Solid-state Reactions in the Carbonylchlorobis(triphenylphosphine)iridium(I)–Hydrogen Chloride System

By **Matthew C. Ball** * and **Janet M. Pope**, Department of Chemistry, University of Technology, Loughborough, Leicester LE11 3TU

The kinetics of addition of HCl gas to the solid complex $[IrClCO(PPh_3)_2]$ to form the *trans*-chloro-octahedral species have been studied. The rate-controlling step is chemical reaction at the phase boundary, with an activation energy of 37 kJ mol^{-1} and an entropy change of -184 J K^{-1} mol^{-1}. The reverse reaction has an activation energy of 51 kJ mol^{-1} and an entropy change of -176 J K^{-1} mol^{-1}. Loss of HCl from the *cis*-chloro-isomer is again controlled by reaction at the phase boundary with an activation energy of 130 kJ mol^{-1} and an entropy change of -92 J K^{-1} mol^{-1}. The enthalpy of dehydrochlorination of each isomer has been measured, and mechanistic implications of the results are discussed.

A LARGE number of complexes of metal ions with the d^8 electron configuration undergo oxidative-addition reactions, and those involving the complex $[IrClCO(PPh_3)_2]$ are probably the most widely studied.[1] This complex is known to react with molecular oxygen, hydrogen, halogens, and the hydrogen halides, as well as many other small molecules, to form six-co-ordinate complexes of d^6 configuration. The reactions with hydrogen chloride in solution give different isomers (*i.e. cis-* or *trans*-dichloro-) depending on the polarity of the solvent,[2] while the reaction of the solid complex with gaseous hydrogen chloride gives only the *trans*-chloro-complex.[3] The kinetics of several of these reactions in solution have been investigated [4] and the object of the present work is to extend the kinetic studies to the solid-state reactions. We report here the results of kinetic and mechanistic studies on reactions (1), (2), and (3).

$$[IrClCO(PPh_3)_2]\ (s) + HCl\ (g) \rightleftharpoons \underset{trans\text{-chloro-isomer}}{[Ir(H)Cl_2CO(PPh_3)_2]\ (s)} \qquad (1),\ (2)$$

$$\underset{cis\text{- and }trans\text{-chloro-isomers}}{[Ir(H)Cl_2CO(PPh_3)_2]\ (s)} \longrightarrow [IrClCO(PPh_3)_2]\ (s) + HCl\ (g) \qquad (3)$$

---

[1] J. P. Collman and W. R. Roper, *Adv. Organometallic Chem.*, 1968, **7**, 54.

[2] D. M. Blake and M. Kubota, *Inorg. Chem.*, 1970, **9**, 989.

[3] L. Vaska, *J. Amer. Chem. Soc.*, 1966, **88**, 5325.

[4] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, 1966, **88**, 3511.

EXPERIMENTAL

Materials.—All iridium analyses were carried out by *X*-ray fluorescence spectroscopy, with the sample diluted with borax to form a disc. The complex $[IrClCO(PPh_3)_2]$ was prepared by the method of Collman and Kang,[5] which requires the reaction of iridium(III) chloride and triphenylphosphine in dimethylformamide, followed by the addition of methanol {Found: Ir, 24·3. $[IrClCO(PPh_3)_2]$ requires Ir, 24·6%}. The complex *trans*-$[Ir(H)Cl_2CO(PPh_3)_2]$ was prepared by passing dry HCl gas (1 atm) over crystals of $[IrClCO(PPh_3)_2]$ at 298 K; 100% conversion of the product took place within 24 h[3] {Found: Ir, 22·9. $[Ir(H)Cl_2CO(PPh_3)_2]$ requires Ir, 23·5%}. I.r. (Nujol mull) spectrum: 2240 [ν(Ir–H)]; 2025 [ν(C–O)]; and 975 and 835 cm^{-1} [δ(Ir–H)]. The complex *cis*-$[Ir(H)Cl_2CO(PPh_3)_2]$ was prepared[6] by passing dry HCl gas into a solution of $[IrClCO(PPh_3)_2]$ (0·22 g) in benzene (40 cm^3) for 1·5 h. During this time the product precipitated from solution. The volume of solvent was reduced under vacuum and the product filtered off; yield 0·19 g (82%) {Found: Ir, 23·1. $[Ir(H)Cl_2CO(PPh_3)_2]$ requires Ir, 23·5%}. I.r. (Nujol mull) spectrum: 2245 [ν(Ir–H)] and 2030 cm^{-1} [ν(C–O)].

In all the experiments involving HCl as a reactant, the apparatus was purged with nitrogen before use.

Kinetic Measurements.—Thermal decompositions were carried out under dry, flowing nitrogen (60 cm^3 min^{-1}) in an all-glass apparatus, using boiling solvents to maintain constant temperatures. Weight losses were recorded through a null-type electrobalance, one arm of which carried a glass fibre and a Pt sample boat; sample weights were always *ca.* 20 mg. The hydrochlorination reaction was followed by measuring the extension of a silica spiral with a cathetometer. In this case the whole apparatus was thermostatted and filled with HCl gas (1 atm) after being purged with nitrogen.

Enthalpimetric Measurements.—Enthalpies of dehydrochlorination for both *cis*- and *trans*-$[Ir(H)Cl_2CO(PPh_3)_2]$ complexes were measured on the calorimeter module of a Du Pont Thermal Analyser. Sample weights were *ca.* 5 mg, and the heating rate chosen was 15 K min^{-1}. The enthalpies were calculated using the heats of fusion of zinc, indium, and tin as standards.

RESULTS

Data from all isothermal runs (23 in all) were converted into α (proportion of complex reacted) against $t/t_{0\cdot5}$ plots (where $t_{0\cdot5}$ = time when α = 0·5), and the results compared with similar plots for models based on diffusion, nucleation, or phase-boundary control of the rate-limiting step.[7] For all three reactions the best fit between experimental and theoretical reduced-time plots was in terms of (4), which is

$$kt = [1 - (1 - \alpha)^{\frac{1}{2}}] \qquad (4)$$

commonly called the ‘contracting-disc’ equation, and which is taken to assume that chemical reaction (*i.e.* bond making or breaking) is the rate-controlling step. Figure 1 shows a comparison between some of the experimental points and the theoretical reduced-time plots. Rate constants were derived and used to calculate Arrhenius parameters for each of the three reactions studied. The Table gives the temperature ranges over which each reaction was studied, with the Arrhenius parameters and enthalpy changes found.

Kinetic and thermochemical parameters

Reaction	Temperature range K	Frequency factor, *A* s^{-1}	Activation energy kJ mol^{-1}	Enthalpy change kJ mol^{-1}
Addition of HCl	304—319(5)	1 × 10^4	37 ± 4	
cis-Decomposition	493—507(5)	3 × 10^8	130 ± 10	98·8
trans-Decomposition	513—531(5)	2 × 10^3	51 ± 5	9·7

Samples of both *cis*- and *trans*-$[Ir(H)Cl_2CO(PPh_3)_2]$ complexes discoloured slightly on heating, and analysis showed a slight increase in iridium content. I.r. spectra of the products were indistinguishable from the original Vaska's complex, and it therefore seems probable that the change in colour is due to slight loss of triphenylphosphine. Optical examination of the starting material $[IrCOCl(PPh_3)_2]$ showed it to be in the form of clear yellow hexagonal plates, most of which had a side length of 20—30 μm, with a few crystals much larger at *ca.* 100 μm. Both *cis*- and *trans*-$[Ir(H)Cl_2CO(PPh_3)_2]$ complexes had the same morphology, but were paler yellow and opaque.

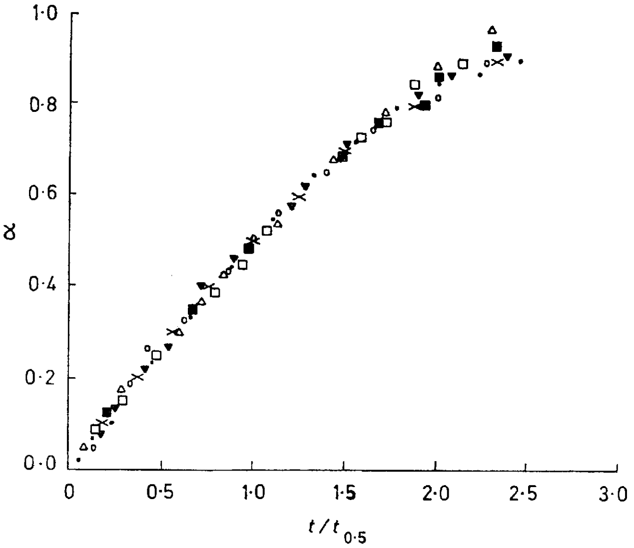


FIGURE 1 Comparison of theoretical and experimental reduced-time plots: reaction 1, (○) 315, (▼) 307 K; reaction 2, (□) 493, (△) 505 K; reaction 3, (●) 518, (■) 531 K; contracting-disc equation, (×)

DISCUSSION

The two-dimensional process suggested by the reduced-time plots is in agreement with the plate morphology of the starting materials. The formation of the *trans*-$[Ir(H)Cl_2CO(PPh_3)_2]$ complex is reversible and activation energies of both forward (37 kJ mol^{-1}) and reverse

---

[5] J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, 1967, **89**, 844.

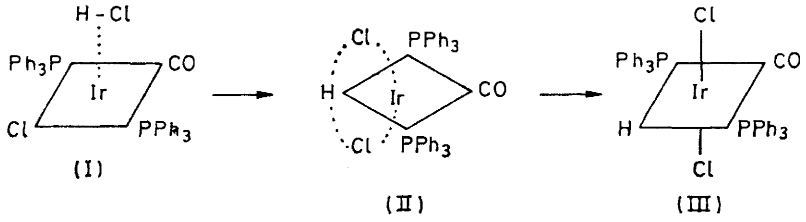
[6] L. Vaska and J. Di Luzio, *J. Amer. Chem. Soc.*, 1962, **84**, 679.

[7] J. H. Sharp, G. W. Brindley, and B. N. N. Achar, *J. Amer. Ceram. Soc.*, 1966, **49**, 379.

(51 kJ mol^{-1}) reactions have been determined. The difference between the two values should be equivalent to ΔH for the reaction. This gives a value of 14 kJ mol^{-1} compared with 9·7 kJ mol^{-1} as determined by calorimetry. When the possible error in these values is considered, this must be regarded as very good agreement.

The frequency factors given in the Table, when converted into entropy values, suggest a loss of entropy in the formation of the transition state for both forward and reverse reactions. The loss of entropy associated with the forward reaction is obviously mainly due to the removal of gaseous HCl in the formation of the transition state. The entropy decrease of -176 J K^{-1} mol^{-1} is however much greater than that associated[8] with the solidification of HCl gas (-101 J K^{-1} mol^{-1}). This presumably means that the transition state is extremely tightly bound, although it is difficult to decide on any formal stereochemistry.

It is obvious that, in the formation of the *trans*-[Ir(H)Cl_2CO(PPh_3)$_2$] complex, chlorine migration must occur, and that the first stage probably involves interaction between Ir orbitals and the bond in the HCl molecule, as follows:



Thus the transition state could be either five-co-ordinate (I) or distorted six-co-ordinate (II). The loss of HCl from (III) results in a tightly bound transition state as shown by the negative entropy change of -184 J K^{-1} mol^{-1}. This adds a little weight to the suggestion of a five-co-ordinate transition state, since it is difficult to visualise any six-co-ordinate species, however distorted, giving rise to such a loss of entropy.

The dehydrochlorination of the *cis*-[Ir(H)Cl_2CO(PPh_3)$_2$] complex, on the other hand, has a very high activation energy and a rather smaller loss of entropy. The large activation energy when combined with the enthalpy value suggests a hypothetical activation energy for the formation of the *cis*-complex of *ca.* 31 kJ mol^{-1}. This is very close to that for formation of the *trans*-complex, and suggests that the same transition state is common to the formation of both *cis*- and *trans*-complexes. The five-co-ordinate species (I) meets this requirement.

The results taken as a whole indicate that the *cis*-[Ir(H)Cl_2CO(PPh_3)$_2$] complex is the thermodynamically stable one in this system, and that the stability of the *trans*-isomer in the solid state is kinetic. Relative energies are shown in Figure 2.

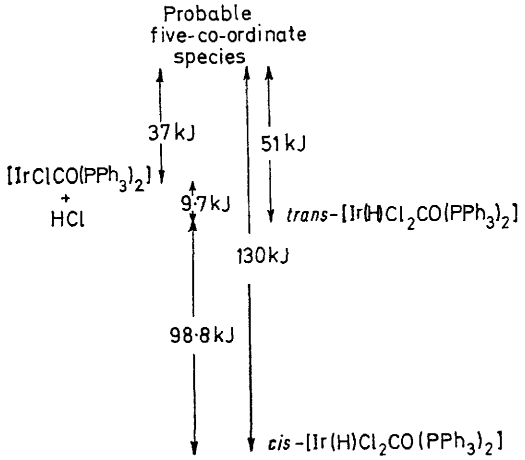


FIGURE 2 Overall energy scheme for the system [IrClCO(PPh_3)$_2$]HCl

The Arrhenius parameters quoted here for the solid-gas reaction lie closer to those[4] for addition of methyl iodide to the [IrClCO(PPh_3)$_2$] complex in benzene solution ($\Delta H^‡ = 24$ kJ mol^{-1}, $\Delta S^‡ = -214$ J K^{-1} mol^{-1}) than to those for addition of oxygen or hydrogen in benzene solution ($\Delta H^‡ = 55$ kJ mol^{-1} for O_2, 45 kJ mol^{-1} for H_2; $\Delta S^‡ = -88$ J K^{-1} mol^{-1} for O_2, -97 J K^{-1} mol^{-1} for H_2), and can be related to the addition of a polar molecule to the d^8 complex in the absence of any solvent effects. The addition of methyl iodide to [IrClCO(PPh_3)$_2$] in dimethylformamide has considerably different Arrhenius parameters ($\Delta H^‡ = 69$ kJ mol^{-1}, $\Delta S^‡ = -42$ J K^{-1} mol^{-1}), which must be due to either a totally different mechanism or to co-ordination of a solvent molecule.

We wish to thank Dr. A. H. Norbury and Mr. S. J. Anderson for their help during this investigation.

[3/012 *Received, 2nd January,* 1973]

---

[8] J. G. Stark and H. G. Wallace, 'Chemistry Data Book,' SI edn. John Murray, London, 1970, p. 52.