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# THE THERMOCHEMISTRY OF ADDUCTS OF OXYGEN AND SULPHUR DIOXIDE WITH CHLOROCARBONYLBIS(TRIPHENYLPHOSPHINE)-IRIDIUM(I)

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## SUMMARY

The enthalpies of removal of $O_2$ from $(O_2)Cl(CO)(PPh_3)_2Ir$ and $SO_2$ from $(SO_2)Cl(CO)(PPh_3)_2Ir$ have been measured by differential scanning calorimetry: 40 kJ are required to break the Ir–$SO_2$ bond and 130 kJ are required to break each Ir–O bond in the crystalline complexes at 298° K. The breaking of the Ir–O bonds is immediately followed by the formation of molecular oxygen from the released peroxide radical leading to an overall exothermic process.

## INTRODUCTION

Recent interest in synthetic oxygen-carrying complexes has been prompted by investigations into the mode of action of hemoglobin. For a short review see ref. 1.

One widely studied[2] complex is the square planar chlorocarbonylbis(triphenylphosphine)iridium(I) which, in benzene or toluene solution, reversibly absorbs molecular oxygen and other molecules. The crystalline oxygen and sulphur dioxide adducts have been the subjects of X-ray structure analysis and show several features which should also be apparent in the strengths of the metal–ligand bonds.

The oxygen adduct[3] has an octahedral structure in which the oxygen molecule, apparently bonded as a peroxide or as a $\pi$ complex, lies in the same plane as the chlorine and carbonyl groups. On the other hand the sulphur dioxide adduct[4] has a tetragonal pyramidal structure in which the sulphur dioxide molecule is attached to the iridium atom by an unusually long Ir–S bond.

The present calorimetric investigation of the quantitative removal of the oxygen or sulphur dioxide ligand was undertaken to determine the strength of bonding of these molecules in the complexes.

## RESULTS AND DISCUSSION

Calorimetric measurements of the enthalpies of reactions (1) and (2) are

$$(O_2)Cl(CO)(PPh_3)_2Ir\ (\text{cryst.}) \rightarrow Cl(CO)(PPh_3)_2Ir\ (\text{cryst.}) + O_2\ (g) \qquad (1)$$

$$(SO_2)Cl(CO)(PPh_3)_2Ir\ (\text{cryst.}) \rightarrow Cl(CO)(PPh_3)_2Ir\ (\text{cryst.}) + SO_2\ (g) \qquad (2)$$

reported in Table 1. The values of $\Delta H$ refer to the peak temperature during the reac-

TABLE 1

ENTHALPIES OF THERMAL DECOMPOSITION IN kJ/mol

| Complex | Reaction | $T_i$ (°K) | $T_p$ (°K) | $T_f$ (°K) | $\Delta H$ at $T_p$°K | $\Delta H$ at 298°K | Wt. loss (%) | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | Calcd. | Found |
| $(O_2)Cl(CO)(PPh_3)_2Ir$ | (1) | 402 | 414 | 425 | $-97\pm4$ | $-92\pm4$ | 3.9 | 3.9 |
| $(SO_2)Cl(CO)(PPh_3)_2Ir$ | (2) | 419 | 457 | 478 | $+35\pm1$ | $+40\pm1$ | 7.6 | 7.9 |

TABLE 2

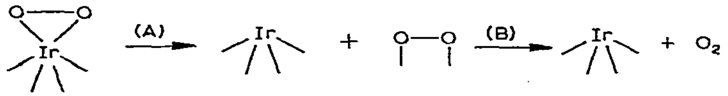
HEAT CAPACITIES OF COMPLEXES IN $J \cdot mol^{-1} \cdot deg^{-1}$

| Temp. (°K) | $C_p$ $Cl(CO)(PPh_3)_2Ir$ | $C_p$ $(O_2)Cl(CO)(PPh_3)_2Ir$ | $C_p$ $(SO_2)Cl(CO)(PPh_3)_2Ir$ |
|---|---|---|---|
| 298 | 925 | 937 | 1046 |
| 300 | 929 | 941 | 1050 |
| 310 | 941 | 962 | 1067 |
| 320 | 950 | 983 | 1084 |
| 330 | 962 | 1004 | 1100 |
| 340 | 975 | 1025 | 1117 |
| 350 | 987 | 1042 | 1130 |
| 360 | 1000 | 1063 | 1146 |
| 370 | 1013 | 1084 | 1163 |
| 380 | 1025 | 1105 | 1180 |
| 390 | 1038 | 1125 | 1197 |
| 400 | 1046 | 1146 | 1213 |
| 410 | 1059 | – | 1230 |
| 420 | 1071 | – | – |

tion ($T_p$) and were corrected to 298°K by means of the measured capacities of the complexes reported in Table 2, together with published data for the heat capacities[5] of oxygen and sulphur dioxide.

The small endothermic value of $\Delta H(2)$ for the breaking of the iridium–sulphur bond in crystalline $(SO_2)Cl(CO)(PPh_3)_2Ir$ indicates a weak bond in comparison with, for example, about 100 kJ required on average to break each metal–sulphur bond in crystalline thiourea complexes[6] $M^{II}[(H_2N)_2CS]_4Cl_2$. The weakness of the iridium–sulphur bond is also apparent from crystallographic data which shows an Ir–S bond length of 0.249 nm compared with about 0.207 nm in other sulphur dioxide complexes[7].

The oxygen adduct shows a strikingly different behaviour in comparison with the sulphur dioxide adduct as indicated by the exothermic removal of the ligand. This rather unusual result lends support to the peroxide formulation of the attached oxygen in the adduct. The breaking of the two iridium–oxygen bonds (step A) should



be followed immediately by the formation of molecular oxygen from rearrangement of the released peroxide radical (step B). The enthalpy of reaction (B) is given by the difference in bond energy, $E(\text{O–O})$, in the oxygen molecule and in the peroxide radical, and is calculated to be $\Delta H(\text{B}) = -352$ kJ from the tabulated[8] bond energies in $O_2$ and $H_2O_2$. The enthalpy of reaction (A), obtained from the relation:

$$\Delta H(1) = \Delta H(\text{A}) + \Delta H(\text{B})$$

is thus 260 kJ/mol indicating that the breaking of each Ir–O bond is an endothermic process requiring 130 kJ.

This calculation neglects the effect of the rearrangements which take place in the other iridium–ligand bonds during reaction (1). Infrared data[1] show that the C–O stretching frequency of the carbonyl group is greater in the oxygen adduct (2000 $\text{cm}^{-1}$) than in the parent compound (1956 $\text{cm}^{-1}$) presumably indicating that the Ir–CO bond is stronger in the parent than in the oxygen adduct. On the assumption that the iridium–phosphine bonds and the iridium–chlorine bond are similarly strengthened during reaction (1), the value of 130 kJ previously calculated for the strength of each Ir–O bond is likely to be a minimum.

The enthalpy of solution of chlorocarbonylbis(triphenylphosphine)iridium in benzene (1 mole complex to 2700 moles benzene) was found to be +2.17 kJ/mol. The enthalpy of solution of gaseous oxygen in benzene was calculated from solubility data[9] as +3.16 kJ/mol. Combination of these values with the enthalpy of reaction (1) leads to $\Delta H(3) = +87$ kJ/mol for reaction (3) which is observed to occur during the formation of the oxygen adduct.

$$O_2\,(\text{soln. } C_6H_6) + \text{Cl(CO)(PPh}_3)_2\text{Ir(soln. } C_6H_6) \rightarrow (O_2)\text{Cl(CO)(PPh}_3)_2\text{Ir(cryst.)} \qquad (3)$$

## EXPERIMENTAL

### *Materials*

The oxygen and sulphur dioxide adducts of $\text{Cl(CO)(PPh}_3)_2\text{Ir}$ (Alfa Inorganics) were made by the methods given by Vaska[1,10].

### *Heats of reaction*

The enthalpies of thermal decomposition were measured in a Perkin–Elmer Differential Scanning Calorimeter using the procedure described elsewhere[11]. Values of $\Delta H$ refer to the peak temperature, $T_p$, of the reaction where the rate of decomposition is greatest. The initial temperature, $T_i$, and the final temperature, $T_f$, refer to the temperature range of the reaction. Uncertainty intervals are standard deviations of the means. A check on the quantitative nature of reactions (1) and (2) was made by measuring the weight change accompanying the loss of the gaseous reaction product, and by recording the infrared spectra of the solid reactants and products.

Heat capacities were obtained as described by O'Neill[12] by comparison of the compounds with synthetic sapphire of known[13] heat capacity.

The heat of solution of $\text{Cl(CO)(PPh}_3)_2\text{Ir}$ in benzene was measured at 298°K in an LKB 8700-1 calorimeter by the procedure outlined by Wadsö[14].

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