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THE MECHANISM OF SUBSTITUTION OF (π-OLEFIN)IRON TETRACARBONYL COMPLEXES BY TRIPHENYLPHOSPHINE: SOLVENT EFFECTS

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Summary

The reaction:

$$(\pi\text{-}CH_2{=}CHPh)Fe(CO)_4 + (2-\alpha)PPh_3 \rightarrow \alpha\, Fe(CO)_4PPh_3 + (1-\alpha)Fe(CO)_3(PPh_3)_2$$
$$+ CH_2{=}CHPh + (1-\alpha)CO$$

has been studied in dichloromethane, acetone, acetonitrile, isopropyl ether and n-hexane. The kinetics indicate that the reaction mechanism is the same as that in toluene. The solvent and temperature effects on the $\alpha/1-\alpha$ ratio further confirm the nature of the proposed intermediates.

Introduction

We previously described [1—3] a study of the mechanism of reaction of π-olefinic ligands in (π-olefin)iron tetracarbonyl complexes with the ligands CO, $SbPh_3$, pyridine, $AsPh_3$ and PPh_3. For all the ligands investigated the results obtained were consistent with formation of $Fe(CO)_4$ as an intermediate. For PPh_3 the final product was a mixture of the complexes $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$. The latter results could not be explained by assuming the formation only of $Fe(CO)_4$ as an intermediate, and further dissociation of this to give $Fe(CO)_3$ as a second intermediate was proposed. Support for this suggestion was obtained from a study of the effect of different concentrations of carbon monoxide on both the ratio $Fe(CO)_4PPh_3/Fe(CO)_3(PPh_3)_2$ and the reaction rate [4]. We describe below a study of solvent effects on the reaction.

Experimental

Dichloromethane, acetone, acetonitrile (AN), isopropyl ether and n-hexane were the solvents used. The last two were purified by distillation over sodium.

Acetone was purified by distillation over Drierite [5] and AN as described by Coetzee et al. [6]. Dichloromethane was purified as described in ref. 7.

(π-CH_2=CHPh)Fe$(CO)_4$ was prepared by treatment of $Fe_2(CO)_9$ with styrene [8] and purified by cryštallisation from pentane. The solvents were throughly deaerated before use. The presence of $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$ was recognised by their IR spectra. Kinetic measurements were carried out with exclusion of light on solutions in the NaCl cells of a Perkin—Elmer IR 257 spectrophotometer, the disappearance of the higher frequency CO stretching bands of the olefinic complex and the appearance of the corresponding CO stretching bands of the monosubstituted and disubstituted complexes being followed. For some solvents it was not possible to follow the appearance of the mono- and di-substituted complexes due to their low solubility. The reactions were followed up to 60—80% completion of reaction, and the 'infinity' values of the absorptions for the mono- and di-substituted complexes were measured at the end of reaction. The concentration of the ligand PPh_3 was always at least ten times as large as that of the olefinic complex. The concentration of styrene, added to observe the mass effect, was also always large with respect to that of the olefin complex in order to avoid significant variation in concentration due to the formation of the olefinic ligand during the course of reaction.

Kinetics were carried out in the temperature range 30—70° C, depending on the particular solvent used.

With AN there was initial formation of the known complex $Fe(CO)_4AN$ [9]. This complex was not isolated, but was recognised by its CO stretching frequencies at 2052, 1965, 1940 cm^{-1} in AN. The concentration of this complex reaches a maximum equilibrium value during the reaction.

Results and discussion

In all the solvents a mixture of the complexes $Fe(CO)_4PPh_3$ and $Fe(CO)_3$-$PPh_3)_2$ is formed, as represented in eqn. 1, in which α represents the fraction of monosubstituted complex per mole of olefinic complex.

$$(CH_2{=}CHPh)Fe(CO)_4 + (2-\alpha)PPh_3 \rightarrow Fe(CO)_4PPh_3 + (1-\alpha)Fe(CO)_3(PPh_3)_2 + CH_2{=}CHPh + (1-\alpha)CO \quad (1)$$

Tables 1—5 list values of k, the pseudo first order rate constants for reaction 1 at various temperatures as a function of the concentration of olefinic ligand for the solvents dichloromethane, acetonitrile, isopropyl ether and n-hexane, respectively. Table 6 shows the final kinetic parameters, including the activation parameters, and the $\alpha/1-\alpha$ ratios for the various solvents at different temperatures.

Figure 1 shows graphs of $1/k$ vs [Styrene] for the various solvents.

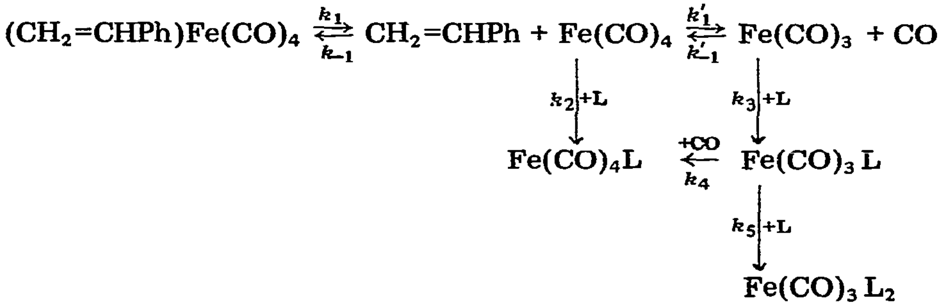
The kinetic behaviour found for all solvents is the same as that for toluene [1—4], from which we assume that the reaction mechanism is the same (eqn. 2) with $L = PPh_3$.

TABLE 1

PSEUDO FIRST ORDER RATE CONSTANTS (k) FOR THE REACTION BETWEEN (π-CH_2=CHC_6H_5)-$Fe(CO)_4$ AND PPh_3 IN CH_2Cl_2 SOLVENT. [PPh_3] = 10^{-1} M, [C] ≈ 2 × 10^{-3} M

T (°C)	10 [Styrene] (M)	10^5 k (sec^{-1})		
		a	*b*	*c*
40	0	8.82	9.07	9.90
40	0.983	7.66	7.30	7.58
40	1.83	6.67	6.91	6.72
40	3.04	5.72	5.74	5.92
40	3.94	5.13	5.15	6.22
40	5.06	4.97	4.93	5.10
30[d]	0	1.89		
30	0	1.83		
30	0.998	1.49		
30	2.17	1.21		
30	2.21	1.25		
30	2.92	1.07		

[a] Values obtained from disappearance of the olefinic complex. [b] Values obtained from appearance of the monosubstituted complex. [c] Values obtained from appearance of the disubstituted complex. [d] At this temperature only the olefinic complex disappearance was followed because the reaction is very slow.



$$\begin{tikzcd}
(CH_2{=}CHPh)Fe(CO)_4 \arrow[r, shift left, "k_1"] & CH_2{=}CHPh + Fe(CO)_4 \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k'_1"] \arrow[d, "k_2"', "+L"] & Fe(CO)_3 + CO \arrow[l, shift left, "k'_{-1}"] \arrow[d, "k_3"', "+L"] \\
& Fe(CO)_4L & Fe(CO)_3L \arrow[l, "+CO", "k_4"'] \arrow[d, "k_5"', "+L"] \\
& & Fe(CO)_3L_2
\end{tikzcd} \qquad (2)$$

Only for acetonitrile does this scheme have to be modified to include the reversible process (eqn. 3).

TABLE 2

PSEUDO FIRST ORDER RATE CONSTANTS (k) FOR THE REACTION BETWEEN (π-CH_2=CHC_6H_5)-$Fe(CO)_4$ AND PPh_3 IN ACETONE. [PPh_3] = 10^{-1} M, [C] ≈ 2 × 10^{-3} M

T (°C)	10 [Styrene] (M)	10^4 k (sec^{-1})		
		a	*b*	*c*
40	0	2.27	2.28	2.37
40	0.94	2.09	1.98	2.04
40	2.57	1.83	1.68	1.96
40	2.98	1.61	1.63	1.68
40	3.99	1.52		1.52
40	5.00	1.40	1.42	1.53
50	0	8.94	8.60	8.90
50	0.902	8.18	7.66	7.30
50	1.605	7.46	7.25	7.34
50	2.60	6.54	6.14	6.32
50	3.94	6.05	5.83	5.60
50	5.19	5.42	5.38	4.38

[a] Values from disappearance of the olefinic complex. [b] Values obtained from appearance of the monosubstituted complex. [c] Values obtained from the appearance of the disubstituted complex.

TABLE 3

PSEUDO FIRST ORDER RATE CONSTANTS (k) BETWEEN (π-CH_2=CHC_6H_5)$Fe(CO)_4$ AND PPh_3 IN ISOPROPYL ETHER. [PPh_3] = 10^{-1} M, [C] ≈ 2 × 10^{-3} M

T (°C)	10 [Styrene] (M)	10^5 k (sec^{-1})		
		a	b	c
40	0	7.18	7.12	7.31
40	0	6.98	7.12	7.02
40	1.10	6.34	6.57	6.14
40	2.20	5.55	5.64	5.58
40	4.27	4.64	4.34	4.43
40	4.67	4.40	4.63	4.58
50 [d]	0	38.9	39.9	
50	0	39.3	38.4	
50	0.917	33.7	30.7	
50	2.22	26.1	27.0	
50	2.96	26.0	26.2	
50	5.20	20.4	20.2	
50	6.32	19.8	18.1	

[a] Values obtained from disappearance of the olefinic complex. [b] Values obtained from appearance of the monosubstituted complex. [c] Values obtained from appearance of the disbustituted complex. [d] The $Fe(CO)_3(PPh_3)_2$ complex precipitates at this temperature.

$$Fe(CO)_4(CH_2{=}CHPh) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CH_2{=}CHPh + Fe(CO)_4 + AN \underset{k_{-s}}{\overset{k_s}{\rightleftarrows}} Fe(CO)_4\,AN \qquad (3)$$

Mechanism 2 would explain the mass retardation effects noted in Table 6 as the ratios k_{-1}/k_m, where k_m takes account of all the stages of disappearance of the intermediate $Fe(CO)_4$. If the dissociation stage of $Fe(CO)_4$ to $Fe(CO)_3$ is an equilibrium, then this ratio becomes k_{-1}/k_2. Analysis of the data of Table 6 assuming mechanism 2, indicates that the solvent influences the values of k_1, the k_{-1}/k_m ratios, and the $\alpha/1-\alpha$ ratios.

Examination of the k_1 values indicates that the solvent effect is very small (maximum variation about 4 times) on passing from solvents of very low dielectric constant (hexane, toluene) to solvents of very high dielectric constant (acetone, AN). Such behaviour is very common for substitution reactions of

TABLE 4

PSEUDO FIRST ORDER RATE CONSTANTS (k) BETWEEN (π-CH_2=CHC_6H_5)$Fe(CO)_4$ AND PPh_3 IN n-HEXANE [a]. [PPh_3] = 10^{-1} M, [C] ≈ 2 × 10^{-3} M

T (°C)	10 [Styrene] (M)	10^5 k (sec^{-1})	
		b	c
40	0	7.00	6.85
40	1.01	5.82	5.91
40	2.59	4.65	4.85
40	3.93	4.41	4.72
40	4.86	3.97	3.83
50	0	28.1	27.7
50	0.90	25.5	28.8
50	2.44	21.5	21.1
50	2.92	20.4	20.6
50	3.87	18.3	18.1
50	5.27	17.7	17.2

[a] In this solvent the $Fe(CO)_3(PPh_3)_2$ complex separates during the reaction. [b] Values obtained from disappearance of the olefinic complex. [c] Values obtained from appearance of the monosubstituted complex.

TABLE 5

PSEUDO FIRST ORDER RATE CONSTANTS (*k*) FOR THE REACTION BETWEEN (π-CH_2=CHC_6H_5)-$Fe(CO)_4$ AND PPh_3 IN ACETONITRILE (AN). [PPh_3] = 10^{-1} *M*, [C] ≈ 2 × 10^{-3} *M*

T (°C)	10 [Styrene] (*M*)	10^4 *k* [a] (sec^{-1})
30	0	0.51
30	1.75	0.49
30	2.74	0.41
30	3.88	0.38
30	4.80	0.35
40	0	2.42
40	0.91	2.09
40	2.15	1.92
40	2.99	1.71
40	3.65	1.75
40	4.59	1.55
50	0	8.29
50	0.96	8.06
50	2.64	7.14
50	3.05	6.97
50	4.95	6.50

[a] Values obtained for disappearance of the olefinic complex.

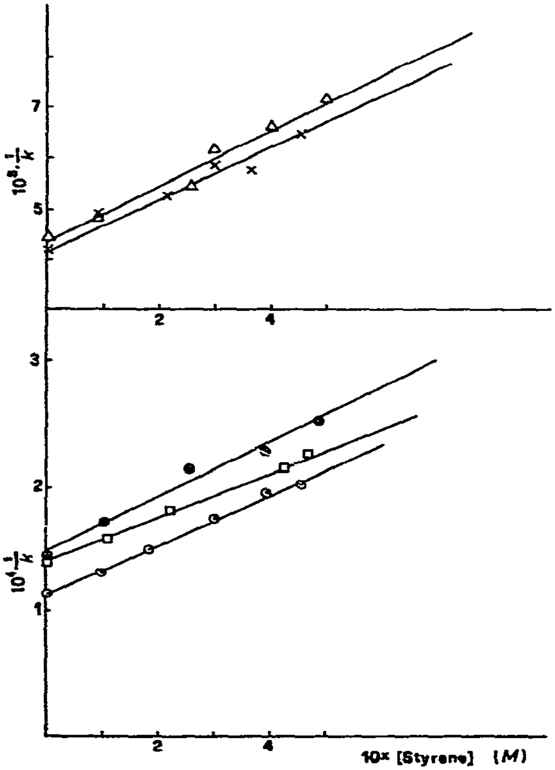


Fig. 1. 1/*k* vs. [Styrene] plots for the reaction between (π-CH_2=CHPh)$Fe(CO)_4$ and PPh_3 in various solvents at 40°; Δ, acetone; X, acetonitrile, ⊖, n-hexane; □, isopropyl ether; ⊙, dichloromethane.

TABLE 6

KINETIC DATA AND ACTIVATION PARAMETERS FOR THE REACTION BETWEEN (π-CH_2=CHC_6H_5)$Fe(CO)_4$ AND PPh_3

Solvent	T (°C)	$10^5 k_1$ (sec^{-1})			k_{-1}/k_m	$\alpha/1-\alpha$	$\Delta E^‡$ (kcal/mole)	$\Delta S^‡$ (cal. mol^{-1} deg^{-1})
		a	b	c				
Dichloromethane	30	1.86			0.243	4.92	32.2	+24
Dichloromethane	40	8.82	9.07	9.9	0.180	4.15		
Acetone	40	22.7	22.8	23.7	0.120	5.32	26.8	+ 9
Acetone	50	89.4	86.0	89.0	0.135	3.99		
Acetonitrile	30	5.11			0.105	2.30	25.5	+ 5
Acetonitrile	40	24.2			0.122	1.80		
Acetonitrile	50	82.9			0.056	1.33		
Acetonitrile	60					1.13		
Acetonitrile	70					0.90		
Isopropyl ether	40	7.08	7.12	7.16	0.125	2.05	33.7	+28
Isopropyl ether	50	39.1	39.2		0.176	1.81		
n-Hexane	40	7.00	6.85		0.123	3.34	28.5	+11
n-Hexane	50	28.1	27.7		0.125	3.17		
Toluene [d]	40	6.80	7.08	7.55	0.112	2.65	31.5	+21
Toluene	50	35.3	34.6	33.7	0.130	2.47		
Toluene	60					2.48		
Toluene	70					2.49		

[a] Values obtained from disappearance of the olefinic complex. [b] Values obtained from appearance of the monosubstituted complex. [c] Values obtained from appearance of the disubstituted complex. [d] The values in this solvent are obtained from ref. 3.

carbonyl complexes proceeding via a dissociation reaction [10]. (The solvent influence arises because the activated complex is solvated differently from the initial one.) In such a case, the ability of the solvent to form a coordinate bond is the most important factor influencing the k_1 values. Thus AN and acetone, solvents having the highest coordination power [11] of those studied, give higher k_1 values. Parallel effects are found in the activation energy parameters (Table 6), which are appreciably lower for these two solvents.

In contrast, the k_{-1}/k_m ratios are not appreciably dependent upon the solvent. This behaviour is easily explained by mechanism 2; if the dissociative stage, involving conversion of $Fe(CO)_4$ into $Fe(CO)_3$ is reversible, then k_1/k_m is equal to k_{-1}/k_2 and the constants k_1 and k_2 then refer to the rate constants of the association stages taking place with the same substrate, $Fe(CO)_4$. The effects of solvation are thus of the same type in both stages and cancel out in the ratio.

There is an appreciable change of $\alpha/1-\alpha$ with temperature. For all the solvents studied this ratio falls with increase in temperature. Again, this may be explained in terms of mechanism 2, since, in the absence of an excess of CO, the ratio $\alpha/1-\alpha$ is mainly influenced by the value of the dissociation rate constant of $Fe(CO)_4$, k'_1, which increases faster (dissociative stage) with temperature than do the rate constants k_2 and k'_{-1} (associative stage).

It is difficult to explain the effect of the solvent on the $\alpha/1-\alpha$ values in terms of individual solvent properties. Because of the complexity of the reaction mechanism, the solvent affects differently the particular reaction intermediate involved [i.e. $Fe(CO)_4$, $Fe(CO)_3$, or $Fe(CO)_3L$], making the net effect difficult to analyse. Nevertheless, specific properties of the solvent (such as its coordinating power) must have considerable influence on $\alpha/1-\alpha$, because of the tendency of the intermediates to increase their coordination number.

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References

1 G. Cardaci and V. Narciso, J. Chem. Soc. Dalton, (1972) 2289.
2 G. Cardaci, Int. J. Chem. Kinet., 5 (1973) 805.
3 G. Cardaci, Inorg. Chem., 13 (1974) 368.
4 G. Cardaci, in preparation.
5 A. Weissberger and E.S. Proskauer, Techniques of Organic Chemistry: Organic Solvents, Interscience, New York, 2nd Edition, 1955.
6 J.F. Cotzee, G.P. Cunninghan, D.K. McCurie and G.R. Podmanabhan, Anal. Chem., 34 (1962) 1139.
7 J.H. Mattews, J. Amer. Chem. Soc., 48 (1926) 562.
8 E. Koerner von Gustorf, M.C. Henry and C. Di Pietro, Z. Naturforsch. B, 21 (1966) 42.
9 E.H. Schubert and R.K. Sheline, Inorg. Chem., 5 (1966) 1071.
10 G. Cardaci, S.M. Murgia and A. Foffani, J. Organometal. Chem., 23 (1970) 265.
11 V. Gutmann, Coordination Chemistry in non-aqueous solutions, Springer Verlag, Vienna, New York, 1968.