Homogeneous Catalytic and Stoicheiometric Hydrogenation of Ethylene by Trishydridocarbonylbis(triphenylphosphine)iridium(III)

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The complex trishydridocarbonylbis(triphenylphosphine)iridium(III), $IrH_3(CO)(PPh_3)_2$, has been found to hydrogenate ethylene catalytically and stoicheiometrically in dimethylformamide at 50°. The rates observed were predicted by equation (i) which could be deduced from a similar equation established previously for the catalyst hydridocarbonyltris(triphenylphosphine)iridium(I), $IrH(CO)(PPh_3)_3$, where $[IrH_3(CO)(PPh_3)_2]_0$ represents the initial concentration of $IrH_3(CO)(PPh_3)_2$. The reaction of ethylene with $IrH_3(CO)(PPh_3)_2$ controls the rate of

$$-\frac{d[C_2H_4]}{dt} = \frac{0{\cdot}01\,[IrH_3(CO)(PPh_3)_2]_0[C_2H_4]}{1 + 828[H_2] + 247[PPh_3]} \qquad \text{(i)}$$

ethylene activation while the inhibitory effect of hydrogen and triphenylphosphine is thought to originate in subsequent competition between reactions of the ethylene intermediate giving ethane and those with hydrogen and phosphine reforming ethylene. The inhibition cannot be explained solely by the effect of the equilibria (ii) and (iii).

$$IrH_3(CO)(PPh_3)_2 \rightleftharpoons IrH(CO)(PPh_3)_2 + H_2 \qquad \text{(ii)}$$

$$IrH(CO)(PPh_3)_3 \rightleftharpoons IrH(CO)(PPh_3)_2 + PPh_3 \qquad \text{(iii)}$$

THE hydrogenation of ethylene catalysed by $IrH(CO)(PPh_3)_3$ in dimethylformamide takes place[1] in the presence of free triphenylphosphine and $IrH_3(CO)(PPh_3)_2$ because of the rapidly established equilibrium (1).

$$IrH(CO)(PPh_3)_3 + H_2 \rightleftharpoons IrH_3(CO)(PPh_3)_2 + PPh_3 \qquad (1)$$

The rates of hydrogenation fit equation (2), in which,

$$-\frac{d[C_2H_4]}{dt} = \frac{k[Ir]_0[C_2H_4]}{1 + k'[H_2] + k''[PPh_3]} \qquad (2)$$

at 50°, $k = 0{\cdot}01$ l mol^{-1} s^{-1}, $k' = 828$ l mol^{-1} and $k'' = 247$ l mol^{-1} when $[Ir]_0 = [IrH(CO)(PPh_3)_3]_0$. It is already known that $IrH(CO)(PPh_3)_2$ can behave as an unstable intermediate in reactions in this system[1,2]

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[1] M. G. Burnett and R. J. Morrison, *J. Chem. Soc.* (*A*), 1971, 2325.

[2] J. F. Harrod and C. A. Smith, *Canad. J. Chem.*, 1970, **48**, 870.

through the equilibria (3) and (4). If the catalyst

$$IrH_3(CO)(PPh_3)_2 \rightleftharpoons IrH(CO)(PPh_3)_2 + H_2 \quad (3)$$

$$IrH(CO)(PPh_3)_3 \rightleftharpoons IrH(CO)(PPh_3)_2 + PPh_3 \quad (4)$$

existed in an equilibrium mixture of all three complexes, each having a significant concentration and the rate determining step were reaction (5), a theoretical rate

$$IrH(CO)(PPh_3)_2 + C_2H_4 \longrightarrow Ir(CO)(C_2H_5)(PPh_3)_2 \quad (5)$$

equation may be derived having a form identical with that of equation (2). However, this equation implies a substantial concentration of $IrH(CO)(PPh_3)_2$ and no other evidence for this conclusion has been found. The investigation has now been continued by a study of the reactions of ethylene and $IrH_3(CO)(PPh_3)_2$, with and without added hydrogen.

Since equilibrium (1) is established rapidly, the concentrations of the iridium complexes which are undoubtedly present, $IrH_3(CO)(PPh_3)_2$ and $IrH(CO)(PPh_3)_3$, are controlled by the hydrogen and phosphine concentrations and should be independent of the identity of the particular compound used initially. However, the use of $IrH_3(CO)(PPh_3)_2$ in the present work permits the study of the faster reactions occurring in the absence of free phosphine. The rates of these reactions all obey equation (2) when $[Ir]_0$ is replaced by $[IrH_3(CO)(PPh_3)_2]_0$ and $[PPh_3] = 0$. The catalytic rate observed on adding phosphine and the rates in the absence of added hydrogen, referred to subsequently as the stoicheiometric reaction, are all consistent with the new form of equation (2).

The evidence now available suggests that the inhibitory terms in the denominator of equation (2) cannot be explained by the equilibria (3) and (4) but must originate in competition reactions involving an intermediate in the complex reaction summarised by (5).

EXPERIMENTAL

$IrH_3(CO)(PPh_3)_2$, $IrH(CO)(PPh_3)_3$, triphenylphosphine, dimethylformamide, hydrogen, and ethylene were obtained and purified as previously described.[1] The apparatus and procedure have been described previously.[1,3]

RESULTS

The partition coefficients of hydrogen, ethylene, and ethane have already been measured.[1]

The Stoicheiometric Reduction of Ethylene by $IrH_3(CO)(PPh_3)_2$.—$IrH_3(CO)(PPh_3)_2$ was found to stoicheiometrically reduce ethylene in dimethylformamide at 50°. The com-

$$IrH_3(CO)(PPh_3)_2 + C_2H_4 \longrightarrow IrH(CO)(PPh_3)_2 + C_2H_6 \quad (6)$$

$$IrH_3(CO)(PPh_3)_2 \longrightarrow \text{Mixed iridium complexes} \quad (7)$$

plete analysis of the iridium-containing products was not attempted. It was noticed that the solution changes from colourless initially to a dark yellow-brown as the reaction proceeds and that the fully reacted solution, when evaporated to dryness at the end of an experiment, contained sufficient $IrH(CO)(PPh_3)_3$ to account for *ca.* 30% of the original complex used. The hydrogen removed as ethane corresponded to the loss of two of the three hydrogen atoms in the original complex.

TABLE 1

The stoicheiometric reduction of ethylene by $IrH_3(CO)(PPh_3)_2$ in DMF solution at 50 °C

Time/min	$10^4[IrH_3(CO)(PPh_3)_2]$/M	$10^4[C_2H_4]$/M [a]	$-10^9d[C_2H_4]/dt$ / mol l^{-1} s^{-1} obs.[a]	calc.
0	54·4	117	591	637
10	18·9	115	290	219
25	13·7	89·8	151	124
40	5·4	116	50	63
55	2·2	89·9	33	20
70	1·2	87·7	10	11

[a] Gas chromatographic analysis; reaction rates calculated from ethane formation.

The observed and predicted rates of ethylene removal are summarised in Table 1. The calculated rates were obtained from equation (8), which was derived from equation (2)

$$-\frac{d[C_2H_4]}{dt} = 0{\cdot}01\,[IrH_3(CO)(PPh_3)_2][C_2H_4] \quad (8)$$

by assuming that no free hydrogen or triphenylphosphine was present and by replacing $[Ir]_0$ by the concentration of $IrH_3(CO)(PPh_3)_2$ present at any time during the reaction calculated using the stoicheiometry of reaction (8). The experimental rates were measured by drawing tangents to the curve given by plotting the concentration of reacted ethylene in solution against time. The concentration of ethylene reacted was found from the pressure of ethane produced, measured by gas chromatography.

The Catalytic Reduction of Ethylene by $IrH_3(CO)(PPh_3)_2$.—The concentrations of phosphine and hydrogen in runs (9) and (13) present during catalysis and given in Table 2 were calculated using the equilibrium constant for reaction (1) determined previously.[1] No allowance had to be made for ethylene–iridium complexes in calculating the concentration of free ethylene since there was no evidence in the study of the stoicheiometric reaction for their formation in measurable amounts. The rates of hydrogenation given in Table 2 were based on the rate of ethane formation measured by gas chromatography but essentially identical rates could be calculated from the observed pressure change. Generally the concentrations of hydrogen and ethylene changed by only a few per cent during the period of observation and the observed rates were virtually constant throughout the run. However, in experiments such as Run 3 in which the rate is high although the concentration of one reactant is low, the rates varied during the experiment in accordance with equation (2). The rates are all quoted at 300 min since this is approximately half the period of observation and it is consequently the time at which the most accurate rate measurement may be made. The agreement of the observed and calculated rates shows that the rate equation is identical with that for the reaction catalysed by $IrH(CO)(PPh_3)_3$.

Samples of $IrH_3(CO)(PPh_3)_2$ stored for long periods in dry air were also tested (Runs 10 and 11). Although the rates of the catalysed reactions were considerably increased, the

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[3] R. J. Morrison, Ph.D. Thesis, The Queen's University of Belfast, 1971.

i.r. spectrum of the solid obtained by evaporating the catalyst solution to dryness at the end of the experiment showed no detectable change in the catalyst. The addition of oxygen also accelerated the catalysed rate, (Run 12), but the catalyst solution then changed from colourless to brown during the reaction. The solid obtained by evaporating the solution at the end of the experiment had an i.r. spectrum with new bands in the iridium hydride or carbon monoxide region together with other bands possibly due to oxygenated products in addition to the spectrum of the original catalyst. There were no bands due to phosphine oxide. No detailed study was made of this system but it was clear that the poor reproducibility and the anomalously fast rates observed previously [1] were due to the effects of catalyst oxidation.

TABLE 2

Kinetic data for the hydrogenation of ethylene using $IrH_3(CO)(PPh_3)_2$ in DMF solution at 50 °C

Run no.	10^4 $[IrH_3(CO)(PPh_3)_2]$/M Initial	10^4 $[H_2]$/M 300 min	10^4 $[C_2H_4]$/M 300 min	10^4 $[PPh_3]$/M 300 min	10^9 $-d[C_2H_4]/dt$/mol l^{-1} s^{-1} obs.	calc.
1	19·8	15·8	99·5	0	81	85
2	60·7	14·4	74·4	0	216	206
3	72·1	14·2	103	0	335	342
4	85·5	13·4	103	0	427	401
5	57·6	1·6	15·2	0	87	77
6	58·7	22·4	35·0	0	63	72
7	59·2	15·2	97·0	0	290	255
8	59·8	3·27	93·2	0	450	439
9	56·4	13·9	104	39·2	179	188
10 [a]	56·9	13·7	97·9	0	375	261
11 [b]	58·0	16·3	77·6	0	240	192
12 [c]	54·3	11·9	97·8	0	315	268
13 [d]	45·7	6·55	93·2	19·4	208	211

[a] Sample stored in air for 1 month. [b] Sample stored in air for 2 weeks. [c] 90 mmHg oxygen added to the reaction mixture. [d] The catalyst is $IrH(CO)(PPh_3)_3$. In no. 13 the surface area in contact with the solution is increased by a factor of 2 using glass ballatini.

Run 13 was performed with $IrH(CO)(PPh_3)_3$ as catalyst in order to show the absence of any surface-promoted catalytic reaction. The rate of Run 13 is in satisfactory agreement with the calculated value although the surface to volume ratio exceeds that used in the other experiments by a factor of *ca.* 2.

DISCUSSION

The Stoicheiometric Reduction of Ethylene by $IrH_3(CO)(PPh_3)_2$.—Preliminary experiments indicated that this reaction occurred very rapidly with complete breakdown of the starting complex. The kinetic study was carried out on a reaction with a convenient rate and in which a large amount of ethane was formed. It can be seen from Table 1 that the calculated and observed rates are in remarkably good agreement considering the random errors likely to be introduced by the rate and concentration data. The experiment is particularly significant because it provides two arguments against $IrH(CO)(PPh_3)_2$ being the most important intermediate in the catalysed reaction.

The mechanism of the stoicheiometric reaction based on the theory advanced previously [1] would include reactions (3), and (9)—(11). Reaction (11) probably takes place in a number of elementary stages but the discussion is unaffected by summarising them in the form shown.

$$IrH(CO)(PPh_3)_2 + C_2H_4 \longrightarrow Ir(C_2H_4)H(CO)(PPh_3)_2 \quad (9)$$

$$Ir(C_2H_4)H(CO)(PPh_3)_2 \longrightarrow Ir(C_2H_5)(CO)(PPh_3)_2 \quad (10)$$

$$Ir(C_2H_5)(CO)(PPh_3)_2 + H_2 \longrightarrow IrH(CO)(PPh_3)_2 + C_2H_6 \quad (11)$$

In the first place, the catalytic experiments described in this and the previous paper [1] suggest that substantial amounts of $IrH(CO)(PPh_3)_2$ must be stabilised under catalytic conditions in order to account for the form of the denominator of the rate equation (2). There are no real differences in the conditions of the stoicheiometric and catalytic reactions apart from the absence of added hydrogen in the former case and the hydrogen apparently only serves to form $IrH_3(CO)(PPh_3)_2$. However, during the stoicheiometric reaction a substantial amount of $IrH(CO)(PPh_3)_3$ is formed together with other iridium decomposition products. Thus, where the scavenging of complexed hydrogen by ethylene and the absence of free triphenylphosphine gives the best chance of a high concentration of $IrH(CO)(PPh_3)_2$, there is clear evidence of the compound's instability. There is no reason to suppose that it will be any more stable under catalytic conditions and the absence of complex decomposition during the catalysis suggests that the intermediate is then only present in very low concentrations if at all.

Secondly, in previous experiments,[1] the effects of the supposed formation of $IrH(CO)(PPh_3)_2$ from $IrH(CO)(PPh_3)_3$ were confused in the large initial pressure changes caused by the solution of ethylene and hydrogen. The half-life to the establishment of the intermediate's equilibrium concentration, calculated from data given by Harrod and Smith,[2] is 0·6 s. However, the corresponding half-life to equilibrium for $IrH_3(CO)(PPh_3)_2$ is 6 min, calculated from the data on the reaction of hydrogen with $IrH(CO)(PPh_3)_3$ given previously,[1] and therefore an increase in pressure due to hydrogen evolution by reaction (4) should be superimposed on the rise in pressure due to ethylene hydrogenation. The latter effect is relatively small and is due to the lower solubility of ethane in dimethylformamide compared to that of ethylene. Despite these apparently favourable circumstances for its detection, there was no evidence of hydrogen formation in the early part of the reaction and neither was there any evidence of deviation from the rate law which might also have been expected because of the non-equilibrium conditions.

The evidence therefore does not support a mechanism involving reactions (3), and (9)—(11) but rather suggests an initial direct ethylene substitution reaction with $IrH_3(CO)(PPh_3)_2$. The stoicheiometry indicates that only 2 of the 3 hydrogen atoms present are transferred to ethylene so that the intermediate $IrH(CO)(PPh_3)_2$ is presumably formed and reacts sufficiently rapidly with free hydrogen to reform $IrH_3(CO)(PPh_3)_2$, thereby avoiding catalyst decomposition.

The Catalytic Reduction of Ethylene by $IrH_3(CO)(PPh_3)_2$.—The discussion in the previous section also applies in part to the results of the catalysed reaction. It is particularly important that there is no evidence[1] of any detectable hydrogen release due to the supposed formation of $IrH(CO)(PPh_3)_2$ since the magnitude of the constant k'' in equation (2) would suggest that during catalysis up to 60% of the initial concentration of $IrH_3(CO)(PPh_3)_2$ must have dissociated. Previously[1] it was argued that in the presence of ethylene some structural change might stabilise $IrH(CO)(PPh_3)_2$ or that it might be stabilised by surface adsorption. No positive evidence has been found for the former explanation and the latter has been eliminated by the absence of a detectable surface effect. The only evidence in favour of $IrH(CO)(PPh_3)_2$ as the rate controlling intermediate is the approximate agreement of experiment with the theoretical prediction that $K_1 = k'/k''$. However, it is quite conceivable that this agreement is fortuitous and therefore misleading. The weight of the evidence above suggests that the rate determining step in catalysis by $IrH_3(CO)(PPh_3)_2$ is the direct reaction of ethylene with the catalyst. The fact that the rate is inhibited by added hydrogen suggests that the ethylene complex produced is involved in competing reactions, one of which forms ethane and the other, with hydrogen, reforms ethylene. This implies that reaction (11) given previously is a complex reaction.

It is particularly striking that hydrogen inhibits the reaction whether phosphine is present or not. When phosphine is present equilibrium (1) ensures that the concentration of $IrH_3(CO)(PPh_3)_2$ rises with that of hydrogen but the catalysed rate still decreases although to a smaller extent than it did in the absence of phosphine when the concentration of $IrH_3(CO)(PPh_3)_2$ is constant. The direct conclusion from the very simple form of the general rate equation (2) is that the rate constants of the ethylene reactions with $IrH_3(CO)(PPh_3)_2$ and $IrH(CO)(PPh_3)_3$ are equal and that the same product is produced in both cases. The inhibition terms then arise by virtue of the same competing reactions as with hydrogen alone but with the addition of a reaction due to phosphine which also reforms ethylene.

The anomalously fast rates observed previously[1] during the first hour of ethylene hydrogenation catalysed by $IrH(CO)(PPh_3)_3$ were previously attributed to the decrease in the concentration of $IrH(CO)(PPh_3)_2$ during the formation of $IrH_3(CO)(PPh_3)_2$. However, once the presence of a large concentration of $IrH(CO)(PPh_3)_2$ is rejected, it is immediately apparent that the reaction forming $IrH_3(CO)(PPh_3)_2$ will also liberate phosphine and if this proceeds as it does in the presence of hydrogen alone,[1] it will come to equilibrium within the first hour. The decrease in the catalytic rate is then simply due to the increase in the concentration of free phosphine as reaction (1) proceeds. The changes in rate predicted on this basis by equation (2) are sufficient to account for the observed rate variations. The absence of any such changes when $IrH_3(CO)(PPh_3)_2$ is used as the catalyst is consistent with this interpretation since phosphine is not liberated in these experiments.

In previous work, catalytic substrates have usually been selected for mechanistic investigation because of the relative rapidity of the catalysed reaction. Such substrates were generally observed to form significant amounts of a catalyst–substrate complex. In the present case, the catalyst–substrate complex is unstable and so low in concentration that the reactions in which it occurs can become rate controlling. Obviously if the catalyst–substrate complex is sufficiently stable, the rate of its reaction with hydrogen may control the catalysed rate and the form of the rate equation will be determined by the reaction system at equilibrium rather than the same system in a kinetic steady state. In that case the catalysed rate may increase with the hydrogen concentration rather than fall. Further investigations of the reduction of a variety of substrates are planned, catalysed by $IrH_3(CO)(PPh_3)_2$ and $IrH(CO)(PPh_3)_3$, in order to test this prediction and the generality of the proposed catalyst mechanism.

We thank Johnson–Matthey for the loan of iridium salts and acknowledge the Postgraduate Studentship from the Government of Northern Ireland (to R. J. M.).

[2/636 *Received, 20th March*, 1972]