

The Reaction of Carbon Dioxide with Rhodium and Iridium Hydroxy Complexes

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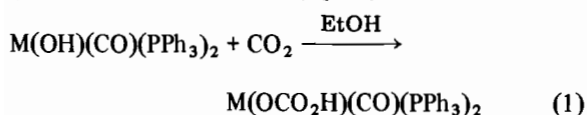
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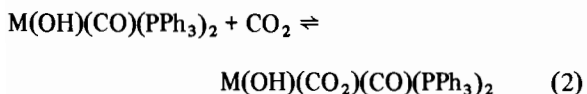
The reactions of trans-M(OH)(CO)(PPh₃)₂ for M = Rh and Ir with CO₂ are described. The rate of reaction of Rh(OH)(CO)(PPh₃)₂ in CH₂Cl₂ and in the presence of traces of water is first order in complex and independent of CO₂ and water concentrations. In the complete absence of water the reaction proceeds by a much faster pathway.

Introduction

An interest in the mechanism of the reactions of CO₂ with metal complexes led us to study the reported [1] uptake of CO₂ by *trans*M(OH)(CO)(PPh₃)₂ for M = Rh and Ir (eqn. 1)



The insertion of CO₂ into a metal bound OH group is believed to be involved in the catalysis of the equilibrium between CO₂ and HCO₃⁻ by carbonic anhydrase. The *trans*-M(OH)(CO)(PPh₃)₂ systems are particularly interesting because of the suggestion [2] that when the complexes are in the solid state, five coordinate CO₂ complexes are formed reversibly (eqn. 2):



The formulation of these complexes as CO₂ adducts was based on their i.r. spectra and the reversibility of the reactions. In this study we have found that the reversible reaction also occurred in CH₂Cl₂ although we believe that the products, which have the same i.r. spectra as those obtained from the solid state reaction, are the bicarbonate complexes. We have used an infra-red stopped-flow spectrometer to follow the kinetics of the reaction of the rhodium complex in an attempt to elucidate the mechanism of this reaction.

Experimental

Both Rh(OH)(CO)(PPh₃)₂ and Ir(OH)(CO)(PPh₃)₂ were prepared by the published methods [3] or directly from the corresponding chloro complexes by dissolving the complex in the minimum quantity of boiling methanol containing NaOH (20-fold excess) under N₂, followed by precipitation of the less soluble hydroxy complex on addition of a large excess of water.

The CH₂Cl₂ solvent was dried immediately prior to use by distillation over P₂O₅ (see discussion). The concentrations of CO₂ and water in CH₂Cl₂ were determined volumetrically. The kinetics of the reaction of Rh(OH)(CO)(PPh₃)₂ with CO₂ were studied using an i.r. stopped-flow spectrometer [4]. The concentrations of Rh(OH)(CO)(PPh₃)₂, CO₂, and product were monitored at 1944, 2332 and 1970 cm⁻¹ respectively with an experimental uncertainty in the wavenumber of ±3 cm⁻¹. The temperature was maintained at (20.5 ± 0.5) °C.

Results and Discussion

It has been well established that the products of the reactions of M(OH)(CO)(PPh₃)₂ (M = Rh, Ir) with CO₂ in ethanol are the bicarbonate complexes, M(OCO₂H)(CO)(PPh₃)₂ [1]. In the absence of solvent or in CH₂Cl₂ the reactions with CO₂ are reversible and the i.r. mull spectra of the products are identical. Different spectra are obtained, however, when the reaction is performed in ethanol. The spectral data are given in Table I. Despite this difference in i.r. spectra, the ³¹P n.m.r. spectra show that the solution species are the same in ethanol and in CH₂Cl₂. In particular the value of J(Rh–P) is typical [5] of a four coordinate Rh(I) complex such as Rh(OCO₂H)(CO)(PPh₃)₂ rather than the suggested five coordinate species, Rh(OH)(CO₂)(CO)(PPh₃)₂. It is possible that the differences in i.r. spectra are due to the incomplete removal of ethanol from the dried samples. It has been suggested [6] that the products from alcohol solutions are

TABLE I. Some Spectral Properties of the Complexes.

Complex	Solvent	$\nu(\text{CO})$ (cm^{-1}) ^a		³¹ P n.m.r. ^b	
		In solution	As paraffin mull	δ (ppm)	J(Rh-P) (Hz)
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	CH_2Cl_2	1963	1954	25.9	—
$\text{Ir}(\text{OH})(\text{CO})(\text{PPh}_3)_2$	CH_2Cl_2	1959(sh), 1938	1938(sh), 1929	28.9	—
$\text{Ir}(\text{OH})(\text{CO})(\text{PPh}_3)_2 + \text{CO}_2$	CH_2Cl_2	1964	1954	25.9	—
$\text{Ir}(\text{OH})(\text{CO})(\text{PPh}_3)_2 + \text{CO}_2$	$\text{C}_2\text{H}_5\text{OH}$	—	1964(br), 1953(br)	25.9	—
$\text{RhCl}(\text{CO})(\text{PPh}_3)_2$	CH_2Cl_2	1977	1964	33.6	125
$\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$	CH_2Cl_2	1954	1950, 1940(sh)	36.5	138
$\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2 + \text{CO}_2$	CH_2Cl_2	1974	1966, 1953(sh)	35.2	133
$\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2 + \text{CO}_2$	$\text{C}_2\text{H}_5\text{OH}$	—	1975(br), 1966(br)	35.2	133

^ash = shoulder, br = broad, all bands strong. ^bChemical shifts relative to external 85% H_3PO_4 .

TABLE II. Observed Rate Constant for the Reaction of $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ with CO_2 in CH_2Cl_2 .^a

Species followed	Frequency (cm^{-1})	Mean rate constant (s^{-1})
$\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$	1944 ± 3	8.2×10^{-2}
CO_2	2332 ± 3	7.6×10^{-2}
$\text{Rh}(\text{OCO}_2\text{H})(\text{CO})(\text{PPh}_3)_2$	1970 ± 3	8.0×10^{-2}

^aThe initial concentrations of $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ and CO_2 were $1 \times 10^{-3} \text{ M}$ and $2 \times 10^{-3} \text{ M}$ respectively and the temperature was $(20.5 \pm 0.5)^\circ\text{C}$.

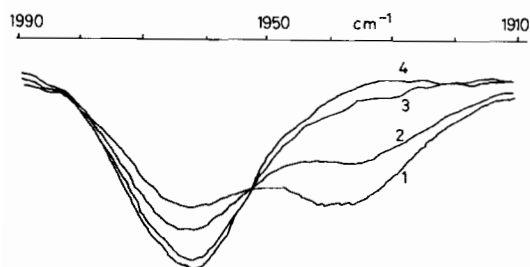


Fig. 1. The i.r. spectra of the reaction of $\text{Ir}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ ($2.5 \times 10^{-3} \text{ M}$) with excess CO_2 in CH_2Cl_2 at five minute intervals.

alcoholates and it might not be possible to distinguish these from bicarbonate complexes by ³¹P n.m.r. spectroscopy.

To obtain $\text{Ir}(\text{OCO}_2\text{H})(\text{CO})(\text{PPh}_3)_2$ from $\text{Ir}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ an excess of CO_2 is required. The i.r. spectra for this reaction in CH_2Cl_2 (Fig. 1) indicate the absence of any long lived intermediate. Nor was any evidence for an intermediate obtained from the low temperature ³¹P n.m.r. spectra for either this or the reaction of the rhodium complex when performed at -78°C . The reaction of the iridium

complex gave a first order rate constant of $ca. 2 \times 10^{-3} \text{ s}^{-1}$. At the present time a detailed study has been done only on the rhodium complex.

The reaction of $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ with CO_2 was studied in CH_2Cl_2 using an i.r. stopped-flow spectrophotometer. This enabled the changes in concentration of both the reactants and of the product to be followed. All three species reacted at the same rate, which was first order in $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ concentration and independent of CO_2 concentration up to a molar excess of 100 (Tables II and III). All individual runs were good first order with standard deviations determined by the precision of the measurements. These results gave a mean rate of $7.8 \times 10^{-2} \text{ s}^{-1}$ at $(20.5 \pm 0.5)^\circ\text{C}$.

To explain these results it is necessary to invoke an initial rate determining step involving $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ but not CO_2 since the rate is independent of CO_2 concentration and CO_2 reacts at the same rate as the rhodium species. The dissociation of OH^- is unlikely but cannot be excluded. The addition of solvent is also thought to be improbable in this solvent and in any event much less likely than in $\text{Pt}(\text{II})$ complexes to be rate determining [7]. Addition of excess PPh_3 was found to increase the inten-

TABLE III. Observed Rate Constants for the Reaction of Rh(OH)(CO)(PPh₃)₂ at Various CO₂ Concentrations.^a

Initial CO ₂ concentration (M)	Mean rate constant (s ⁻¹)
1 × 10 ⁻³	7.4 × 10 ⁻²
2 × 10 ⁻³	7.8 × 10 ⁻²
1 × 10 ⁻²	7.8 × 10 ⁻²
1 × 10 ⁻¹	7.7 × 10 ⁻²

^aThe initial concentration of Rh(OH)(CO)(PPh₃)₂ was 1 × 10⁻³ M and the temperature was (20.5 ± 0.5) °C. Rates were measured at 1944 and 1970 cm⁻¹.

sity of ν(CO) in both the reactant and product (this does not occur with RhCl(CO)(PPh₃)₂) but at PPh₃ concentrations below 3 × 10⁻² M there was no effect on the rate so the main pathway cannot involve dissociation of the phosphine ligand. Hydroxy bridged phosphine complexes of platinum and palladium are known but the bridge is very unreactive [8]. The rate of the reaction was, however, found to be dependent on water in the solvent with a faster pathway being available in the absence of water. In the kinetic experiments the total expected change cannot be observed because some of the reaction occurs after mixing but before observation starts. Any reaction with a half life shorter than about 10⁻³ s will be virtually complete before observation is possible [4]. The increase in transmission, corresponding to a decrease in concentration, observed for Rh(OH)(CO)(PPh₃)₂ was greater in undried CH₂Cl₂ (ca. 2 × 10⁻² M in water) or dried CH₂Cl₂ to which water had been added than in dried CH₂Cl₂ (<2 × 10⁻³ M in water)*. The concentration of water had no effect on the total amount of product formed and so it appears that the reaction is slower in the presence of water. The rate of this

*For the reaction of 1 × 10⁻³ M Rh(OH)(CO)(PPh₃)₂ with 4 × 10⁻³ M CO₂ the changes in transmission observed at 1950 cm⁻¹ during kinetic experiments were, for wet and dried CH₂Cl₂, 8.9 and 4.5% respectively.

slower reaction was found to be independent of the concentration of added water and in very dry solutions it was possible to see evidence of the faster reaction. It thus appears that under the usual experimental conditions the rate determining step involves water. Kinetic studies of reactions in aqueous solution, such as that between Co(OH)(NH₃)₅²⁺ and CO₂ [9], have indicated that it is the O–H bond that is cleaved. A possible explanation of the observations reported in this study is that charge separation of the O–H bond leads to unfavourable entropy effects due to hydrogen bonded water.

Related systems are now being investigated to see if this behaviour is more general.

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