Solvent Effect in the Insertion Reaction of Iron(II) Carbonyls

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The CO insertion reaction for the complex $[Fe(CO)_2(PMe_3)_2(Me)(CN)]$ is second order in many solvents. The solvent effect on the kinetics and the equilibria is very small. This fact is attributed to the small interaction between the reactive intermediate and the solvent, and to the small variation of the dipole moment during the course of the reaction.

We have recently studied the insertion reaction (1), where

$$[Fe(CO)_2L_2(Me)X] + {}^{13}CO \rightleftharpoons [Fe(CO)_2L_2(COMe)X] \quad (1)$$

X = CN, NCS, or I, and L = PMe_3, in toluene, and we have found that the speed of the reaction is a function of X and of the different isotopomers formed.[1]

We describe here the solvent effect on the kinetics and the equilibria of the same reaction with X = CN, in which both the starting and the final complexes have a *cis* configuration,[1] with the aim of obtaining further information on the reaction mechanism.

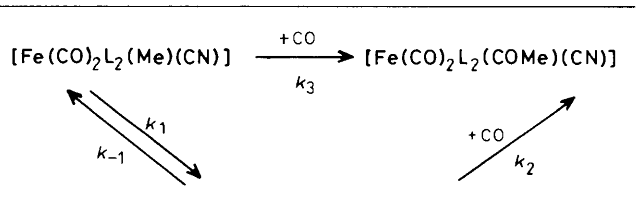
The study of the solvent effect presents certain difficulties, both general and particular. The general difficulty lies in the fact that different complex interactions are involved in the solvent effect, and it is difficult to distinguish the different influences. Such interactions have been described by different parameters such as donor number (d.n.),[2] polarity,[3] acidic properties,[4] *etc.* The specific difficulty lies in the fact that the CO is not very soluble, so it is impossible to have an excess of it in solution, and also that it is necessary to know the solubility of CO in all the solvents at the different temperatures. This is probably the reason why the L-promoted insertion has been studied more with L = PR_3, $P(OR)_3$, RNC, or NR_3[5–10] (R = alkyl or aryl) than with L = CO.[11]

Results and Discussion

The kinetics and the equilibria were studied in solvents with different donor numbers and different dielectric constants. The constancy of the CO concentration was obtained by performing the reaction in the presence of a large quantity of CO in the gas phase. The kinetics were followed by monitoring both the disappearance of the methyl derivative (ν_{CO} in n-hexane, 2 004 cm^{-1}) and the appearance of the acetyl derivative (ν_{CO} in n-hexane, 2 021 cm^{-1}). The results obtained were in good agreement (within 8%). The results of the kinetics are reported in Table 1 and refer to the disappearance of the methyl derivative. Reaction (1) is driven towards the products but does not proceed to completion. Since the CO concentration is constant, reaction (1) can be considered a first-order equilibrium reaction of the type (2) where $k_I = k_{II}[CO]$. Equation (3) was used to calculate k_I; a = initial concentration of **A**, X_e = **B** at equilibrium, and X = concentration of **B** at time t.

$$\mathbf{A} \underset{k_{-I}}{\overset{k_I}{\rightleftharpoons}} \mathbf{B} \quad (2)$$

$$\frac{k_I a}{X_e} = \frac{1}{t} \ln \frac{X_e}{X_e - X} \quad (3)$$



Scheme.

The reported second-order constants, obtained by dividing the pseudo-first-order constants by the CO concentration, are the average of two or three runs, which agree to within 5%. The rate and equilibrium constants at 295 K are reported in Table 2, along with the dielectric constants and several measures of solvent polarity and co-ordinating ability.

From the reported results it can be seen that the rate is fairly high compared to other insertion reactions,[5,9,11] and that the variation of k_{II} and K_{eq} is small on varying the d.n. and the dielectric constants of the solvent, even if there is no correlation between k_{II} and d.n., polarity, or dielectric constant.

The results obtained can be explained by two mechanisms, shown in the Scheme: (*i*) a methyl migration to CO and a simultaneous attack by CO; (*ii*) the formation of a five-co-ordinated intermediate, followed by attack of the incoming CO. Mechanism (*i*) would give an overall rate constant $k_I = k_3[CO]$. For mechanism (*ii*), $k_I = k_1k_2[CO]/k_{-1} + k_2[CO]$, which, assuming $k_{-1} > k_2[CO]$, is transformed into the expression $k_I = k_1k_2[CO]/k_{-1}$.

It is difficult to choose between the two mechanisms, and in the past the same experimental results have been interpreted in different ways by different authors.[9,11] We are in favour of mechanism (*ii*) because of its lower steric requirements. The large steric hindrance of this complex is proved by the fact that with other Lewis bases the equilibrium is driven towards the reagents, while for analogous complexes the reaction goes to completion.[9,12] Moreover, the only alkyl group that can easily be bound to the metal is the methyl group.[13,*] The small solvent effect can be ascribed to the fact that the solvent does not interact very much with the reactive intermediate and, due to the steric hindrance, enters very little into the co-ordination sphere. In fact the second-order rate constants vary only by a factor of 6 over the full range of solvents while for the less hindered complex $[Mn(CO)_5Me]$ they vary by a factor of 44.[11] These results are also in accordance with those of Wright and Baird[15] who found that for the CN derivative no charged intermediate is involved in the reaction path.

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[*] Recent results obtained by our group[14] show that other alkyl groups can be bound to the metal if a different synthetic route is followed.

Table 1. Equilibrium and second-order rate constants for reaction (1)

Solvent	Temp. (°C)	K_{eq}/ dm^3 mol^{-1}	10^3[CO]/ mol dm^{-3}	k_{II}/ dm^3 mol^{-1} s^{-1}	$\Delta H^{\neq}$/ kJ mol^{-1}	$\Delta S^{\neq}$/ J K^{-1} mol^{-1}
Cyclohexane	15	3 900				
	22	2 800	7.6	0.99	34	52
			5.1	0.95		
			1.9	0.88		
	30	2 050				
Toluene	5	14 000	8.2	0.31 *		
			5.46	0.26 *		
			2.05	0.28 *		
	8	12 800				
	15	11 000	7.4	1.00 *		
			3.7	0.88 *		
			1.8	0.86 *		
	22	6 700	6.9	1.74 *	44	75
			4.6	1.46 *		
			1.7	1.74 *		
	30	3 300				
1-Chloro-octane	5	19 700				
	15	9 300				
	22	6 000	8.1	1.00	54	109
			5.4	1.09		
			2.0	1.20		
	30	3 000				
	40	1 500				
	47	900				
$O(CH_2CH_2OEt)_2$	5		6.5	0.44		
			4.3	0.38		
			1.6	0.39		
	15	11 600				
	22	7 600	6.6	1.95	28	20
			4.4	1.73		
			1.6	1.66		
$HCONMe_2$	22	21 700	3.2	5.16	53	96
			2.1	5.05		
			0.8	4.20		
	30	12 000				
	38	7 000				
MeCN	5	36 900				
	22	23 200	4.0	6.90	86	209
			1.0	6.02		
	30	11 500				
	40	3 800				

[a] These data allow an estimate of $\Delta H^{\ddagger}$ = 72 kJ mol^{-1} and $\Delta S^{\ddagger}$ = 17 J K^{-1} mol^{-1}.

Table 2. Solvent effect on rates and equilibrium constants at 22 °C

Solvent	$10k_{II}$/dm^3 mol^{-1} s^{-1}	K_{eq}/dm^3 mol^{-1}	ε^a	d.n.^{a}	Polarity E_T^b	Polarity $(A + B)^c$
Cyclohexane	0.94	2 800	2.0	<0.1	31.2	0.09
Toluene	1.65	6 700	2.4	*ca.* 0.2	33.9	0.67
1-chloro-octane	1.10	6 000	5.0^d		*ca.* 34	
$O(CH_2CH_2OEt)_2$	1.78	7 600	5.7^d		37.5	
$HCONMe_2$	4.80	21 700	36.1	26.6	43.8	1.23
MeCN	6.46	23 200	38.0	14.1	46.0	1.22

[a] From ref. 2. [b] See ref. 3. [c] See ref. 4. [d] From ref. 11.

As far as the equilibrium constants are concerned, they too vary very little (factor of 8 only), and this can be ascribed both to the steric hindrance and to the fact that the dipole moment of the CN derivative varies very little when a methyl group transforms into an acetyl group.

Experimental

Solvents were purified and dried by standard methods. The complex $[Fe(CO)_2(PMe_3)_2(Me)(CN)]$ was prepared as described previously.[16] Its stability was checked in each solvent under a nitrogen atmosphere. The solubility of CO is reported in the literature,[11,17] and was extrapolated from these data.

The kinetics were followed by introducing a solution of the complex (1.3 × 10^{-3} mol dm^{-3}) into a thermostatted reactor containing the required atmosphere (carbon monoxide or carbon monoxide–nitrogen). The reactions were carried out under pseudo-first-order conditions, the CO concentration being constant. Aliquots of the solution were withdrawn at appropriate times through a serum cap, and transferred to a 0.1-mm NaCl cell. The rates of the disappearance of the methyl complex and of the appearance of the acetyl complex were followed with an i.r. spectrometer (Perkin-Elmer 337) and were linear with no detectable curvature up to 2—3 half-lives. Light did not affect the rate.

The equilibrium concentrations required for the determination of the equilibrium constant $K_{eq} = [Fe(CO)_2(PMe_3)_2(COMe)(CN)]/[Fe(CO)_2(PMe_3)_2(Me)(CN)][CO]$ were obtained after allowing the system to react until no further change was detectable by i.r. measurement.

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Received 20*th March* 1986; *Paper* 6/548