition of the oxygen adduct have been studied, principally by Vaska [1]. His work showed that two deoxygenation reactions occurred, namely thermal decomposition, producing gaseous oxygen and the original d^8 complex, and photochemical decomposition, which is rapid in the presence of gaseous oxygen, and results in the formation of triphenylphosphine oxide and a Ir^{IV} species. The enthalpy of decomposition of the solid adduct has been measured by Ashcroft and Mortimer [2] using the method of dynamic calorimetry.

The present work is an investigation into the mechanism of the deoxygenation reaction, and follows a previous publication [3] on the hydrogen chloride adducts.

Experimental

$\text{IrCOCl}(\text{PPh}_3)_2$ was prepared by the method of Collman and Kang [4], and

the oxygen adduct was prepared from this by reaction with gaseous oxygen in benzene solution. Infrared absorption (Nujol mull) gave peaks [1] at 1995 cm^{-1} [$\nu(\text{C}-\text{O})$] and 855 cm^{-1} [$\delta(\text{Ir}-\text{O})$]. X-ray fluorescence analysis of samples diluted with borax gave Ir contents of 24.5% for the original complex [$\text{IrCOCl}(\text{PPh}_3)_2$ calcd.: 24.6%] and 23.4% for the oxygen adduct [$\text{IrO}_2\text{COCl}(\text{PPh}_3)_2$ calcd.: 23.7%].

Microscopic examination. The original Vaska's compound appeared as yellow plates, the majority of which were $20\text{ }\mu\text{m} \times 30\text{ }\mu\text{m}$ with relatively few much larger. The adduct was orange in colour, also occurring as plates, but much smaller in size ($20\text{ }\mu\text{m} \times 15\text{ }\mu\text{m}$) with a tendency to clump together. Attempts were made to follow the reaction microscopically to confirm the kinetic evidence, but these were unsuccessful, because no means could be found to detect the boundary between the reactant and product phases.

Kinetic measurements. Weight-loss vs. time measurements were made using a C.I. microforce balance and recorder, and the all-glass apparatus was designed so that a stream of pre-heated dry nitrogen ($25\text{-}28\text{ ml min}^{-1}$) could be passed over the sample; constant temperatures were maintained by boiling solvents. Sample weights were always $25\text{ mg} \pm 10\%$, and infrared spectra were taken of reaction products.

The weight-loss data were converted to fraction reacted (α) by assuming a theoretical weight-loss of 3.95%, corresponding to the loss of one mole of oxygen per mole of adduct. A few runs were made to very long times and α values of between 0.98 and 0.99 could be reached. The time scale was made dimensionless by using the concept of "reduced time", i.e. the ratio of the time to reach a given value of α to that ($t_{0.5}$) required to reach $\alpha = 0.5$. Graphs of α vs. $t/t_{0.5}$ were constructed and compared with similar plots calculated from equations which described possible rate controlling steps. These covered the three main possibilities of oxygen diffusion, nucleation of product, or growth of the interphase boundary. Additional geometric growth factors gave nine theoretical equations [5] for comparison. These equations are all of the form $F(\alpha) = kt$, where $F(\alpha)$ describes the particular mechanism followed. Comparison of experimental and theoretical reduced time plots allows the form of $F(\alpha)$ to be determined. Rate constants could then be calculated and used to determine Arrhenius parameters.

Results

Two rate-controlling steps were observed in the decomposition in nitrogen, depending on the temperature range studied. The low temperature (379-397 K) runs followed the Avrami-Erofeyev equation ($n = 2$):

$$[-\ln(1-\alpha)]^{\frac{1}{2}} = kt$$

and a comparison of theory and experiment is shown in Fig. 1. Rate constants derived using this equation gave an Arrhenius plot from which the activation energy and frequency factor were calculated to be 232 kJ mol^{-1} and $10^{21.4}\text{ sec}^{-1}$, respectively.

The best fit in the high temperature range (405-422 K) was in terms of the

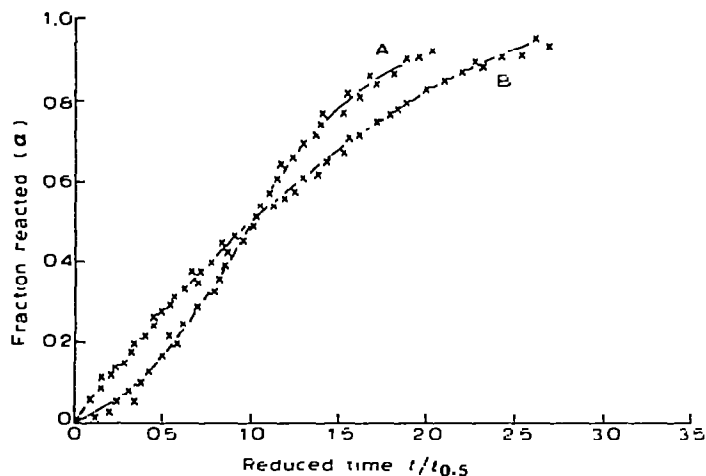


Fig. 1. Comparison of experimental A: Avrami-Erofeyev equation, and theoretical B: contracting disc equation, curves.

contracting disc equation:

$$1 - (1 - \alpha)^{\frac{1}{2}} = kt$$

and data are included in Fig. 1. The activation energy and frequency factor calculated from these results were 180 kJ mol^{-1} and $10^{14.2} \text{ sec}^{-1}$, respectively.

Discussion

The Arrhenius parameters show that the nucleation process has a much higher activation energy (i.e. temperature coefficient) than the growth process. It is therefore to be expected that the rate-controlling step should change as the temperature is raised, since the rate of the nucleation process increases more rapidly than that of the lower energy process. It is satisfying that this expected

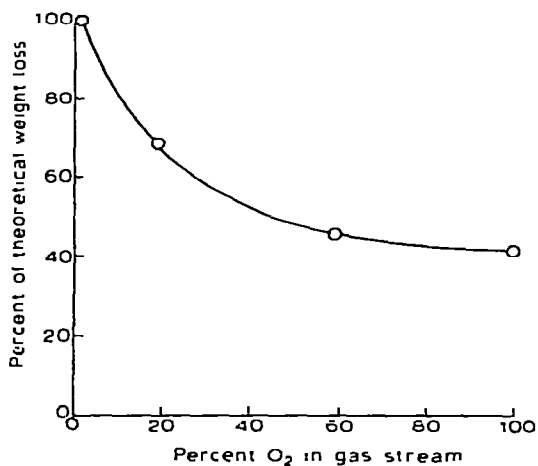


Fig. 2. Effect of oxygen pressure on weight loss at 405 K.

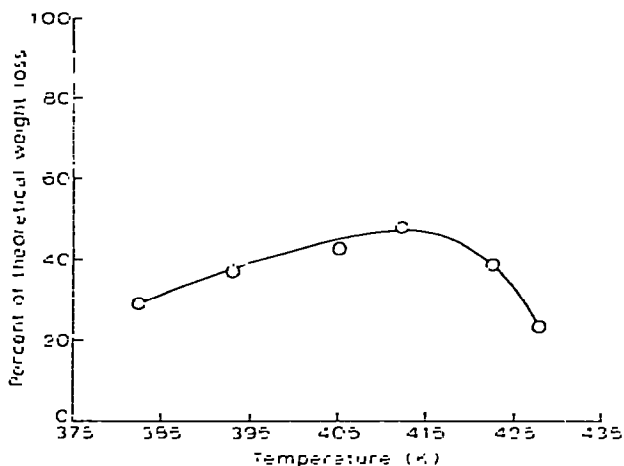


Fig. 3. Effect of temperature on weight loss in pure oxygen.

change in mechanism has been observed in this case. The high frequency factors for the nucleation and growth process suggest a bimolecular bulk process rather than a surface reaction [6], and the formal geometry of both rate-controlling steps is in agreement with the observed morphology of both reactant and product.

The activation energy for the phase boundary reaction (180 kJ mol^{-1}) when combined with the reaction enthalpy measured by Ashcroft and Mortimer [2] (-97 kJ mol^{-1} at 414 K), suggests an activation energy for the forward reaction, i.e. the pick-up of atmospheric oxygen by Vaska's compound, of about 280 kJ mol^{-1} .

The results obtained from the runs carried out under oxygen are illustrated in Figs. 2 and 3, and are best interpreted as describing a balance between the thermal deoxygenation reaction, which is favoured in nitrogen, and the photochemical decomposition studied by Vaska [1], which is increasingly favoured as the oxygen pressure is increased (Fig. 2). The shape of Fig. 3 is determined by the temperature-dependence of the photochemical oxidation and the sublimation of triphenylphosphine oxide. This latter step was confirmed by IR analysis of the sublimate collected on a cold finger.

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