Mechanism and Equilibrium Constants of the Reaction between Carbon Monoxide and Triphenyl-phosphine-, -arsine-, and -stibine-dicarbonyl-(1–2-η:3–4-η-1,4-diphenyl-1-azabuta-1,3-diene)iron

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Equilibrium and rate data have been measured for the ligand-substitution reaction $[Fe(\eta^4-C_6H_5CH=CHCH=NC_6H_5)(CO)_2L] + CO \rightleftharpoons [Fe(\eta^4-C_6H_5CH=CHCH=NC_6H_5)(CO)_3] + L$ where $L = PPh_3$, $AsPh_3$, or $SbPh_3$. The reaction proceeds *via* a dissociative equilibrium of the η^4 complexes to σ unsaturated complexes. Variations of the equilibrium and rate constants appear to be mainly associated with the basicity of the ligands.

RECENTLY, the reaction mechanisms of tetrahapto-heterodieneiron tricarbonyls [1–3] (heterodiene = α,β-unsaturated aldehydes and ketones or α,β-unsaturated Schiff bases) with ligands of the type MR_3 ($M = P$, As, or Sb; $R = $ alkyl or phenyl) have been studied. The results indicate that with the less basic MR_3 ligands ($M = As$ or Sb) the mechanism proceeds by a partial dissociation of the heterodiene ligand, followed by the introduction of the MR_3 ligand into the intermediate unsaturated complex, and then chelation of the heterodiene ligand with the substitution of a CO group. With more basic ligands (MR_3: $M = P$) there is an associative process parallel to the above mechanism which leads to the same final products. The results of such mechanistic studies agree with some synthetic studies recently carried out by other authors [4]. The tricarbonyl complexes in which the heterodiene ligand is an α,β-unsaturated Schiff base react with $AsPh_3$ and $SbPh_3$ but the reaction does not go to completion. This fact was attributed to the carbon monoxide obtained during the reaction which reforms the initial tricarbonyl complex $[Fe(\eta^4-C_6H_5CH=CHCH=NC_6H_5)(CO)_3]$. This is unexpected, however, since the $[Fe(\eta^4-C_6H_5CH=CHCH=NC_6H_5)(CO)_2L]$ complexes do not react with PPh_3 even under very drastic conditions ($>90\ °C$), notwithstanding the very much greater basicity of PPh_3 in relation to carbon monoxide. This behaviour induced us to study, both from the kinetic and thermodynamic point of view, the reaction of the $[Fe(\eta^4-C_6H_5CH=CHCH=NC_6H_5)(CO)_2L]$ complexes with carbon monoxide.

EXPERIMENTAL

Materials.—The $[Fe(\eta^4-C_6H_5CH=CHCH=NC_6H_5)(CO)_2L]$ ($L = PPh_3$, $AsPh_3$, or $SbPh_3$) complexes were prepared as described in ref. 3 and $[Fe(\eta^4-C_6H_5CH=CHCH=NC_6H_5)(CO)_3]$ as in refs. 5 and 6. The reactions were carried out in toluene which was purified by distillation on metallic Na, and stored under nitrogen. Carbon monoxide was prepared by the method of Gilliland and Blanchard [7] and purified by bubbling through Fiester's solution [8]. Solubility data for CO in toluene are taken from ref. 9.

Kinetic Measurements.—The apparatus used for the kinetics is accurately described in ref. 10. Particular care was taken to eliminate traces of oxygen since the complexes with $L = SbPh_3$ and $AsPh_3$ are very sensitive to it. The analytical course of the reaction was followed by observing the appearance of the CO stretching band at

the highest frequency of $[Fe(\eta^4-C_6H_5CH=CHCH=NC_6H_5)(CO)_3]$ using a Perkin-Elmer 257 spectrophotometer and 0.5 mm NaCl cells. The concentration range of the complexes is 2×10^{-3}—4×10^{-3} mol dm⁻³.

Since there are various experimental conditions the methods for measuring the rate constant are different.

(*i*) $L = AsPh_3$ *or* $SbPh_3$. (*a*) *Absence of free ligand* L. Reaction (1) proceeds to completion. Since the kinetic

$$[Fe(\eta^4-C_6H_5CH=CHCH=NC_6H_5)(CO)_2L] + CO \longrightarrow$$
$$A$$
$$[Fe(\eta^4-C_6H_5CH=CHCH=NC_6H_5)(CO)_3] + L \quad (1)$$
$$E$$
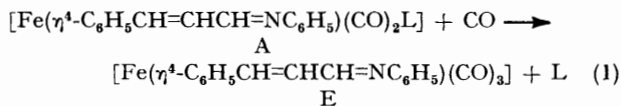
conditions were of pseudo-first order ($P_{CO} = $ constant) the equation used is (2) where D_∞ and D_t are the absorbances at time $t = \infty$ and t respectively.

$$2.3 \log[D_\infty/(D_\infty - D_t)] = k_I t \quad (2)$$

(*b*) *Ligand* L *in excess.* Reaction (1) does not proceed to completion. Since P_{CO} and [L] are constant reaction (1) can be considered a first-order equilibrium reaction of

$$A \underset{k_{-I}}{\overset{k_I}{\rightleftharpoons}} E \quad (3)$$

the type (3) where $k_I = k_f[CO]$ and $k_{-I} = k_r[L]$. The equation (4) used to calculate k_I is shown below [11] where

$$\frac{k_I a}{x_e} = \frac{1}{t} \ln \frac{x_e}{x_e - x} \quad (4)$$

$a = $ initial concentration of A, $x_e = $ concentration of E at equilibrium, and $x = $ concentration of E at time t.

(*ii*) $L = PPh_3$. With this ligand there is an equilibrium reaction even in the absence of free PPh_3 and the concentration of the latter varies during the reaction. The CO concentration is constant since P_{CO} is constant. The situation may be represented by equation (5) where $L = PPh_3$ and $k_I = k_f[CO]$. There can be two cases.

$$A \underset{k_r}{\overset{k_I}{\rightleftharpoons}} L + E \quad (5)$$

(*a*) PPh_3 is absent at the beginning of the reaction so that $[L] = [E]$. In such a case the kinetic equation $dx/dt = k_I(a - x) - k_r x^2$ can be integrated to give equation (6) [11],

$$k_I = \frac{x_e}{t(2a - x_e)} \ln \frac{a x_e + x(a - x_e)}{a(x_e - x)} \quad (6)$$

where x_e is the equilibrium concentration of L and E, x is the concentration at time t of L and E, and a is the initial concentration of A.

(b) [L] ≠ [E]. This is the case where the PPh₃ ligand is added at the beginning of the reaction so the concentrations of L and E are not equal. In such a case the kinetic equation obtained for reaction (1) is as shown below

$$dx/dt = k_I(a - x) - k_r(b + x)x \quad (7)$$

where b is the initial concentration of L. If $M = (a - x_e)/[x_e(b + x_e)]$, this expression becomes $dx/[a - (Mb + 1)x - Mx^2] = k_I dt$. This equation may be integrated by conventional methods.[12] If we use the substitutions $n = (Mb + 1)$ and $p = [4aM + (Mb + 1)^2]^{\frac{1}{2}}$ the integrated equation gives rise to (8) which is the equation used by us to

$$\ln \frac{(2Mx + n + p)(n - p)}{(2Mx + n - p)(n + p)} = k_I pt \quad (8)$$

calculate the k_I values. Although the equilibrium constants of reaction (1) with L = PPh₃ at the lowest temperature (35 °C) are imprecise because additional non-equilibrium processes take place (see below), the values of the rate constants are more reliable since they are less affected by the x_e value than the equilibrium constants.

Equilibrium Measurements.—The equilibrium concentrations required to determine the equilibrium constants of reaction (1), $K_{eq} = [E][L]/[A][CO]$, were obtained from i.r. spectrophotometric measurements. Such constants were always determined using reaction (1) in the forward direction *i.e.* from reagents to products. In only one case (L = AsPh₃) were measurements also made in the opposite direction and the values obtained agree within the limits of experimental error (Table 1).

TABLE 1

Equilibrium and kinetic constants for reaction
(1), L = AsPh₃, in toluene

$\frac{\theta_c}{°C}$	$\frac{10[AsPh_3]}{mol\ dm^{-3}}$	$\frac{P_{CO}}{atm\ ^b}$	$\frac{10^5 k_I}{s^{-1}}$	$\frac{10^2 k_t}{dm^3\ mol^{-1}\ s^{-1}}$	$K_{eq}\ ^a$
18.4		1.0	26.70		
		1.0	24.90		
		0.40	23.30		
		0.25	23.20		
		0.14	20.10		
		0.10	17.60		
		0.10	18.00		
	1.51	0.10	0.42	0.58	317
	3.00	0.10	0.17	0.23	390
	3.00	0.25	0.43	0.24	
	5.01	0.25	0.26	0.14	331
	3.02	0.50	0.83	0.23	326
30.2	1.51	0.10	1.70	2.69	
	2.77	0.10	0.93	1.47	559
	3.00	0.10	0.86	1.35	507
	5.07	0.10	0.58	0.92	566
42.0	2.99	0.10	6.16	11.42	806
	3.00	0.10	5.65	10.48	690
	3.99	0.10	4.63	8.59	767
	5.04	0.10	3.43	6.35	813
	0.33	0.02			800 ᶜ
	0.66	0.02			852 ᶜ

ᵃ These data allow an estimate of $\Delta H^\ominus = 29 \pm 2$ kJ mol⁻¹ and $\Delta S^\ominus = 148 \pm 6$ J K⁻¹ mol⁻¹. ᵇ 1 atm = 101 325 Pa. ᶜ Obtained from the reverse reaction.

The measurement of K_{eq} for the complexes with L = PPh₃ is more affected by error since the equilibrium position is uncertain due to parallel non-equilibrium reactions taking place which bring about the formation of [Fe(CO)₃(PPh₃)₂]⁻, [Fe{N(C₆H₅)=CHCH=CHC₆H₅}(CO)₄], and [Fe(CO)₅]. The parallel reactions become more important at the lowest

temperature (35 °C). In such cases the equilibrium constants were not measured.

RESULTS AND DISCUSSION

Kinetic Results.—The complexes [Fe(η⁴-C₆H₅CH=CH-CH=NC₆H₅)(CO)₂L] (L = AsPh₃ or SbPh₃) react with carbon monoxide, in the absence of an excess of free ligand, to form [Fe(η⁴-C₆H₅CH=CHCH=NC₆H₅)(CO)₃]. Such a reaction is not one of equilibrium. The results obtained are shown in Tables 1 and 2. The kinetics

TABLE 2

Equilibrium and kinetic constants for reaction (1),
L = SbPh₃, in toluene

$\frac{\theta_c}{°C}$	$\frac{10[SbPh_3]}{mol\ dm^{-3}}$	$\frac{P_{CO}}{atm}$	$\frac{10^5 k_I}{s^{-1}}$	$\frac{10^2 k_t}{dm^3\ mol^{-1}\ s^{-1}}$	$K_{eq}\ ^*$
18.4		1.00	62.30		
		0.50	58.80		
		0.20	44.70		
		0.14	38.00		
		0.10	33.70		
	1.00	0.20	2.17	1.49	
	3.00	0.20	0.79	0.54	541
	1.50	0.10	0.62	0.85	
	3.00	0.10	0.28	0.38	573
	5.01	0.10	0.16	0.22	597
30.2	1.47	0.10	3.32	5.26	1 000
	3.00	0.10	1.63	2.58	852
	5.00	0.10	0.98	1.55	920
42.0	3.21	0.10	6.66	12.36	1 270
	5.04	0.10	4.92	9.12	1 340

* These data allow an estimate of $\Delta H^\ominus = 26 \pm 2$ kJ mol⁻¹ and $\Delta S^\ominus = 143 \pm 6$ J K⁻¹ mol⁻¹.

are of pseudo-first order and the rate constants (k_I) vary with the pressure of carbon monoxide. Plotting $1/k_I$ against $1/P_{CO}$ gives a straight line with a non-zero intercept (Figure). Such results can be rationalized on the basis of the Scheme.
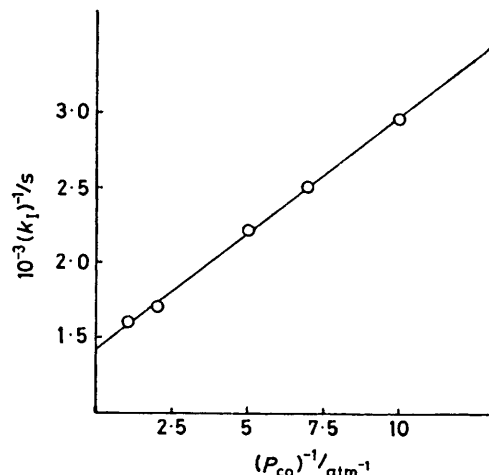
Plot of $1/k_I$ against $1/P_{CO}$ for reaction (1) with L = SbPh₃ at 18.4 °C in toluene

Applying the steady-state approximation to the intermediate B in the Scheme when the reaction is not at equilibrium and assuming that $k_2[CO][B] \gg k_{-2}[C]$, we obtain equation (9) for the pseudo-first-order rate constant, k_I, from which we get equation (10). From (10) it can be seen that the values of the intercept and

slope of the Figure correspond to $1/k_1$ and k_{-1}/k_1k_2 respectively. From these values, k_{-1}/k_2 are calculated. At 18.4 °C for L = SbPh$_3$, $k_1 = 6.99 \times 10^{-4}$ s^{-1} and

$$k_{\mathrm{I}} = \frac{k_1k_2[\mathrm{CO}]}{k_{-1} + k_2[\mathrm{CO}]} \qquad (9)$$

$k_{-1}/k_2 = 0.108$ mol dm^{-3}; for L = AsPh$_3$, $k_1 = 2.71 \times 10^{-4}$ s^{-1} and $k_{-1}/k_2 = 0.054$ mol dm^{-3}. The values of k_1 decrease going from L = SbPh$_3$ to AsPh$_3$. This is in agreement with the greater basicity of AsPh$_3$, which by

$$1/k_{\mathrm{I}} = \frac{k_{-1}}{k_1k_2[\mathrm{CO}]} + 1/k_1 \qquad (10)$$

increasing the electronic density of the metal stabilizes the bond with the heterodiene group. The values of k_{-1}/k_2 decrease with an increase in the basicity of the ligand. Since k_{-1} and k_2 both correspond to associative processes, the increase in L basicity disfavours both

SCHEME
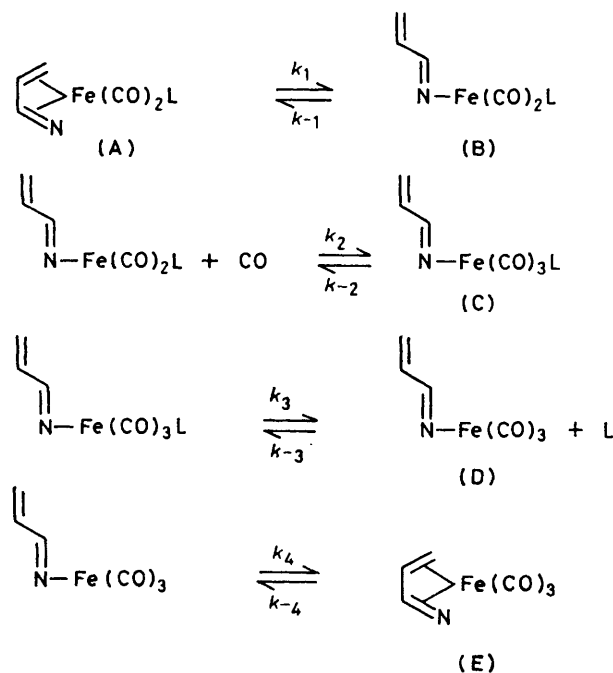
processes, but the chelation process is more disfavoured than the other.

As regards the PPh$_3$ ligand, it is not possible to calculate the rate constant, k_1, of the first dissociative process because the reaction is in equilibrium. The same situation is to be found when AsPh$_3$ or SbPh$_3$ are in excess. In such cases it is possible to calculate from the equilibrium position the values of k_f which are shown in Tables 1—3. In these cases, applying the steady-state approximation to the intermediates B, C, and D of the

$$k_f = \frac{k_1k_2k_3k_4}{k_{-1}k_3k_4 + k_{-1}k_{-2}k_4 + k_2k_3k_4[\mathrm{CO}] + k_{-1}k_{-2}k_{-3}[\mathrm{L}]} \qquad (11)$$

Scheme, equation (11) is obtained for k_f, from which we get equation (12). Since the reactant and product

of the Scheme are in equilibrium, so also are the intermediates and thus the equilibrium constant follows from equation (13). By substituting (13) in the last term of

$$\frac{1}{k_f} = \frac{k_{-1}}{k_1k_2} + \frac{k_{-1}k_{-2}}{k_1k_2k_3} + \frac{1}{k_1}[\mathrm{CO}] + \frac{k_{-1}k_{-2}k_{-3}}{k_1k_2k_3k_4}[\mathrm{L}] \qquad (12)$$

(12), equation (14) is obtained. Plotting $1/k_f$ against [L] with [CO] = constant gives a straight line whose slope is $1/K_{\mathrm{eq}}k_{-4}$. Hence, values of k_{-4} can be calculated

$$K_{\mathrm{eq}} = \frac{k_1k_2k_3k_4}{k_{-1}k_{-2}k_{-3}k_{-4}} \qquad (13)$$

$$\frac{1}{k_f} = \frac{k_{-1}}{k_1k_2} + \frac{k_{-1}k_{-2}}{k_1k_2k_3} + \frac{1}{k_1}[\mathrm{CO}] + \frac{[\mathrm{L}]}{K_{\mathrm{eq}}k_{-4}} \qquad (14)$$

and are reported in Table 4. Within the limit of experimental error at the various temperatures, the values of k_{-4} for AsPh$_3$ and SbPh$_3$ are the same. This is in accord with the Scheme since the final step is independent of the ligand L. The values of k_{-4} calculated in this way agree with those measured for the reverse reaction with

TABLE 3

Equilibrium and kinetic constants for reaction (1), L = PPh$_3$, in toluene at $P_{\mathrm{CO}} = 1$ atm

$\dfrac{\theta_c}{^\circ\mathrm{C}}$	$\dfrac{10^3[\mathrm{PPh_3}]}{\mathrm{mol\ dm^{-3}}}$	$\dfrac{10^3 k_f}{\mathrm{dm^3\ mol^{-1}\ s^{-1}}}$	K_{eq} *
50		5.23	0.35
		5.56	0.36
	1.66	4.61	0.39
	1.75	4.81	0.45
	1.90	5.76	0.38
	1.96		0.42
	3.75	5.06	0.43
42		1.33	0.24
		1.28	0.24
		1.37	0.29
	1.29	1.13	0.29
	2.28	1.30	
	2.34	1.15	0.25
35		0.37	
		0.35	
	2.06	0.34	
	2.75	0.32	
	5.22	0.32	
	5.22	0.34	

* These data allow an estimate of $\Delta H^{\ominus} = 45 \pm 2$ kJ mol^{-1} and $\Delta S^{\ominus} = 134 \pm 6$ J K^{-1} mol^{-1}.

PPh$_3$. The effect of [PPh$_3$] and the value of k_f for the reaction with PPh$_3$ could not be measured because the concentration of PPh$_3$ could not be varied over a wide enough range.

Thermodynamic Results.—The equilibrium constants of reaction (1) at various temperatures are shown in Tables 1—3.

The thermodynamic stability of the various complexes follows the order: PPh$_3$ > CO $\gg$ AsPh$_3$ > SbPh$_3$. This agrees with the results obtained for other carbonyl and carbonyl nitrosyl complexes.[10,13]

The values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are positive (see footnotes to Tables 1—3). The value of $\Delta S^{\ominus}$ can be explained on the basis of a decreased solvation of the tricarbonyl complex due to a smaller dipole moment. For the

three ligands studied the values of $\Delta S^\ominus$ are equal within the limits of experimental error. This is reasonable on the basis of the similar structure and steric hindrance of the ligands studied. As a consequence, the thermodynamic stability depends primarily on the value of $\Delta H^\ominus$ which can be associated with the energy of the Fe–L bond, so that such values give indications of the relative energy of the Fe–P, Fe–As, and Fe–Sb bonds in the complexes studied. The trend in bond energies

TABLE 4

Calculated k_{-4} values (s^{-1}) at various temperatures in toluene

$\dfrac{\theta_c}{^\circ C}$	AsPh$_3$	SbPh$_3$	PPh$_3$ *
18.4	2.08×10^{-6}	2.07×10^{-6}	
30.2	9.06×10^{-6}	8.66×10^{-6}	
42	4.28×10^{-5}	4.47×10^{-5}	3.97×10^{-5}

* Value calculated from the activation parameters of ref. 3.

agrees with the order of basicity of the ligands, in accordance with the fact that for such bonds it is the contribution of the $\sigma \longrightarrow$ Fe bond which is predominant.

Conclusions.—The kinetic and thermodynamic results of this work and of ref. 3 support the proposed Scheme.

For the L = PPh$_3$ ligand it was not possible to carry out a kinetic study of reaction (1) but there is no reason why there should be a variation from the mechanism found for AsPh$_3$ and SbPh$_3$. Instead, a kinetic study was previously carried out for the reverse of reaction (1), and it was found that the mechanism proceeds along two parallel paths, one of the dissociative type as represented in the Scheme and one associative with L, until the intermediate C is formed.[3]

Under the experimental conditions of this work ([L] = 10^{-3} mol dm^{-3}) the associative path is negligible (*ca.* 0.05%) compared to the dissociative path. For this reason it can be assumed that the reaction mechan-

ism for L = PPh$_3$ also corresponds to the Scheme. However, in certain experimental conditions, some non-equilibrium processes can take place, which lead to the formation of [Fe(CO)$_3$(PPh$_3$)$_2$], [Fe{N(C$_6$H$_5$)=CHCH= CHC$_6$H$_5$}(CO)$_4$], and [Fe(CO)$_5$]. Their presence can be explained by assuming that the intermediates C and D react with CO or PPh$_3$.

The reason why the complex [Fe(η^4-C$_6$H$_5$CH=CHCH= NC$_6$H$_5$)(CO)(PPh$_3$)$_2$] cannot be obtained stems from the fact that the formation of [Fe{N(C$_6$H$_5$)=CHCH=CHC$_6$H$_5$}- (CO)$_2$(PPh$_3$)$_2$] from intermediate B is thermodynamically inhibited due to the presence of three very basic σ ligands.[14]

REFERENCES

[1] G. Cardaci and S. Sorriso, *Inorg. Chem.*, 1976, **15**, 1242.
[2] G. Cardaci and G. Bellachioma, *Inorg. Chem.*, 1977, **16**, 3099.
[3] G. Bellachioma and G. Cardaci, *J.C.S. Dalton*, 1977, 2181.
[4] C. R. Graham, G. Scholes, and M. Brookhart, *J. Amer. Chem. Soc.*, 1977, **99**, 1180.
[5] S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, 1967, **6**, 20.
[6] G. Cardaci and G. Bellachioma, *J.C.S. Dalton*, 1976, 1735.
[7] W. L. Gilliland and A. A. Blanchard, *Inorg. Synth.*, 1946, **2**, 81.
[8] A. I. Vogel, ' A Textbook of Practical Organic Chemistry,' 3rd edn., Longmans Green, London, 1957, p. 186.
[9] G. Reichenbach, G. Innorta, and A. Foffani, *Inorg. Chim. Acta*, 1969, **3**, 139.
[10] G. Innorta, G. Reichenbach, and A. Foffani, *J. Organometallic Chem.*, 1970, **22**, 731.
[11] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' Wiley, New York, 1961, p. 186.
[12] Z. G. Szabo, in ' Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1969, vol. 2, p. 43.
[13] R. J. Angelici and C. M. Ingemanson, *Inorg. Chem.*, 1969, **8**, 83.
[14] F. Porta, S. Cenini, S. Giordano, and M. Pizzotti, *J. Organometallic Chem.*, 1978, **150**, 261.