NO_2^- stretching vibrations in the $[Co(NH_3)_nNO_2]^{2+}$ complex indicate that the nitro ligand produced by the parallel disproportionation reaction prevents any further formation of the nitrosyl complexes. The nitro complex is destroyed only by heating the complex under vacuum to 200°, and these conditions are sufficient to destroy the ammine complex also. Although the reaction system cannot be considered catalytic at the higher nitric oxide pressures, the formation of the undesirable nitro ligands may be prevented by going to lower partial pressures of NO where the disproportionation reaction does not occur.

These results clearly show that the reactivity of nitric oxide coordinated to cobalt(II) can be greatly enhanced by forming complexes with strong bases. The presence of the $[Co^{III}(NH_3)_nNO]^{2+}$ in a zeolite appears to facilitate the intramolecular reaction between the nitrosyl and ammonia ligands. This illustrates the unique function of zeolites as solvents.

Acknowledgment. The authors wish to acknowledge the support of this work by The Robert A. Welch Foundation under Grant No. A-257.

References and Notes

(1) C. C. Chao and J. H. Lunsford, *J. Phys. Chem.*, **76**, 1546 (1972).

(2) Y. Y. Huang, *J. Catal.*, **32**, 482 (1974).

(3) J. W. Jermyn, T. J. Johnson, E. F. Vansant, and J. H. Lunsford, *J. Phys. Chem.*, **77**, 2964 (1973).

(4) C. Naccache and Y. Ben Taarit, *Trans. Faraday Soc.*, **2**, 1475 (1973).

(5) C. C. Chao and J. H. Lunsford, *J. Phys. Chem.*, **78**, 1174 (1974).

(6) J. B. Peri, *J. Phys. Chem.*, **78**, 588 (1974).

(7) P. Finn and W. Jolly, *Inorg. Chem.*, **11**, 893 (1972).

(8) D. Gwost and K. G. Caulton, *Inorg. Chem.*, **13**, 414 (1974).

(9) P. Gans, *J. Chem. Soc. A*, 943 (1967).

(10) (a) E. F. Vansant and J. H. Lunsford, *J. Chem. Soc., Chem. Commun.*, 830 (1972); (b) *Trans. Faraday Soc.*, **69**, 1028 (1973).

(11) E. F. Vansant, Thesis for the Agregate of Higher Education, University of Antwerp, Antwerp, Belgium, 1974.

(12) E. F. Vansant and J. H. Lunsford, *Advan. Chem. Ser.*, **No. 121**, 441 (1973).

(13) R. Howe and J. H. Lunsford, to be submitted for publication.

(14) C. C. Chao and J. H. Lunsford, *J. Amer. Chem. Soc.*, **93**, 71 (1971).

(15) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N.Y., 1963.

(16) S. Pinchas and I. Laulicht, "Infrared Spectra of Labeled Compounds," Academic Press, London, 1972, p 28.

(17) (a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed., Interscience, New York, N.Y., 1972, p 696; (b) W. Beck, A. Melnikoff, and R. Stahl, *Chem. Ber.*, **99**, 3721 (1966).

(18) J. B. Raynor, *J. Chem. Soc.*, 997 (1966).

(19) P. Gans, *Chem. Commun.*, 144 (1965).

(20) K. Otto, M. Shelef, and J. T. Kummer, *J. Phys. Chem.*, **74**, 2690 (1970).

(21) P. G. Douglas and R. D. Feltham, *J. Amer. Chem. Soc.*, **94**, 5254 (1972).

Mechanism of Formation of (α,β) Unsaturated Aldehyde- and Ketone–Iron Tricarbonyl Complexes from the Corresponding Iron–Tetracarbonyl Complexes

G. Cardaci

Contribution from the Institute of Physical Chemistry, University of Perugia, 06100 Perugia, Italy.

Received June 20, 1974

Abstract: The kinetics of the reaction:

$$(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_4 \rightarrow \alpha(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_3 + (1-\alpha)Fe(CO)_5 + (1-\alpha)C_6H_5CH{=}CHCOR + (2\alpha-1)CO \quad (1)$$

where R = H, CH_3, and C_6H_5 and α is the fraction of chelate complex $(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_3$ *per* mole of reagent complex, has been followed. The reaction is first order with respect to $(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_4$, and the first-order rate constants (k_c) decrease with increase in concentration of $C_6H_5CH{=}CHCOR$ and are a function of CO concentration. $(1-\alpha)/\alpha$ changes linearly with $1/[C_6H_5CH{=}CHCOR]$ and also changes with CO pressure according to a square law. The results exclude an intramolecular chelation mechanism. A mechanism involving $Fe(CO)_3$ intermediate, which is responsible for the formation of the chelate complex, is suggested.

Many (π-*cis*-1,3-diene)$Fe(CO)_3$ complexes have been described in the literature,[1] since the preparation of (π-1,3-butadiene)$Fe(CO)_3$.[2] The nature of the iron–diene ligand bond has stimulated much interest from both theoretical and structural viewpoints.[3,4] Recently some π-hetero-1,3-diene complexes of iron carbonyl have also been described in which the heteroatom is oxygen[5] or nitrogen.[6] These complexes also have a structure similar to that of (π-*cis*-1,3-diene)$Fe(CO)_3$ complexes, with heteroatom lone pairs which do not participate in bonding to the iron.[7]

The iron atom is unique in its inclination to coordinate 1,3-diene or 1,3-heterodiene planar ligands.[1] This may depend both on the high stability of such structures and/or on the particular reaction mechanism involved. In order to clarify this mechanism a kinetic study of the formation reaction was undertaken. These complexes are obtained by photochemical reaction between the diene ligand and $Fe(CO)_5$ [8] or by thermal reaction between the diene and $Fe_2(CO)_9$.[6]

In both methods of preparation, the percursor of the (π-diene)$Fe(CO)_3$ is the corresponding (π-diene)$Fe(CO)_4$ complex. However, since the $(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_4$ and $(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_3$ are more stable than the corresponding (π-diene) complexes, the reaction studied kinetically is the formation of $(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_3$ from the corresponding $(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_4$ (with R = H, CH_3, C_6H_5).

For the reaction with R = H, literature reports[9] suggest the following stoichiometry

$$2(\pi\text{-}C_6H_5CH{=}CHCHO)Fe(CO)_4 \longrightarrow (\pi\text{-}C_6H_5CH{=}CHCHO)Fe(CO)_3 + Fe(CO)_5 + C_6H_5CH{=}CHCHO$$

but no mention was made of possible reaction mechanisms.

Recently, other authors[6] have assumed an internal chelation mechanism on the basis of the different reactivity of the complexes $(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_4$ in the two forms, s-cis and s-trans.

Table I. Infrared C–O Stretching Frequencies

Complex	Solvent[a]	ν(C–O), cm^{-1}	ν(C–O),[b] cm^{-1}
(π-$C_6H_5CH{=}CHCHO$)Fe(CO)$_4$	T	2094, 2037, 2020, 1998	1677
	H	2101, 2091, 2039, 2030, 2020, 2000	1694, 1687
	S	2097, 2090, 2031, 2021, 2013, 1994	1677
	A	2090, 2022, 1991	Not observable
(π-$C_6H_5CH{=}CHCOCH_3$)Fe(CO)$_4$	T	2093, 2034, 2022, 1992	1680
	H	2095, 2032, 2020, 1993	1684
	A	2092, 2025, 1988	Not observable
(π-$C_6H_5CH{=}CHCOC_6H_5$)Fe(CO)$_4$	T	2090, 2033, 2019, 1994	1651
	H	2092, 2032, 2021, 1993	1653
	A	2093, 2027, 1991	Not observable
(π-$C_6H_5CH{=}CHO$)Fe(CO)$_3$	T	2072, 2017, 1991	
	H	2074, 2010, 1992	
	A	2067, 2007, 1987	
(π-$C_6H_5CH{=}CHCOCH_3$)Fe(CO)$_3$	T	2064, 2010, 1988	
	H	2067, 2010, 1990	
	A	2064, 2002, 1987	
(π-$C_6H_5CH{=}CHCOC_6H_5$)Fe(CO)$_3$	T	2067, 2012, 1990	
	H	2067, 2010, 1987	
	A	2067, 2007, 1991	

[a] Key; T = CCl_4, H = *n*-hexane, S = CS_2, A = acetone. [b] Ir CO stretching of the organic ligand.

Table II. Percent Fe(CO)$_5$ and (1 −)α/α Values for Reaction 1 in Acetone, at 40° and at Various Concentrations of $C_6H_5CH{=}CHCOR$ and Carbon Monoxide ([(π-$C_6H_5CH{=}CHCOR$)Fe(CO)$_4$] = (5–6) × 10^{-3} *M*)

R	10^2[$C_6H_5CH{=}$ CHCOR], *M*	P_{CO}, atm	10^2[CO], *M*	% Fe(CO)$_5$	(1 − α)/ α
H	0	0	0	41	0.70
	2.25			16	0.19
	6.00			12	0.14
	10.50			10	0.11
CH_3	0			46	0.85
	2.00			17	0.20
	6.00			12	0.13
	10.00			11	0.12
C_6H_5	0			34	0.51
	0.50			22	0.28
	0.68			17	0.21
	1.00			15	0.17
	2.00			12	0.14
	5.00			9	0.10
	10.00			8	0.09
	0		1.06	82	4.75
	0.61			67	2.00
	0.70			55	1.35
	0.97			55	1.38
	1.31			51	0.96
	2.11			33	0.50
	5.37			26	0.34
	0	0.75	0.79	76	3.20
		0.50	0.53	71	2.50
				71	2.47
		0.25	0.26	61	1.54
				62	1.42
	0.97	0.75	0.79	50	1.02
		0.50	0.53	41	0.70
		0.25	0.26	27	0.37

Experimental Section

The complexes (π-$C_6H_5CH{=}CHCOR$)Fe(CO)$_4$ and (π-$C_6H_5CH{=}CHCOR$)Fe(CO)$_3$ (R = H, CH_3, C_6H_5) were prepared, as described previously,[6,9] by reaction of the appropriate (α,β) unsaturated aldehyde or ketone with $Fe_2(CO)_9$ in benzene. All were purified by crystallization from *n*-pentane. (π-$C_6H_5CH{=}CHCOCH_3$)Fe(CO)$_4$, not described previously, was prepared by reaction between $Fe_2(CO)_9$ and $C_6H_5CH{=}CHCOCH_3$ (mole ratio, 1/1) in benzene at room temperature. When the suspension of $Fe_2(CO)_9$ had completely reacted, the solution was evaporated to dryness; the solid (π-$C_6H_5CH{=}CHCOCH_3$)Fe(CO)$_4$ was purified from (π-$C_6H_5CH{=}CHCOCH_3$)Fe(CO)$_3$, also formed in small quantities, by fractional recrystallization from *n*-pentane and obtained as a yellow solid (mp 53–54°). *Anal.* Calcd: C, 53.53; H, 3.21. Found: C, 53.72; H, 3.32. The nmr spectrum (CCl_4 solvent) shows three bands: $\tau_{C_6H_5}$ 2.35, τ_{CH_3} 7.23, τ_{AB} 4.80 ppm. The τ_{AB} is attributed to the trans protons of the olefin bond, which show four bands corresponding to an AB pattern. From this pattern, τ_A 4.43 and τ_B 5.17 ppm and J_{AB} = 11 Hz are measured.

(π-$C_6H_5CH{=}CHCHO$)Fe(CO)$_4$ shows the carbonyl CO and the aldehyde CO stretching modes doubled in apolar solvents (*e.g.*, *n*-hexane, CS_2). This is due to the presence of two conformers, s-cis and s-trans, as previously suggested in the literature.[6] The methyl and phenyl group stabilize the s-cis conformation.[10] Table I shows the ir CO stretching frequencies of the complexes in different solvents.

All the complexes are sensitive to oxygen when in solution, and even decompose in deaerated solvents, extent of decomposition depending on the particular solvent used. The kinetic runs were carried out in acetone since in this solvent there was less decomposition.

Kinetic measurements were performed in closed flasks, with an aliquot being removed using a syringe. Great care was taken to avoid sucking in air during aliquot removal. The final products were more stable than the reactants, but still were susceptible to slow decomposition. Decomposition of the reacting complexes could be greatly reduced by carrying out the reaction in a large excess of olefin. The kinetics were followed by measuring the decrease in intensity of the CO stretching band at a higher frequency than that of the starting complex as well as the increase in intensity of the CO band at higher frequencies than that of the chelate complex.

When the appearance of the chelate complex was followed, the final absorbance of the complex could not be determined experimentally because of extensive decomposition. On the other hand, the absorbance could not be deduced from the initial concentration of the reactant because Fe(CO)$_5$ was also formed as a side-product as well as the final chelate complex. The formation of Fe(CO)$_5$ depends on many factors, which are analyzed below. To circumvent this difficulty it was assumed that the decomposition of the chelate complex is negligible during the initial phase of the kinetics. The absorbance values for completion of reaction were then extrapolated from the concentration of the chelate at a certain time, *t*, for a certain decrease in the olefinic complex to the total concentration of the olefinic complex itself. The values of the rate constants obtained using this method are comparable (within 5% experimental error) to those obtained by following the disappearance of the olefinic complex.

Several of the reactions were carried out under variable carbon monoxide pressure, prepared as described in the literature.[11] A CO partial pressure lower than atmospheric was obtained by dilution with nitrogen using Mohr bottles to measure gas volumes. The apparatus[12] used for these runs consisted of a thermostated flask with magnetic stirrer, attached to a thermostated buret which main-

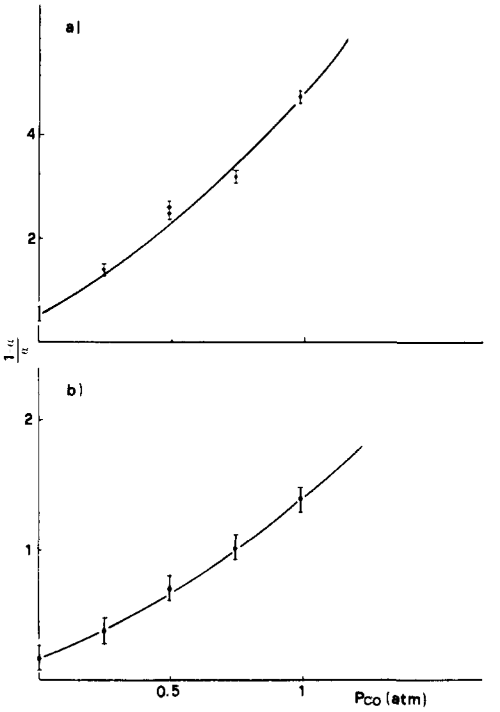

Figure 1. $(1-\alpha)/\alpha$ *vs.* P_{CO} for reaction 1 in acetone with R = C_6H_5: (a) $[C_6H_5CH{=}CHCOC_6H_5]$ = 0; (b) $[C_6H_5CH{=}CHCOC_6H_5]$ = 9.74×10^{-3} *M*.

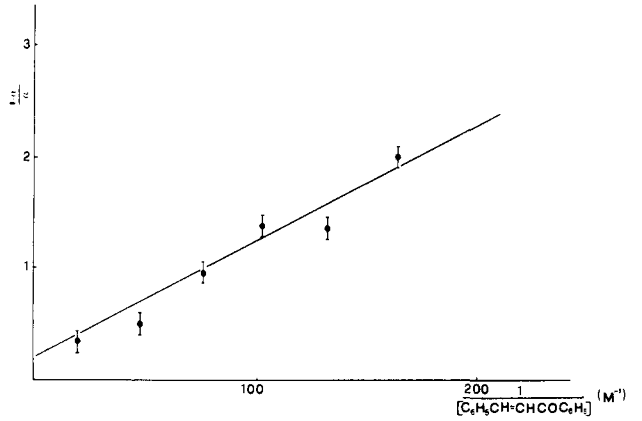

Figure 2. $(1-\alpha)/\alpha$ *vs.* $1/[C_6H_5CH{=}CHCOC_6H_5]$ for reaction 1 at P_{CO} = 1 atm in acetone and at 40°.

tained a constant CO pressure over the solution. The CO concentration in acetone was taken from ref 13. The quantity of $Fe(CO)_5$, formed during these reactions was measured using ir spectroscopy. Since the CO stretching modes of $Fe(CO)_5$ overlap those of both the olefinic complex and the chelate complex, the solution was first distilled before measuring the $Fe(CO)_5$ concentrations. The reaction of the olefinic complexes with $SbPh_3$ was also studied kinetically.

Spectrophotometric measurements were performed in 0.5-mm NaCl cells on a Perkin-Elmer 257 instrument. The nmr spectra were obtained on a Jeol JNM-C-60HL instrument using tetramethylsilane as reference.

Results

Table II lists the percentage of $Fe(CO)_5$ and the $(1-\alpha)/\alpha$ ratios obtained for reaction 1 at various $C_6H_5CH{=}CHCOR$ and CO concentrations. An increase in the quantity of $Fe(CO)_5$ with increase in concentration of $C_6H_5CH{=}CHCOR$ and CO pressure is observed. At constant olefin concentration the $(1-\alpha)/\alpha$ ratios vary with CO pressure according to a square law, as shown in Figure 1. At constant CO pressure (1 atm) there is a linear dependence of $(1-\alpha)/\alpha$ on $1/[C_6H_5CH{=}CHCOR]$ (Figure 2).

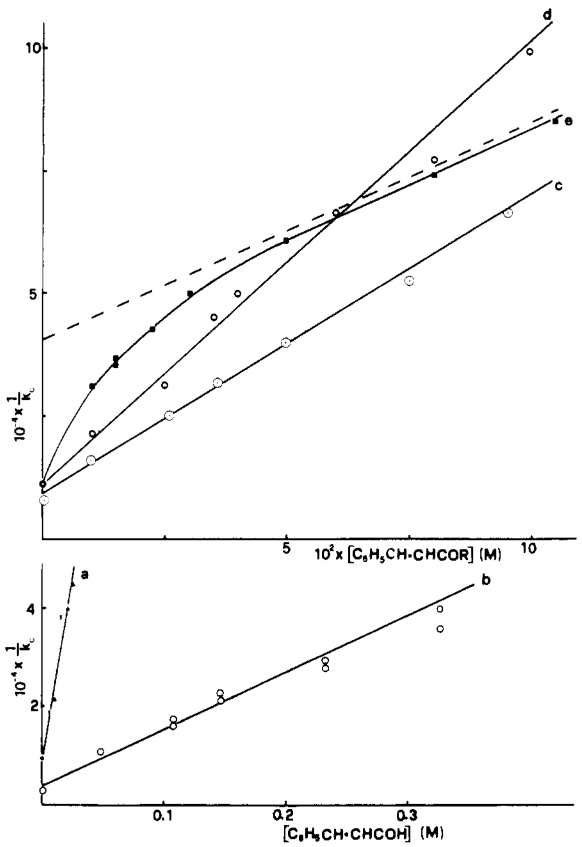

Figure 3. $1/k_c$ *vs.* $[C_6H_5CH{=}CHCOR]$ for reaction 1 in acetone: line a, R = H, T = 30°, P_{CO} = 0, $[(\pi\text{-}C_6H_5CH{=}CHCOH)Fe(CO)_4] \sim 7 \times 10^{-3}$ *M*; line b, R = H, T = 40°, P_{CO} = 0, $[(\pi\text{-}C_6H_5CH{=}CHCOH)Fe(CO)_4] = (4\text{–}7) \times 10^{-3}$ *M*; line c, R = CH_3, T = 40°, P_{CO} = 0, $[(\pi\text{-}C_6H_5CH{=}CHCOCH_3)Fe(CO)_4] \sim 6 \times 10^{-3}$ *M*; line d, R = C_6H_5, T = 40°, P_{CO} = 0, $[(\pi\text{-}C_6H_5CH{=}CHCOC_6H_5)Fe(CO)_4] \sim 6 \times 10^{-3}$ *M*; curve e, R = C_6H_5, T = 40°, P_{CO} = 1 atm, $[(\pi\text{-}C_6H_5CH{=}CHCOC_6H_5)Fe(CO)_4] = {\sim}6 \times 10^{-3}$ *M*.

Table III. Pseudo-First-Order Rate Constants (*k*) for Reaction 2 of the Text at 40° in Acetone

R	$10^3[C]$,[a] *M*	$10[C_6H_5CH{=}CHCOR]$, *M*	$10[SbPh_3]$, *M*	10^4k, sec^{-1}
H	6.60	0	6.65	3.48
	3.30	0	1.43	3.52
	3.15	0	1.57	3.68
	2.66	6.35	1.21	3.20
	3.50	8.50	1.01	2.80
	3.60	30.00	1.00	2.37
	3.90	40.00	1.00	2.48
	3.85	100.00	1.00	1.76
CH_3	5.79	0	0.20	1.60
	6.10	0	0.50	1.60
C_6H_5	6.10	0	0.21	0.92
	5.92	0.52	0.93	0.93

[a] [C] = concentration of $(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_4$.

The kinetic results indicate that reaction 1 is first order with respect to complex. The rate constants (k_c) decrease with increase in the concentration of olefinic ligand and are a function of CO concentration. In the absence of CO, $1/k_c$ values change linearly with $C_6H_5CH{=}CHCOR$ concentration (Figure 3, lines a, b, c, d), while for a constant CO concentration of 1 atm a curve, with a tendency toward an asymptotic line, is found (Figure 3, curve e).

The kinetic results for reaction 2 are shown in Table III.

$$(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_4 + SbPh_3 \longrightarrow Fe(CO)_4SbPh_3 + C_6H_5CH{=}CHCOR \quad (2)$$

The results indicate that the reaction is first order with respect to olefin complex and that the $1/k$ values vary linearly with the concentration of $C_6H_5CH{=}CHCOR$. It may be noted that the rate constants obtained for this reaction in the absence of olefinic ligand correspond to the extrapolated values of Figure 3.

Discussion

The kinetic results obtained for reaction 2 indicate that the substitution mechanism is the same as that observed for similar complexes.[14,15] The mechanism is

$$(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_4 \underset{k_{-1}}{\overset{k1}{\rightleftarrows}}$$

$$C_6H_5CH{=}CHCOR + Fe(CO)_4 \xrightarrow[+SbPh_3]{k_2} Fe(CO)_4SbPh_3 \qquad (3)$$

and the rate constant at zero concentration of olefinic ligand corresponds to the rate constant k_1.

A mechanism which might explain the simultaneous formation of chelate complex and $Fe(CO)_5$ for reaction 1 is

$$\begin{tikzcd}
(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_4 \arrow[r, shift left, "k_1"] \arrow[r, leftarrow, shift right, "k_{-1}"'] \arrow[d, "-CO"', "k"] & C_6H_5CH{=}CHCOR \\
(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_3 & + \; Fe(CO)_4 \arrow[d, "k_2"', "+CO"] \\
 & Fe(CO)_5
\end{tikzcd} \qquad (4)$$

However, this may be rejected for the following reasons. (a) The chelation reaction is completely blocked by an excess of olefin (Figure 3) (for the $(\pi\text{-}C_6H_5CH{=}CHCOC_6H_5)$-$Fe(CO)_4$ complex, at a concentration of 5×10^{-1} *M* of $C_6H_5CH{=}CHCOC_6H_5$, the reaction does not begin for at least 12 hr). (b) The rate constant at zero ligand concentration should correspond to $k_1 + k$ according to eq 4, whereas the value observed is k_1. (c) The ratio $(1 - \alpha)/\alpha$ should equal $k_1k_2[CO]/(k_{-1}k[L] + k_2k[CO])$ with $L = C_6H_5CH{=}CHCOR$, whose expression would predict that, for constant concentration of L, $(1 - \alpha)/\alpha$ *vs.* P_{CO} shows asymptotic behavior with a limiting value $(1 - \alpha)/\alpha = k_1/k$. Instead Figure 1 clearly shows that $(1 - \alpha)/\alpha$ follows a square dependence.

However, the kinetic results suggest that the dissociative step of the olefin is common both to the step giving the chelate complex and to that leading to $Fe(CO)_5$. Hence we suggest the mechanism

$$(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_4 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}$$

$$\begin{tikzcd}
C_6H_5CH{=}CHCOR + Fe(CO)_4 \arrow[r, "k_3", "+CO"'] \arrow[d, shift right, "k_1'"'] & Fe(CO)_5 \\
Fe(CO)_3 + CO \arrow[u, shift right, "k_{-1}'"'] \arrow[r, "k_2", "+C_6H_5CH{=}CHCOR"'] & (\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_3
\end{tikzcd} \qquad (5)$$

The dissociation of $Fe(CO)_4$ to $Fe(CO)_3$ has previously been suggested as a step in the substitution reaction of (π-monoolefin)iron tetracarbonyl by PPh_3[16,17] to explain the simultaneous formation of $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$ and this suggestion is supported by the effect of CO pressure on the ratio $[Fe(CO)_4PPh_3]/[Fe(CO)_3(PPh_3)_2]$.[18] The species $Fe(CO)_3$ has also been observed as a product of the photolysis of matrix-isolated $Fe(CO)_5$[19,20] at low temperatures and was assigned a structure having symmetry C_{3v}, which is also that most convenient for coordination of diene ligands.

Assuming the stationary state approximation for the species $Fe(CO)_4$ and $Fe(CO)_3$, the expression for the rate constant is given by

$$\frac{1}{k_c} = \frac{1}{k_1} + \frac{k_1k_2[L]^2 + k_{-1}k_{-1}'[CO][L]}{k_1k_2k_3[CO][L] + k_1k_1'k_2[L] + k_1k_{-1}'k_3[CO]^2} \qquad (6)$$

in which L is the ligand $C_6H_5CH{=}CHCOR$. When $[CO] \rightarrow 0$, this equation reduces to

$$\frac{1}{k_c} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_1'}[L] \qquad (7)$$

Equation 7 explains the linear behavior observed in Figure 3, lines a, b, c, d.

Equation 6 explains the nonlinear behavior, with intercept $1/k_1$, observed at constant CO pressure, shown in Figure 3 curve e. An analytical treatment of eq 6 predicts that an asymptotic curve with a limiting slope of $k_{-1}/(k_1k_3[CO] + k_1k_1')$ would be given. This is different than the slope of eq 7, because of the presence of the term $k_1k_3[CO]$, and this accounts for the smaller slope of the dotted line in Figure 3.

The ratio

$$\frac{1 - \alpha}{\alpha} = \frac{k_3k_1[CO]^2}{k_1'k_2[L]} + \frac{k_3}{k_1'}[CO] \qquad (8)$$

obtained on the basis of the mechanism 5, explains the square-law dependence observed in Figure 1b. The nonzero intercept of Figure 1a may be explained by the CO given off during reaction 1. Equation 8 rationalizes the linear behavior shown by Figure 3.

To conclude, it may reasonably be stated that the proposed mechanism explains all the experimental results. This mechanism may be generalized to all the iron carbonyl complexes, which give the intermediate $Fe(CO)_4$ in the first step of reaction. This explains the unique behavior of iron carbonyl complexes in its tendency to coordinate dienes.

Acknowledgment. This work was supported in part by the Italian National Research Council.

References and Notes

(1) H. W. Quinn and J. H. Tsai, *Advan. Inorg. Chem. Radiochem.*, **12**, 243 (1969).
(2) H. Reihlem, A. Gruhl, G. von Hessling, and O. Pfrengle, *Justus Liebigs Ann. Chem.*, **482**, 161 (1930); B. F. Hellam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958).
(3) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 1 (1964).
(4) M. I. Davis and C. S. Speed, *J. Organometal. Chem.*, **21**, 401 (1970).
(5) S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, **6**, 20 (1967).
(6) A. M. Brodie, B. F. G. Johnson, P. L. Jòsty, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 2031 (1972).
(7) A. De Cian and R. Weiss, *Acta Crystallogr., Sect. B*, **28**, 3264, 3273 (1972).
(8) E. Koerner von Gustorf, F. W. Grevels, C. Krüger, G. Olbrich, F. Mark, D. Shulz, and R. Wagner, *Z. Naturforsch. B*, **27**, 392 (1972).
(9) K. Stark, J. E. Lancaster, H. D. Murdoch, and E. Weiss, *Z. Naturforsch. B*, **19**, 284 (1964).
(10) S. Sorriso and G. Cardaci, in preparation.
(11) W. L. Gillliand and A. A. Blanchard, *Inorg. Syn.*, **2**, 81 (1946).
(12) G. Innorta, G. Reichenbach, and A. Foffani, *J. Organometal. Chem.*, **22**, 731 (1970).
(13) J. Horiuti, *Sci. Pap. Inst. Phys. Chem. Res., Tokyo*, **17**, 125 (1931).
(14) G. Cardaci and V. Narciso, *J. Chem. Soc., Dalton Trans.*, 2289 (1972).
(15) G. Cardaci, *Int. J. Chem. Kinet.*, **5**, 805 (1973).
(16) G. Cardaci, *J. Organometal. Chem.*, **76**, 385 (1974).
(17) G. Cardaci, *Inorg. Chem.*, **13**, 368 (1974).
(18) G. Cardaci, *Inorg. Chem.*, **13**, 2974 (1974).
(19) M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1351 (1973).
(20) M. Poliakoff, *J. Chem. Soc., Dalton Trans.*, 210 (1974).