Mechanism of the Homogeneous Hydrogenation of Olefins catalysed by Chlorocarbonylbis(triphenylphosphine)iridium(I) with and without Basic Cocatalysts

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The complex chlorocarbonylbis(triphenylphosphine)iridium(I), $IrCl(CO)(PPh_3)_2$, has been found to catalyse the hydrogenation of olefins, (RHC=CHR), in dimethylformamide at 50° (R = H) and at 80° (R = CO_2Me or CO_2H), at a rate which increases to a maximum value during an initial induction period. The induction period does not occur in hydrogenations carried out in toluene at 80° (R = CO_2Me), and may be removed in dimethylformamide by addition of *p*-methoxyphenol. In the presence of basic cocatalysts in dimethylformamide, the catalyst is converted into trihydridocarbonylbis(triphenylphosphine)iridium(III), $IrH_3(CO)(PPh_3)_2$, during the induction period. The induction period in the absence of cocatalyst is attributed to the involvement of an iridium–olefin intermediate in a radical chain process depending on the solvent or its impurities. The mechanism of the reactions is discussed in terms of an iridium–olefin intermediate, the concentration of which is determined partly by the equilibria existing between the stable iridium complexes present and partly by the kinetic competition of the reactions forming and removing the intermediate.

THE kinetics of olefin hydrogenation catalysed by chlorocarbonylbis(triphenylphosphine)iridium, $IrCl(CO)(PPh_3)_2$, have previously [1] been interpreted in terms of the equilibrium formation of a five-co-ordinate alkyl iridium intermediate accompanied by a certain amount of a four-co-ordinate intermediate formed by phosphine dissociation. The rate determining step was identified as hydrogen attack on the four-co-ordinate intermediate. In polar solvents such as dimethyl sulphoxide or dimethylacetamide an induction period was observed [2] during which the rate increased to a final constant value. This was attributed to an initial slow dissociation of triphenylphosphine from $IrCl(CO)(PPh_3)_2$ thought to occur in these solvents.

In previous studies of ethylene hydrogenation catalysed by $IrH(CO)(PPh_3)_3$ [3] and $IrH_3(CO)(PPh_3)_2$,[4] we found that a similar equilibrium interpretation was not possible and concluded that the concentration of the alkyl intermediate was controlled by kinetic competition rather than by the equilibria between iridium complexes. The present investigation was undertaken to find if a similar mechanism applied to the hydrogenation of olefins catalysed by $IrCl(CO)(PPh_3)_2$.

In the course of the work, it was found that a trace of a radical inhibitor, *p*-methoxyphenol, removed the induction period observed, in polar solvents and that, contrary to the previous report,[2] no spectroscopic evidence of the phosphine dissociation from $IrCl(CO)(PPh_3)_2$ could be found. Furthermore a detailed analysis of the original data [1,2] together with our additional experiments showed a marked disagreement between theory and experiment. Although no induction periods were observed in toluene, the same type of variations between theory and experiment could also be observed in this solvent. It is therefore concluded that the earlier theory [1] must be incomplete and that, in general, the rate of olefin hydrogenation is not solely controlled by equilibrium factors combined with a single rate-determining step but may also be affected by the kinetic competition of subsequent reactions involving the olefin intermediate. The induction period is attributed to radical side-reactions leading to a changed rate-determining step for alkane formation.

A parallel investigation was also carried out on the base cocatalysed hydrogenation of ethylene using $IrCl(CO)(PPh_3)_2$ in dimethylformamide. It was found that the base dehydrochlorination of $IrH_2Cl(CO)(PPh_3)_2$ was a relatively slow process and that the cocatalysed

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[1] W. Strohmeier and T. Onoda, *Z. Naturforsch.*, 1969, **24b**, 1493.

[2] B. R. James and N. A. Memon, *Canad. J. Chem.*, 1968, **46**, 217.

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

[4] M. G. Burnett and R. J. Morrison, *J.C.S. Dalton*, 1973, 632.

hydrogenation rate was controlled by the concentration of $IrH_3(CO)(PPh_3)_2$ formed.

EXPERIMENTAL

Reagents.—$IrH_3(CO)(PPh_3)_2$, $IrH(CO)(PPh_3)_3$, triphenylphosphine, dimethylformamide, hydrogen, and ethylene were prepared or purified as previously described.[3] Identical samples of $IrCl(CO)(PPh_3)_2$ were prepared by the methods of Vaska and DiLuzio[5] and Vrieze *et al.*[6] $IrH_2Cl(CO)(PPh_3)_2$ was prepared by the method of Vaska and DiLuzio.[7] The physical and spectroscopic properties of these compounds agree with those in the literature. Sodium chloride, hydroxide, and acetate, lithium hydroxide (AnalaR; B.D.H.), and sodium perchlorate, maleic acid, *p*-methoxyphenol, and triethylamine (Reagent Grade; B.D.H.), were all used as supplied. White Spot nitrogen and argon (British Oxygen Co.) were also used as supplied.

p-Toluidine (Reagent Grade; B.D.H.) was recrystallised from ethanol–acetone. Dimethylacetamide and toluene (Reagent Grade; Hopkins and Williams) were redistilled and stored over 5A molecular sieve. Dimethyl maleate was prepared by the silver salt method[8] when required free of *p*-methoxyphenol but otherwise the ester was used as supplied by Kodak Ltd., containing 20 p.p.m. *p*-methoxyphenol. Dimethyl fumarate was prepared either by heating pure dimethyl maleate or by esterifying pure fumaric acid. The solid products were recrystallised from acetone and gave identical i.r. spectra.

Apparatus and Procedure.—The apparatus and procedure used at 50° have already been described.[3] At 80°, a small-volume reflux condenser held at 25° was fitted to the reaction vessel to prevent solvent condensation in the transducer gas line. When using toluene at 80°, the procedure was further modified due to the large vapour pressure of toluene and its ability to dissolve vacuum grease. A known weight of catalyst was placed in the reaction vessel which had been fitted with a vacuum-tight rubber injection seal. The toluene was initially vacuum-degassed and an atmosphere of argon was then used to force it through a hypodermic needle into the reaction vessel. The latter contained 100 Torr of argon to prevent the solvent boiling too rapidly. The catalyst solution was allowed to come to equilibrium for 10—15 min before the addition of hydrogen and olefin. Liquid reactants were injected by a hypodermic syringe through the rubber seal and the total initial pressure was adjusted to 1 atm by the addition of argon where necessary. The effective volume of the reaction vessel used in these experiments was 251 ml.

RESULTS

Partition coefficients for ethylene and hydrogen in dimethylformamide at 50° have already been reported.[3] The partition coefficients for hydrogen at 80° are −0·088 (dimethylacetamide) and 0·107 (dimethylformamide). The corresponding coefficient in toluene has been calculated from data given by Landholdt-Bornstein (0·102).[9] This is less than the value calculated from Table 1 of ref. 10 (0·110), but the latter is not consistent with the high temperature data given in Figure 151 of ref. 9.

TABLE 1

The rate and equilibrium constants for reaction (1)

		$10^3[IrCl(CO)(PPh_3)_2]/M$		$10^3[H_2]/M$				
Number	$t/°C$	Initial	Equilib.	Initial	Equilib.	$10^3R/s^{-1}$	$k_{-1}/mol^{-1}\,l\,s^{-1}$	$10^4K_1/M$
(1)	25	2·22	0·08	1·30	1·26	2·05	1·56	0·50
(2)	25	2·35	0·11	0·99	0·97	1·50	1·51	0·46
(3)	30	5·39	0·39	1·41	1·26	2·51	1·84	0·98
(4)	40	5·41	0·66	1·78	1·61	3·96	2·18	2·22
(5)	40	5·75	0·55	1·79	1·61	3·85	2·17	1·70
(6)	50	5·41	1·20	1·67	1·55	4·94	2·49	4·41
(7)	50	24·46	4·40	2·00	1·94	6·45	2·73	4·26
(8)	50	5·37	0·91	2·31	2·19	7·51	2·85	4·43
(9)	50	5·77	1·00	2·33	2·21	7·65	2·80	4·84
(10)	50	5·41	0·88	2·32	2·20	7·31	2·78	4·76
(11)	50	5·36	2·95	0·43	0·34	2·10	2·76	4·18
(12)	50	5·30	2·11	0·69	0·62	2·70	2·61	4·13
(13)	50	0·78	0·19	1·61	1·54	5·06	2·50	4·85

Mean value $K_1 = 4{\cdot}46 \times 10^{-4}$M (50°).

Reactions of $IrCl(CO)(PPh_3)_2$.—*Equilibrium and kinetics of* $IrH_2Cl(CO)(PPh_3)_2$ *formation*. The rate of attainment of equilibrium (1), and the final equilibrium concentrations

$$IrH_2Cl(CO)(PPh_3)_2 \rightleftharpoons IrCl(CO)(PPh_3)_2 + H_2 \quad (1)$$

have been measured by the fall in hydrogen pressure accompanying the formation of $IrH_2Cl(CO)(PPh_3)_2$ in dimethylformamide. In all these experiments the hydrogen consumed was a relatively small fraction of the total in the reaction vessel so that the hydrogen concentration could be assumed to be constant and the reaction system analysed as if it consisted of two opposed first-order reactions.

$$-\frac{d\ln([IrCl(CO)(PPh_3)_2] - [IrCl(CO)(PPh_3)_2]_e)}{dt} = R \quad (2)$$

The subscript e denotes the equilibrium concentration and

$$R = k_1 + k_{-1}[H_2]$$

The results were in excellent agreement with equation (2) and the values of R, K_1, and k_{-1} are given in Table 1 for a wide range of conditions.

The i.r. spectrum of the hydride formed has been shown by Taylor, Young, and Wilkinson[11] to be the H-*cis*, PPh_3-

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[5] L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, 1961, **83**, 2784.

[6] K. Vrieze, J. P. Collman, C. T. Sears, jun., and M. Kutoba, *Inorg. Synth.*, 1968, **11**, 101.

[7] L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, 1962, **84**, 679.

[8] A. I. Vogel, 'A Textbook of Practical Organic Chemistry,' Longmans, London, 1966, p. 388.

[9] Landholdt-Bornstein, 'Zahlenwerte und Funktionen,' Berlin, 1962, vol. II, Part 2b, pp. 1—70 and 1—186.

[10] W. Strohmeier and T. Onoda, *Z. Naturforsch.*, 1969, **24**b, 515.

[11] R. C. Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, 1966, **5**, 20.

trans isomer. The product remains in this form even after 4 h at 50° in dimethylformamide. After a long period in impure solvents, an i.r. band appears at 1745 cm^{-1} (within the range 1725—1771 cm^{-1} attributed to H-*trans*) [12] but the isomer giving rise to this absorption could not be detected in the solid isolated from a solution which had been used as a catalyst.

Solvolysis. Solutions of 10^{-4}M-IrCl(CO)(PPh$_3$)$_2$ in dimethylacetamide and dimethylformamide were stored at *ca.* 21° under nitrogen for periods of up to 6 months without any detectable change occurring in the absorption band at 387 nm. A sample of the dimethylformamide solution was also kept at 80° for 5 h without producing any significant change in the absorption. The spectrum of IrCl(CO)(PPh$_3$)$_2$ from 200 to 500 nm was the same at 80° as that observed at 25°.

Catalysis of Olefin Hydrogenation by IrCl(CO)(PPh$_3$)$_2$.—*In the absence of a base.* (a) *Ethylene in dimethylformamide at* 50°. A preliminary experiment showed that even in the presence of 0·02M-ethylene there was no detectable complex formation. A typical catalysed reaction of hydrogen and ethylene shown in Figure 1 starts slowly but accelerates to a final apparently constant rate. The induction period is defined as the intercept on the time axis of the linear region extrapolated to zero reaction. After the induction period defined in this way subsequent variation in rate can hardly be detected since the slight curvature of the plot is masked by the variation in the ethylene analyses (Figure 1). The reaction is sufficiently slow to cause only small changes in the ethylene and hydrogen concentrations during the experiment so that an approximately constant rate would normally have been expected throughout the experiment.

The dependence of the final rate measured at 1200 min on the ethylene, hydrogen, and iridium concentration is shown in Figure 2. The numbers next to the points in Figure 2 give the induction periods in minutes. Although it was intended to vary only one concentration at a time, it was found in practice that it was impossible in these experiments to match the conditions exactly. The actual observed rates are represented by the open points. The solid points represent rates which have been corrected for the error introduced by a deviation from the nominal concentrations. The corrections are made assuming the catalysed rate follows the rate equation (3), in which the

$$-\frac{d[C_2H_4]}{dt} = \frac{0{\cdot}0025[C_2H_4][IrCl(CO)(PPh_3)_2]_o}{1 + 2240[H_2]} \qquad (3)$$

subscript o denotes the initial concentration. No correction was necessary for experiments represented by a solid point only. The corrections do not affect the trends in the results but their absence would produce an appearance of greater random variation than really exists. The theoretical basis for equation (3) will be discussed later but it is apparent that the curves drawn in Figure 2 which were calculated from equation (3) only reproduce the trends of the results, although the equation is clearly sufficiently accurate for calculation of the corrections required.

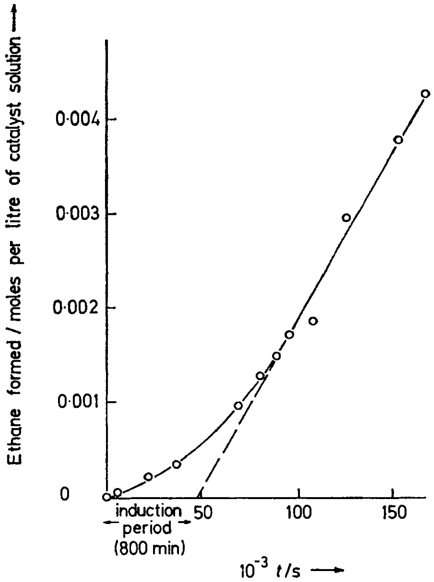

FIGURE 1 Formation of ethane at 50° in dimethylformamide

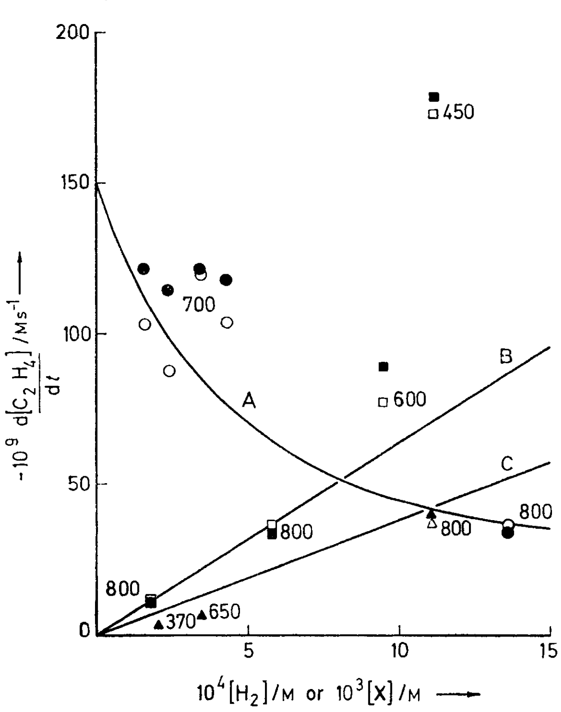

FIGURE 2 Variation in rate of ethylene hydrogenation with concentration of reactants. Concentrations when constant: [IrCl(CO)(PPh$_3$)$_2$] = 6 × 10^{-3}M, [H$_2$] = 1·3 × 10^{-3}M, [C$_2$H$_4$] = 10^{-2}M. Curve A calculated for variation of [H$_2$] ●. Curve B calculated for variation of [IrCl(CO)(PPh$_3$)$_2$]$_o$ ■. Curve C calculated for variation of [C$_2$H$_4$] ▲. Open symbols represent uncorrected rates. The numbers next to the points give the observed induction periods in minutes.

The effect of various treatments and additives is given in Table 2, Nos (1)—(7). It should be emphasised that in none of these experiments was there any evidence from the i.r. spectra of the solids isolated from the reactant solutions that the catalyst was present in any other form than IrCl(CO)(PPh$_3$)$_2$ and H-*cis*, P-*trans*-IrH$_2$Cl(CO)(PPh$_3$)$_2$. It can be seen that every treatment produces some increase in the final rate excepting triphenylphosphine addition which inhibits it. The calculated rates given for experiments (2)—(7) are based on experiment (1) corrected for the slight changes in individual conditions by equation (3).

Although considerable changes in the induction periods occur in experiments (1a) and (2)—(7), the most dramatic

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[12] J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, **1965**, 7391.

change is in experiment (1b) in which no induction period is observed. The effect of maturing the catalyst solution is invariably to shorten the induction period and to increase the final rate; the greatest effect however is produced by maturing in the presence of a reacting mixture of hydrogen and ethylene [Nos. (1a) and (1b)]. Experiments (8)—(13) are the results of base-cocatalysis and are dealt with later.

TABLE 2

The effects of treatment and additives on the rate of ethylene hydrogenation using $IrCl(CO)(PPh_3)_2$ in dimethylformamide at 50°

Number	$10^3[Ir]_0$/M	Additive	$10^3[C_2H_4]$/M	$10^3[H_2]$/M	$-10^9d[C_2H_4]/dt$ / mol l^{-1} s^{-1} Obs.	Calc.	Induction period/min	pK_a of conjugate acid
(1a)	5·73		11·1	1·36	36·3	36·3	800	
(1b) *	5·77		8·74	1·37	188	28·6		
(2) *	5·58		10·6	1·21	115	36·8	425	
(3) *	5·69		5·61	1·40	82·7	17·8	400	
(4) *	6·43		8·88	1·17	171	36·4	500	
(5)	5·24	0·026M $NaClO_4$	10·4	1·45	57·5	29·6	800	<0
(6)	5·65	0·036M NaCl	10·3	1·46	46·7	31·5	800	<0
(7)	5·57	0·009M PPh_3	12·4	1·47	7·6	37·2	800	3
(8)	5·68	0·007M NaOH **	7·03	1·05	153	153	40	15·7
(9)	5·93	0·007M NaOH **	7·55	1·04	191	240	40	15·7
(10)	5·57	0·031M LiOH	8·00	1·20	194	223	150	15·7
(11)	5·40	0·021M NEt_3	10·0	1·30	176	260	150	10·7
(12)	5·85	0·031M p-C_7H_9N	8·75	1·25	200	252	150	5·1
(13)	5·40	0·040M HCOONa	12·0	1·10	200	339	150	3·8

The symbol $[Ir]_0$ in column 2 represents the initial concentration of $IrCl(CO)(PPh_3)_2$.

* (1b) Using the catalyst solution from Experiment (1a) which had reacted for 48 h. (2) Catalyst solution held under 1 atm ethylene for 24 h at 50° before use. (3) Catalyst solution held under 1 atm hydrogen for 24 h at 50° before use. (4) Catalyst solution held under 1 atm nitrogen for 60 h at 50° before use. ** Saturated solution. Sufficient solid present to give 0·06M NaOH on complete solution.

The composition of the solvent was analysed chromatographically using a 2-m 5% fluorosilicone oil column at 100°. Initially no impurities could be detected but analysis of the solvent after it had been used in an experiment showed the presence of 3 low-boiling impurities at a maximum concentration of 1 part in 2000 parts of solvent.

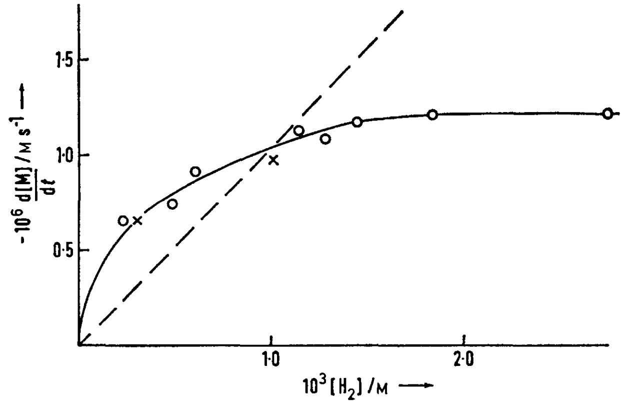

FIGURE 3 Variation in rate of dimethyl maleate hydrogenation with hydrogen concentration at 80° in toluene – – – calculated using equation (11). ○ Rates measured in the presence of 5×10^{-6}M p-methoxyphenol. × Initial rate in the absence of p-methoxyphenol. $[(CHCO_2Me)_2] = 0{\cdot}18$M, $[IrCl(CO)(PPh_3)_2] = 0{\cdot}92 \times 10^{-3}$M

(b) *Dimethyl maleate and maleic acid in dimethylformamide, dimethylacetamide, and toluene at* 80°. The data given by Strohmeier and Onoda [1] contain no experiments showing the variation of rate with hydrogen concentration although this would provide an important test of the proposed mechanism. The rates shown in Figure 3 were measured by the rate of change of hydrogen pressure during the hydrogenation of dimethyl maleate in toluene. The broken line is calculated from the rate expression given by Strohmeier and Onoda using the revised constants which have been found to improve the fit of the theory and the original data. The original rates appear to be about 20% faster than in comparable experiments in this work but the discrepancy between theory and experiment depends more on the zero order with respect to the hydrogen concentration above 5×10^{-4}M than on a simple numerical disagreement. The theory predicts an order only slightly less than 1 over the whole range shown in Figure 3. The numerical disagreement may originate in the more efficient removal of oxygen by the vacuum-degassing technique used in this work as opposed to the nitrogen-purging method used by Strohmeier and Onoda.[12] A slight degree of catalyst oxidation can change the rate by several orders of magnitude.[2]

Most of the measurements given in Figure 3 were made in the presence of 5×10^{-6}M of p-methoxyphenol, since dimethyl maleate isomerises rapidly to dimethyl fumarate in the absence of a radical inhibitor. However, the reaction rate of dimethyl maleate in toluene is not affected by the presence of the inhibitor. Without added p-methoxyphenol, the rate decreases over a period of 2 h to the value corresponding to the hydrogenation of dimethyl fumarate but its initial value is equal to that found when the inhibitor is used.

The inhibitor also removes the induction period observed during the hydrogenation of dimethyl maleate in dimethylformamide. In the absence of inhibitor, the reaction plot was a sigmoid curve probably because the induction period (curve A, Figure 4) was accompanied by the formation of dimethyl fumarate which is only slowly hydrogenated. The final rate is comparable to that found using dimethyl fumarate (curve C). In the presence of inhibitor, the catalysed rates for both dimethyl maleate and dimethyl fumarate are reduced (curves B and D) and the induction periods disappear. Induction effects are much less pronounced using maleic acid in both dimethylformamide and dimethylacetamide but preliminary experiments have shown similar decreases in the catalysed rate in the presence of 5 × 10^{-6}M *p*-methoxyphenol.

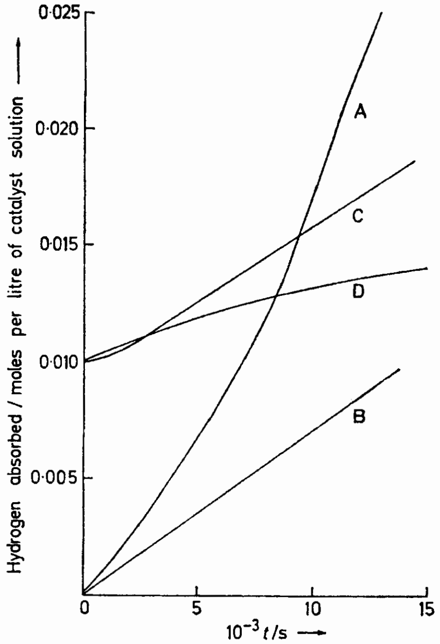

FIGURE 4 The absorption of hydrogen by 0·18M substrate in dimethylformamide at 80°, catalysed by 0·95 × 10^{-3}M IrCl(CO)$(PPh_3)_2$. A, dimethyl maleate; B, dimethyl maleate + 5 × 10^{-6}M *p*-methoxyphenol; C, dimethyl fumarate; D, dimethyl fumarate + 5 × 10^{-6}M *p*-methoxyphenol

In the presence of a base. The addition of a base to the catalyst in dimethylformamide at 50° decreased the induction period and sharply increased the catalysed rate of ethylene hydrogenation. The i.r. spectrum of the solid extracted from the catalyst solution at the end of the experiment showed that the major constituent was $IrH_3(CO)(PPh_3)_2$ together with the chloride of the base used and small amounts of $IrHCl_2(CO)(PPh_3)_2$. The $IrHCl_2(CO)(PPh_3)_2$ was presumably responsible for the slight white precipitate observed in experiments (8)—(10) and (13) since its solubility is less than 10^{-4}M at 50° whereas sodium and lithium chlorides are both soluble at concentrations greater than 0·01M. During the induction period the yellow colour of $IrCl(CO)(PPh_3)_2$ slowly vanished in experiments (10)—(13) but in experiments (8) and (9) the colour slowly darkened to a reddish brown before disappearing entirely. These differences did not apparently significantly affect the final rate. The rates given in column 7 of Table 2 for experiments (8)—(13) have been calculated using the empirical rate equation obtained in a previous study[3] of the $IrH_3(CO)(PPh_3)_2$ system and assuming that the complex is finally entirely in that form.

DISCUSSION

In the following discussion, the constants of the equilibria[1,2] supposed to control the hydrogenation rate are estimated and are then used to test the fit of the theoretical rate equation to the rate data for dimethyl maleate, maleic acid, and ethylene.

Reactions of $IrCl(CO)(PPh_3)_2$.—*Solvolysis.* Despite careful investigation the spectroscopic experiments reported by James and Memon[2] could not be repeated. It was possible to produce similar results by deliberately arranging a very slight leakage of air into the sealed spectrometer cell and such a cause is at the moment the only available explanation of the discrepancy. It seems on the whole likely that the dissociation equilibrium postulated by James and Memon[2] lies almost entirely to the left.

$$IrCl(CO)(PPh_3)_2 \rightleftharpoons IrCl(CO)(PPh_3) + PPh_3 \quad (4)$$

Olefins. There is no evidence for the formation of an ethylene complex at the ethylene concentrations used in this work but Strohmeier and Fleischmann[13] have made a study of equilibrium (5) for $M = (CHCO_2Me)_2$ in toluene at temperatures *ca.* 20°. The value of K_5 extrapolated to 80° is given in Table 3.

$$IrCl(CO)M(PPh_3)_2 \rightleftharpoons IrCl(CO)(PPh_3)_2 + M \quad (5)$$

James and Memon reported that complex formation with maleic acid is prevented by adding triphenylphosphine so that equilibrium (6) must also be considered

$$IrCl(CO)M(PPh_3)_2 \rightleftharpoons IrCl(CO)M(PPh_3) + PPh_3 \quad (6)$$

in evaluating their results at 80° in dimethylacetamide. Since they believed that equilibrium (4) was responsible for the effect of phosphine, their results were given as equilibrium constants K_4 and K_7. In fact, in the

$$IrCl(CO)(PPh_3) + M \rightleftharpoons IrCl(CO)M(PPh_3) \quad (7)$$

absence of reaction (4), the system must be dominated by equilibrium (8), that is, at 80° very little

$$IrCl(CO)(PPh_3)_2 + M \rightleftharpoons IrCl(CO)M(PPh_3) + PPh_3 \quad (8)$$

$IrCl(CO)M(PPh_3)_2$ is present. This conclusion is consistent with the analysis of the kinetic results given later in the discussion.

$$\therefore \quad K_8 = K_4K_7 \quad \text{(quoted in ref. 2)}$$
$$= K_6/K_5$$

The value of K_6/K_5 for $M{=}(CHCO_2H)_2$ at 80° is given in Table 3.

TABLE 3

Measured and fitted equilibrium and rate constants for the hydrogenation of dimethyl maleate and maleic acid by $IrCl(CO)(PPh_3)_2$ at 80°

	10^3K_1/M	K_5/M	10^3K_6/M	$10^3K_6/K_5$	k_9/mol l^{-1} s^{-1}
$(CHCOOMe)_2$ in toluene	5·54 [a]	5·87 [b]	6·48 *	1·10	3·33 *
$(CHCOOH)_2$ in dimethylacetamide	4·87 [c]			1·96 [c]	2·46 *

* These values are fitted using kinetic data, the remainder are independently measured. The value of K_1 in toluene is less than that in reference (a), 5·97 × 10^{-3}M, because of the smaller partition coefficient used in this work (0·102 compared to 0·110).

[a] W. Strohmeier and F. J. Müller, *Z. Naturforsch.*, 1969, **24**b, 931. [b] W. Strohmeier and R. Fleischmann, *Z. Naturforsch.*, 1969, **24**b, 1217. [c] B. R. James and N. A. Memon, *Canad. J. Chem.*, 1968, **46**, 217.

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[13] W. Strohmeier and R. Fleischmann, *Z. Naturforsch.*, 1969, **24**b, 1217.

Hydrogen. The reaction of hydrogen and $IrCl(CO)(PPh_3)_2$ appears from this and the previous work [14-16] to be a simple oxidative addition equilibrium. Although

$$IrH_2Cl(CO)(PPh_3)_2 \rightleftharpoons IrCl(CO)(PPh_3)_2 + H_2 \quad (1)$$

the pressure of hydrogen was followed for up to 4 h after the hydride had been formed, no evidence could be found of any subsequent pressure changes showing indirectly that triphenylphosphine does not slowly dissociate from $IrCl(CO)(PPh_3)_2$. If $IrCl(CO)(PPh_3)_2$ had dissociated, a comparable fraction of the hydride would also have broken up. The constancy of the measured values of K_1 over a wide range of conditions (Table 1), is further evidence that $IrCl(CO)(PPh_3)_2$ is unlikely to be involved in side-reactions.

It is noticeable that the rates of reaction (−1) are relatively unaffected by the solvent, *e.g.* k_{-1} (80°) $= 4{\cdot}8$ (dimethylformamide) and $8{\cdot}4$ l mol^{-1} s^{-1} (toluene).[15] The absence of any large effect is caused by decreases in the enthalpy of activation being balanced by decreases in the entropy, *e.g.* $\Delta H^{\ddagger} = 15{\cdot}3$ (dimethylformamide) and $45{\cdot}4$ kJ (toluene) [14,15] when $\Delta S^{\ddagger} = -190$ (dimethylformamide) and -100 J K^{-1} (toluene).[14,15] It has previously been suggested [3] that this is associated with an increasingly polar transition state in the more polar solvents.

The data in Table 1 apply to the formation of the H-*cis*, PPh_3-*trans*-isomer. The subsequent isomerisation seems too slow to affect the catalysis experiments except under basic conditions when a different hydride is formed.

Catalysis of Olefin Hydrogenation by $IrCl(CO)(PPh_3)_2$ *in the Absence of a Base.—Induction period.* The previous explanation [2] of the increasing catalysed rate early in the reaction depended on the existence of the solvolytic reaction (4) for which there now seems to be little evidence. It is now suggested that the rate-determining step in the catalytic reaction in dimethylformamide can be changed by the intervention of a radical chain process.

The main evidence in support of this hypothesis is the absence of an induction period in experiments conducted with *p*-methoxyphenol. The fact that the concentration of the inhibitor is 10^{-3} that of the catalyst strongly suggests the presence of a chain process.

The effects of pre-treating the catalyst solution (Table 2) show that the induction processes are promoted by $IrH_2Cl(CO)(PPh_3)_2$ but that the most effective agents are the reactive intermediates present during the catalysed reaction. Ethylene alone has apparently no more effect on the induction period than nitrogen and nitrogen is unlikely to be chemically involved in the system. This is consistent with the absence of significant concentrations of an iridium–ethylene complex. The importance of the olefin in determining the extent to which the hydrogenation accelerates during the induction period is clearly shown by the fact that the ethylene and dimethyl maleate rates are very much increased but that the hydrogenation of maleic acid is only slightly affected. It may also be significant that there is no induction period when using toluene as a solvent since toluene is one of a class of non-polar solvents known not to participate in radical reactions such as, for instance, the induced decomposition of peroxides.[17] Radical substitution reactions at metal centres are well established amongst non-transition metals [18] and may well play an unsuspected part in transition metal catalysis. Evidence of the intervention of radical intermediates in hydrogenation catalysis has already appeared.[19]

The identity of the radical processes which are producing the induction periods are the subject of current investigation.* The impurities introduced into the solvent during the hydrogenation of ethylene could have been present in the ethylene but it is possible that they are the products of the radical reactions. Their concentrations, assuming a molecular weight of the order of 100, are comparable to that of the catalyst.

The mechanism of the catalysed reaction. The mechanism proposed by Strohmeier [1] depends on the equilibria (1), (5), and (6) and the rate determining step (9). The last step may well involve radical intermediates and its rate may be strongly dependent on the solvent but in the present analysis the reaction can be summarised by equation (9). If the complex $IrCl(CO)(PPh_3)$ combines

$$IrH_2Cl(CO)(PPh_3)_2 \rightleftharpoons IrCl(CO)(PPh_3)_2 + H_2 \quad (1)$$

$$IrCl(CO)M(PPh_3)_2 \rightleftharpoons IrCl(CO)(PPh_3)_2 + M \quad (5)$$

$$IrCl(CO)M(PPh_3)_2 \rightleftharpoons IrCl(CO)M(PPh_3) + PPh_3 \quad (6)$$

$$IrCl(CO)M(PPh_3) + H_2 \longrightarrow IrCl(CO)(PPh_3) + MH_2 \quad (9)$$

rapidly with triphenylphosphine to reform $IrCl(CO)(PPh_3)_2$, the equilibrium concentration of $IrCl(CO)M(PPh_3)$ may be expressed by equation (10).

$$[IrCl(CO)M(PPh_3)] = \frac{K_6[M][IrCl(CO)(PPh_3)_2]_o}{K_6[M] + [PPh_3](K_5 + K_5[H_2]/K_1 + [M])} \quad (10)$$

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* The induction periods and isomerisation reactions have subsequently been found to be due to small concentrations, (*ca.* 5×10^{-5}M), of oxidised impurities present in the dimethylformamide and dimethyl maleate as normally prepared. If both solvent and substrate are redistilled and also stored under argon the induction and isomerisation effects disappear.

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The rate of olefin removal is given by the rate of reaction (9).

$$-\frac{\mathrm{d[M]}}{\mathrm{d}t} = k_9[\mathrm{IrCl(CO)M(PPh_3)}][\mathrm{H_2}] =$$
$$\frac{k_9K_6[\mathrm{M}][\mathrm{IrCl(CO)(PPh_3)_2}]_o[\mathrm{H_2}]}{K_6[\mathrm{M}] + [\mathrm{PPh_3}](K_5 + K_5[\mathrm{H_2}]/K_1 + [\mathrm{M}])} \quad (11)$$

In order to test this equation it is necessary to estimate the concentration of triphenylphosphine.

$$[\mathrm{PPh_3}] = [\mathrm{IrCl(CO)M(PPh_3)}] + [\mathrm{PPh_3}]_o$$

On substituting the expression in equation (10) above for $[\mathrm{IrCl(CO)M(PPh_3)}]$, the concentration required is obtained as the solution to the quadratic equation (12),

$$T[\mathrm{PPh_3}]^2 + (1 - [\mathrm{PPh_3}]_oT)[\mathrm{PPh_3}] - ([\mathrm{PPh_3}]_o + [\mathrm{IrCl(CO)(PPh_3)_2}]_o) = 0 \quad (12)$$

in which $T = (1/K_6[\mathrm{M}])(K_5 + K_5[\mathrm{H_2}]/K_1 + [\mathrm{M}])$. In all the above equations the subscript o denotes an initial concentration.

The unknown constants, k_9 and K_6, required to fit the data using equations (10) and (11), are obtained by successive approximations. The constants derived for the data published by Strohmeier and Onoda [1] and James and Memon [2] are given in Table 3. The details of the experimental conditions and the observed and fitted rates are given in Tables 4 and 5.* All but 3 of the 24 rate measurements for dimethyl maleate are randomly scattered about the values predicted by the rate equation but the observations numbered 25, 26, and 27 in Table 1 of ref. 1 give rates which are each a factor of *ca.* 2 too large. The disagreement occurs in the presence of large concentrations of triphenylphosphine. The value of K_6 ($1{\cdot}55 \times 10^{-2}$M), proposed by Strohmeier and Onoda [1] makes these results statistically indistinguishable from the others but they do so by worsening the fit elsewhere. The percentage coefficient of variation then becomes 20% compared with 11% using the constants in Table 3. Moreover detailed examination of the results reveals that the variations between the observed and theoretical values are no longer entirely random.

The data for 10 of the 16 independent experiments given for maleic acid [2] also fit with a coefficient of variation of 12% using the constants in Table 3 but the remaining 6 experiments with varying hydrogen concentrations exceed the theoretical prediction by a factor rising to 2 at the lowest concentrations. The unusually large coefficient of variation calculated in the analysis of both sets of data is confirmed by the poor reproducibility found by James and Memon when they performed duplicate experiments (Table 5). The concentrations of maleic acid used in this work are so small that $[\mathrm{M}] < (K_5 + K_5[\mathrm{H_2}]/K_1)$ and therefore K_6 cannot be estimated. This inequality implies that the concentration of $\mathrm{IrCl(CO)M(PPh_3)_2}$ is negligible and justifies the assumption originally made in estimating K_6/K_5. The failure of the theory exactly parallels the failure for dimethyl maleate shown in Figure 3 where the disagreement also occurs on varying the hydrogen concentration.

It must therefore be concluded that the theory proposed by Strohmeier and Onoda [1] fails to predict the effect of hydrogen or triphenylphosphine concentrations over the whole range although it does have some limited success in correlating data at low triphenylphosphine and constant hydrogen concentrations. The mechanism consequently cannot be correct although the rate data probably fit an empirical rate equation similar to (11).

The results obtained using ethylene were unfortunately not performed with added inhibitor and the maturing experiments suggest that unless the conditions are exactly duplicated considerable changes in rate can be produced. However the general trend of the observations can themselves cast light on the mechanism of hydrogenation. Equation (3) was deduced from equation (13) which follows if the mechanism proposed by Strohmeier and Onoda is correct but with reaction (−5) as the new rate determining step.

$$i.e.\ -\frac{\mathrm{d[C_2H_4]}}{\mathrm{d}t} = \frac{k_{-5}[\mathrm{C_2H_4}][\mathrm{IrCl(CO)(PPh_3)_2}]_o}{1 + [\mathrm{H_2}]/K_1} \quad (13)$$

The simplification produced by studying the hydrogenation of ethylene lies in the absence of $\mathrm{IrCl(CO)(C_2H_4)(PPh_3)_2}$ and the consequent absence of significant concentrations of triphenylphosphine formed by dissociation. The uncertainty involved in estimating the free triphenylphosphine concentration is thereby removed. The changed rate-determining step was not unexpected in view of the exactly similar result obtained with the catalysts $\mathrm{IrH(CO)(PPh_3)_3}$ [3] and $\mathrm{IrH_3(CO)(PPh_3)_2}$.[4] The value of K_1 is taken from Table 1. The persistent effects of the induction processes may well account for the apparent discrepancies shown in Figure 2 but the completely unpredicted inhibition by triphenylphosphine shown in Table 2 cannot be explained using Strohmeier and Onoda's theory. The simplest explanation of the triphenylphosphine inhibition lies in the kinetic competition of reactions involving the iridium–olefin intermediate. The simplest form of such a mechanism is to suppose that $\mathrm{IrCl(CO)M(PPh_3)_2}$ and $\mathrm{IrCl(CO)M(PPh_3)}$ behave as reactive intermediates and that both are in the steady state concentration. This assumption leads to equation (14), and readily accounts

$$-\frac{\mathrm{d[C_2H_4]}}{\mathrm{d}t} =$$
$$\frac{k_9k_{-5}k_6[\mathrm{IrCl(CO)(PPh_3)_2}]_o[\mathrm{C_2H_4}][\mathrm{H_2}]}{\{k_9(k_5 + k_6)[\mathrm{H_2}] + k_5k_{-6}[\mathrm{PPh_3}]\}\{1 + [\mathrm{H_2}]/K_1\}} \quad (14)$$

for the inhibition by triphenylphosphine. Also in the absence of triphenylphosphine, equation (14) simplifies to equation (15) which is identical in form with equation (3).

$$-\frac{\mathrm{d[C_2H_4]}}{\mathrm{d}t} = \frac{k_5k_6[\mathrm{IrCl(CO)(PPh_3)_2}]_o[\mathrm{C_2H_4}]}{(k_5 + k_6)(1 + [\mathrm{H_2}]/K_1)} \quad (15)$$

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* Tables 4 and 5 have been deposited at the National Lending Library under the Supplementary Publications Scheme (SUP. No. 20638, 3 pp.). Details of the Scheme are given in Notice to Authors No. 7 in the index of issue *J. Chem. Soc. (A)*, 1970.

Clearly in this limiting form the mechanism has become practically equivalent to that assumed in deducing equation (13). Indeed if $k_6 > k_5$ equations (15) and (13) are identical but this situation can only exist as long as there are no reactions competing with reaction (9), *i.e.* with the reaction of hydrogen. There are a number of variants to this approach possible but all depend on a combination of an equilibrium expression, such as equation (10), with a steady-state expression. The result is the characteristic product of two terms in the denominator of the theoretical rate expression. In equation (14), the equilibrium term is $(1 + [H_2]/K_1)$ while the term $\{k_9(k_5 + k_6)[H_2] + k_5k_{-6}[PPh_3]\}$ is produced by the steady state assumption.

A similar approach, combining kinetic and equilibrium factors, may be successful in solving the problem of the failure of Strohmeier and Onoda's theory for dimethyl maleate and maleic acid. The equilibrium term in the denominator would be identical with the denominator of equation (11) while the kinetic term would originate in the competition of reactions involving the iridium–olefin intermediate generated in reaction (9). If the latter contained a large hydrogen contribution, the kinetics would appear to agree with those predicted by equation (11) except that the order with respect to hydrogen would be almost zero at the higher hydrogen concentrations. The anomaly of the apparent decrease in the inhibitory effect of triphenylphosphine at high concentrations seems likely to remain. It is possible, in view of the cocatalysis due to even weak bases shown in Table 2, that triphenylphosphine itself can behave simultaneously as a cocatalyst and as an inhibitor.

The acceleration produced by ionic additives (Table 2) points to a strongly polar transition state in the rate-determining step similar to that suggested in the formation of $IrH_2Cl(CO)(PPh_3)_2$. The absence of evidence of chloride ion inhibition argues against the existence of a chloride ion dissociative mechanism. A polar solvent such as dimethylacetamide might be expected to accelerate a reaction involving a polar transition state [2] but it is apparent from Table 3 that the constants are all very similar to those in toluene. Although the theory behind these constants is in doubt they remain useful as an empirical means of predicting rates and their similarity shows that under comparable conditions the rate of catalysis is similar in toluene and dimethylacetamide. It is possible that the change in substrate type has brought this about but it is also possible that the situation is similar to that of the reaction of $IrCl(CO)(PPh_3)_2$ and hydrogen in which the reduced enthalpy of activation in dimethylformamide compared to that in toluene was balanced by a reduced entropy of activation.

Finally, it must be remembered that the possible radical character of the rate-determining step could be complicating the observed kinetics. A detailed investigation of the effect of inhibitors and radical initiators is at present being carried out.

Catalysis of Olefin Hydrogenation by $IrCl(CO)(PPh_3)_2$ *in the Presence of a Base.*—It was originally supposed that the intermediate $IrH(CO)(PPh_3)_2$ could be generated in large concentrations in catalytic systems [3] but subsequently evidence was found that the intermediate could only be present in very low concentrations.[4] The use of strong bases as dehydrochlorinating agents has already been shown [20] to produce products consistent with the formation of the intermediate $IrH(CO)(PPh_3)_2$ but it is evident from the present results that the dehydrochlorination is relatively slow so that $IrH(CO)(PPh_3)_2$ never rises above the level found using $IrH_3(CO)(PPh_3)_2$ as a catalyst. The presence of small quantities of $IrHCl_2(CO)(PPh_3)_2$ in the solid isolated from the complex solution suggest that the dehydrochlorination is not irreversible but the cocatalysis by the feeble base formate shows that equilibrium (16) is readily moved to

$$IrH_2Cl(CO)(PPh_3)_2 + B \rightleftharpoons IrH(CO)(PPh_3)_2 + BH^+ + Cl^- \quad (16)$$

the right. The triphenylphosphine molecule is only 0·8 pK units less basic than the formate ion in water so that there is even a possibility that the inhibitor might catalyse the formation of $IrH(CO)(PPh_3)_2$ and produce anomalously fast inhibited rates. The existence of such anomalies has already been pointed out but the possibility of triphenylphosphine cocatalysis has yet to be confirmed.

It must be concluded that although it is possible to generate $IrH(CO)(PPh_3)_2$ by basic cocatalysis, hydrogen and triphenylphosphine are such effective reactants with the intermediate that the resulting system amounts to one in which $IrH_3(CO)(PPh_3)_2$ is slowly generated from $IrCl(CO)(PPh_3)_2$. The mechanism is consequently finally controlled by the factors already outlined for the catalyst system $IrH_3(CO)(PPh_3)_2$.

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