Kinetics and Mechanism of Mono- and Di-olefin Exchange at Five-coordinate Iron(o)

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Exchange of various mono-olefins with styrene in $[Fe(CO)_4(PhCH{=}CH_2)]$ proceeds *via* a dissociative process, involving an $Fe(CO)_4$ intermediate. Ligand exchange in system (i) (enone = benzylideneacetone, cinnamaldehyde, chalcone, or dypnone; polyene = cyclohexa- and cyclohepta-1,3-diene, cycloheptatriene, cyclo-octatetraene,

$$[Fe(CO)_3(\eta^4\text{-enone})] + \text{polyene} \rightleftharpoons [Fe(CO)_3(\eta^4\text{-polyene})] + \text{enone} \qquad \text{(i)}$$

or 1,4-diphenylbuta-1,3-diene) is stepwise, involving a rate-determining dechelation of the π-bound CO moiety. Both associative and dissociative pathways are found. The influence of diene structure and enone substituent is discussed.

ALTHOUGH many studies have been reported on the kinetics and mechanism of carbonyl- and olefin-substitution reactions by Group 5 ligands, relatively little work has been carried out on reactions in which olefins or polyolefins function as nucleophiles in substitution reactions.[1] These are of interest not only in view of the expected difference in nucleophilicity between Group 5 ligands and olefins, but also because many transition-metal-catalysed reactions of olefins and polyolefins involve olefin as a substituting ligand at a metal centre. We here report our studies on the olefin exchange of the types (1) and (2).

$$[Fe(CO)_4(PhCH{=}CH_2)] + \text{olefin} \rightleftharpoons [Fe(CO)_4(\text{olefin})] + PhCH{=}CH_2 \qquad (1)$$

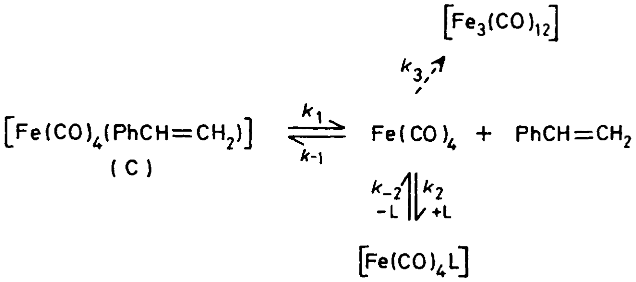
$$[Fe(CO)_3(\eta^4\text{-enone})] + \text{polyene} \rightleftharpoons [Fe(CO)_3(\eta^4\text{-polyene})] + \text{enone} \qquad (2)$$

RESULTS AND DISCUSSION

(*a*) *Mono-olefin Exchange.*—The complexes $[Fe(CO)_4L]$ (L = styrene or methyl acrylate) have been prepared previously;[2,3] tetracarbonyl(cyclo-octene)iron was prepared by displacement of styrene from tetracarbonyl(styrene)iron and isolated as a rather unstable oil which decomposes to $[Fe_3(CO)_{12}]$ fairly rapidly.† During the course of this work, a preparation of $[Fe(CO)_4L]$ (L = cyclo-octene) from $[Fe_2(CO)_9]$ was also reported.[4] Tetracarbonyl(cycloheptene)iron is much less stable in the free state, decomposing rapidly to $[Fe_3(CO)_{12}]$; it is, however, stable in solution in the presence of excess of cycloheptene.

The ν(C–O) frequencies for the complexes are given in the Experimental section. Despite overlap in the spectra, reactions between $[Fe(CO)_4(PhCH{=}CH_2)]$ and an olefin may conveniently be followed by monitoring either the disappearance of the absorption at 2 085 cm^{-1} due to the initial complex or the appearance of the absorptions due to $[Fe(CO)_4(\text{olefin})]$ at 2 101, 2 072, and 2 074 cm^{-1} (olefin = methyl acrylate, cyclo-octene, and cycloheptene respectively). The rate constants quoted in Table 1 have been obtained by the former method. Surprisingly, cyclohexene did not displace styrene, while reaction with acrylonitrile did not proceed to yield a single product. Reaction (1) is potentially reversible and equilibrium constants have been determined indirectly for several olefins.[5] However, with the concentrations of olefin used in this study, complete displacement of styrene is observed, and the reaction has been treated mechanistically as irreversible.

A mechanism involving dissociation of the iron–styrene bond may be invoked to explain the results (Scheme 1).



SCHEME 1 L = Methyl acrylate, cycloheptene, or cyclo-octene

Neglecting k_3 and k_{-2} for the moment, application of the steady-state approximation to $Fe(CO)_4$ yields the rate law (3) and therefore (4) where $k_{obs.}$ is the observed

$$\frac{-d[C]}{dt} = \frac{k_1k_2[C][L]}{k_{-1}[\text{styrene}] + k_2[L]} \qquad (3)$$

$$k_{obs.} = \frac{k_1k_2[L]}{k_{-1}[\text{styrene}] + k_2[L]} \qquad (4)$$

pseudo-first-order rate constant. Data for these reactions in the absence of added styrene are presented in Table 1.

For cases where $k_2[L] \gg k_{-1}[\text{styrene}]$, equation (4) reduces to $k_{obs.} = k_1$. As predicted, $k_{obs.}$ is independent of [L] at all except the lowest concentrations of olefin studied (see below). Additionally, the k_1 values obtained are identical within experimental error, and are thus independent of the nature of L as required by the mechanism.

It may be noted that, particularly in the case of cyclo-

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† Such thermal instability of $[Fe(CO)_4(\text{olefin})]$ complexes is well established; see for example, J. C. Barborak, L. W. Dasher, A. T. McPhail, J. B. Nicholas, and K. D. Onan, *Inorg. Chem.*, 1978, **17**, 2936.

TABLE 1

Rate constants for reactions of $[Fe(CO)_4(PhCH{=}CH_2)]$ and of (1b)—(1d) with cycloheptatriene

Substrate	Ligand	[L]/[substrate]	$10^4k_{obs.}$/ s^{-1}	10^4k_1/ s^{-1}
$[Fe(CO)_4(PhCH{=}CH_2)]$ [a]	Cycloheptene	8.5	4.38, 4.75	9.12
		17.0	5.20, 5.38	±0.88
		34.0	8.63, 8.22	
		68	8.83, 8.22	
		94	9.45, 9.34	
		111	10.25, 10.66	
		129	10.02, 9.64	
		154	9.74, 10.17	
	Cyclo-octene	8.5	9.02, 8.72	9.98
		17.0	9.90, 9.92	±0.36
		34	9.85, 9.56	
		68	10.01, 9.99	
		94	9.45, 10.01	
		111	9.66, 10.20	
		129	9.41, 9.42	
		154	10.33, 9.84	
	Methyl acrylate	10	9.67, 9.82	10.22
		20	9.98, 9.67	±0.31
		40	10.38, 10.38	
		80	10.66, 10.65	
		110	10.74, 9.54	
		130	10.54, 10.28	
		150	10.33, 10.31	
		180	10.82, 10.90	
(1b) [b]	Cycloheptatriene	10	3.81, 3.94	
		20	5.08, 5.42	
		40	7.88, 9.66	
		80	10.32, 9.92	
		160	18.86, 18.86	
(1c)	Cycloheptatriene	10	0.77, 1.04	
		20	1.15, 1.22	
		40	2.52, 2.62	
		80	4.97, 5.50	
		160	6.49, 6.74	
(1d)	Cycloheptatriene	12.5	2.59, 2.56	
		25	3.50, 3.21	
		40	3.32, 3.39	
		80	5.76, 5.76	
		160	11.12, 10.56	

[a] Reactions carried out at 60 °C in light petroleum (b.p. 100—120 °C); initial complex concentration was 3.0×10^{-3} mol dm^{-3} in all cases. [b] Reactions carried out at 90 °C in toluene; initial concentration of (1b)—(1d) was 4.9×10^{-3} mol dm^{-3} in all cases.

heptene, a decrease in $k_{obs.}$ is observed in the reactions involving the lower concentrations of olefin, although rate measurements based on disappearance of $[Fe(CO)_4(PhCH{=}CH_2)]$ are still first order. This behaviour is ascribed to a contribution of the reversible k_{-2} step at low [L], coupled with decomposition of the $Fe(CO)_4$ intermediate (k_3 in the mechanism). Experimentally, this is evident in the observations that (*a*) conversion of $[Fe(CO)_4(PhCH{=}CH_2)]$ into $[Fe(CO)_4L]$ is not quantitative in these reactions and (*b*) the rate of appearance of $[Fe(CO)_4L]$ is not first order, reaching a maximum followed by a decrease due to decomposition. The k_1 values quoted in Table 1 have been determined by a linear least-squares analysis using only those reactions which resulted in quantitative conversion into $[Fe(CO)_4L]$.

The effect of added styrene on the reaction with methyl acrylate also confirms the mechanism. Rearrangement of equation (4) yields (5). Thus, for constant [L], a plot of $1/k_{obs.}$ against [styrene] is linear (Figure 1).

$$\frac{1}{k_{obs.}} = \frac{k_{-1}[\text{styrene}]}{k_1k_2[L]} + \frac{1}{k_1} \qquad (5)$$

Cardaci and co-workers[5-9] have studied in detail the reaction of $[Fe(CO)_4(PhCH{=}CH_2)]$ with CO, pyridine, and EPh_3 (E = P, As, or Sb) to yield $[Fe(CO)_4L]$. The mechanism observed is analogous, although reaction with PPh_3 is complicated by concomitant formation of $[Fe(CO)_3(PPh_3)_2]$. The k_1 value obtained (10.4×10^{-4} s^{-1}) for reaction with PPh_3 in hexane at 60 °C (extrapolated from data[7] at lower temperatures) compares well with the k_1 values obtained here. Previous work has also shown that k_1 is solvent dependent, increasing with the dielectric constant of the solvent as expected,[7] and that the effects of substituent (X) on k_1 in the reactions of $[Fe(CO)_4(XCH{=}CH_2)]$ with PPh_3 are also consistent with the proposed mechanism.[8] Recently, it has been shown that complexes of the type $[Fe(CO)_4(PhCH{=}CHCH{=}NR)]$ react with PPh_3 in a similar fashion.[10]

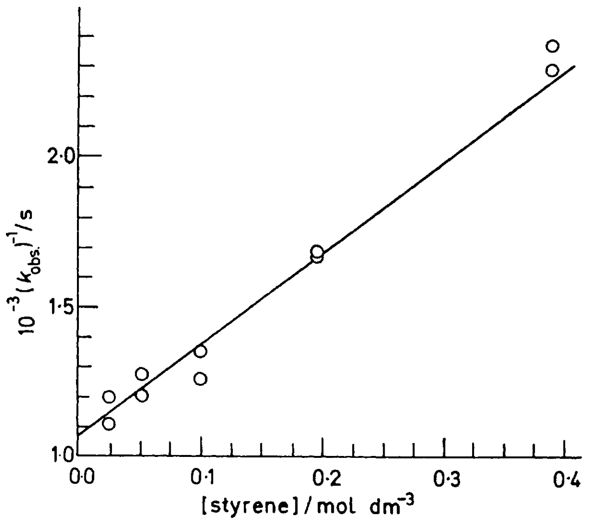

FIGURE 1 Plot of $1/k_{obs.}$ against [styrene] for reaction of $[Fe(CO)_4(PhCH{=}CH_2)]$ with methyl acrylate

From Figure 1, a value of k_2/k_{-1} of 1.06 ± 0.06 is obtained. From previous work,[8] it has been shown that k_2/k_{-1} is a reflection of the nucleophilicity of the various ligands compared to styrene. By combination with previously obtained values,* the reactivity order obtained is $C_5H_5N > PPh_3 > AsPh_3 \approx SbPh_3 > CO >$ methyl acrylate.

(*b*) *Polyene Exchange*.—The displacement of the α,β-unsaturated ketone from complexes of type (1) has proved to have considerable synthetic utility in complexing of unstable polyenes,[11] and is particularly interesting with regard to the remarkable selectivity observed on reaction with tautomeric diene mixtures.[12-14] In this work, we have investigated primarily the displacement of enone from complexes (1a)—(1d) (Scheme 2) with cyclohexa-1,3-diene and cycloheptatriene and the reaction of (1a) with a series of polyenes to elucidate the effect of ketone substituent and polyene structure on the mechanism of this reaction. Part of this work has

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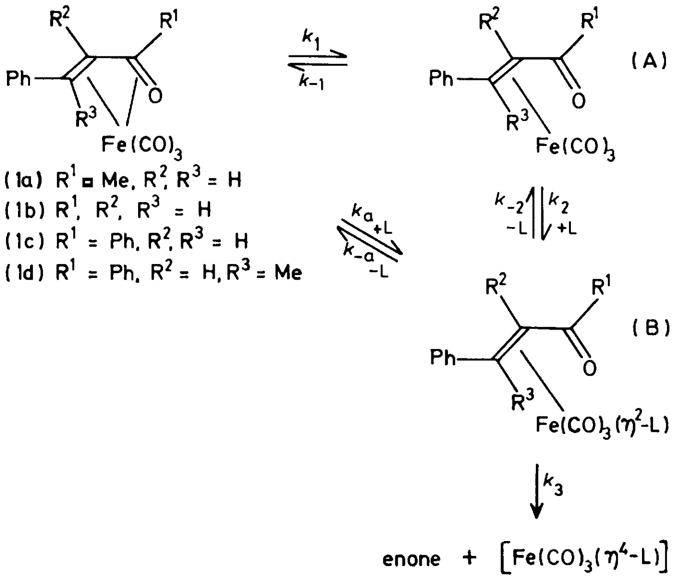
* Taken from ref. 8, at 50 °C; k_2/k_{-1} values are, however, essentially independent of temperature.

already been described,[15] and the overall results are consistent with the recent qualitative observations of Brookhart and Nelson.[16] It has been shown in the displacement of enone from (1a) by cyclohexa-1,3-diene that the rate exhibits the expected first-order dependence on the concentration of (1a).[14]



SCHEME 2 L = Cyclohexadiene, cycloheptadiene, cycloheptatriene, cyclo-octatetraene, or 1,4-diphenylbutadiene

Variation of polyene. Kinetically well behaved reactions were observed at 70 °C in toluene between (1a) and cyclohexa-1,3-diene, cyclohepta-1,3-diene, cyclo-octatetraene, cycloheptatriene, and 1,4-diphenylbuta-1,3-diene. All the product $[Fe(CO)_3(polyene)]$ complexes have previously been well characterized from syntheses using other iron carbonyl reagents.[17-19] Displacement with cyclo-octa-1,5-diene (1,5-cod) proceeded with concomitant isomerization of $[Fe(CO)_3(1,5\text{-cod})]$ to $[Fe(CO)_3(1,3\text{-cod})]$, while exchange with 1,3-cod itself was extremely slow at 70 °C. Reaction with norbornadiene resulted in extensive decomposition. Although there is considerable overlap in the i.r. spectra of reactants and products below 2 000 cm^{-1}, the reactions may be monitored by i.r. spectroscopy using the disappearance of the absorption due to (1a) at 2 064 cm^{-1} or the appearance of a band at *ca.* 2 045 cm^{-1} due to the product $[Fe(CO)_3(polyene)]$; $k_{obs.}$ values were obtained using the former method.

The proposed mechanism is shown in Scheme 2. Application of the steady-state approximation to intermediates (A) and (B) yields the rate equation (6) and therefore (7). More simplified versions of this rate law and mechanism have been invoked in similar systems.

$$\frac{-\mathrm{d}[(1)]}{\mathrm{d}t} = [(1)]\left(k_\alpha[\mathrm{L}] + \frac{k_\beta[\mathrm{L}]}{k_\gamma + k_\delta[\mathrm{L}]}\right) \qquad (6)$$

$$k_{obs.} = \frac{k_\beta[\mathrm{L}]}{k_\gamma + k_\delta[\mathrm{L}]} + k_\alpha[\mathrm{L}] \qquad (7)$$

where

$$k_\alpha = k_3k_a/(k_{-a} + k_3)$$
$$k_\beta = k_3(k_1k_2k_{-a} + k_1k_2k_3 - k_ak_{-2}k_{-1})/(k_{-a} + k_3)$$
$$k_\gamma = k_{-a}k_{-1} + k_{-2}k_{-1} + k_3k_{-1}$$

and

$$k_\delta = k_{-a}k_2 + k_3k_2$$

Thus, substitution of bidentate ligands in $[M(CO)_4(chelate)]$ complexes (M = Cr, Mo, or W) may be explained by a purely S_N1 ring opening ($k_{-a} = k_a = k_{-2} = 0$),[20] or by the assumption that $k_1 \gg k_a$,[21,22] while it has recently been shown that substitution of complexes of type (1) by Group 5 ligands to yield $[Fe(CO)_3(\eta^2\text{-enone})L]$ and $[Fe(CO)_3L_2]$ complexes may be explained assuming $k_{-a} = k_{-2} = 0$.[23-26]

Plots of $k_{obs.}$ against polyene concentration for reaction of (1a) with the various polyenes are shown in Figure 2. Solubility limited studies using diphenylbutadiene to a maximum ligand : complex ratio of 95 : 1. The derived rate constants (k_α, k_β/k_δ, and k_γ/k_δ) listed in Table 2 were obtained by fitting of the experimental data to the theoretical model of equation (7) by means of a non-linear least-squares computer program. Initial estimates were obtained graphically and then refined by an iterative Taylor-differential correction routine. In addition, an overall standard deviation is given which reflects the fit of the experimental data to the theoretical model. The value of this standard deviation for each system is close to the standard deviation of the difference between duplicate runs for $k_{obs.}$ values in that system (see Experimental section) and shows that the mechanistic model is consistent with the experimental results. The curves drawn in Figure 2 are those calculated on the basis of equation (7). Particularly for reactions with cycloheptatriene, the precision of the derived rate constants is limited by the lack of $k_{obs.}$ values at ligand concentrations greater than the practical limit of 1 mol dm^{-3}. Standard deviations of the derived rate constants

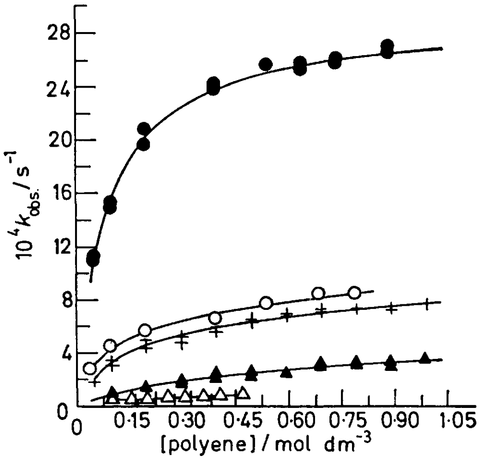


FIGURE 2 Plot of $k_{obs.}$ against [polyene] for reactions of (1a) with cyclohexa-1,3-diene (●), cyclo-octatetraene (○), cyclohepta-1,3-diene (+), cycloheptatriene (▲), and 1,4-diphenylbuta-1,3-diene (△)

TABLE 2

Derived rate constants for reactions of $[Fe(CO)_3(\eta^4\text{-enone})]$ complexes

Complex[a]	θ_c / °C	Polyene[b]	10^4k_α / $dm^3\ mol^{-1}\ s^{-1}$	$10^4k_\beta/k_\delta$ / s^{-1}	$10k_\gamma/k_\delta$ / $mol\ dm^{-3}$	$10^4\sigma$[c] / s^{-1}
(1a)	70	chpt	0.83 (0.83)[d]	3.6 (1.5)	3.9 (1.7)	0.13
	70	chpd	1.4 (0.6)	7.1 (0.7)	1.3 (0.2)	0.28
	70	chd	0.4 (1.2)	28.6 (1.1)	0.82 (0.07)	0.45
	70	cot	2.5 (1.4)	7.2 (1.1)	0.79 (0.2)	0.29
	70	bd	1.3 (0.1)	0.26 (0.03)	*e*	0.049
(1b)	90	chpt	15.9 (3.4)	5.1 (1.8)	0.30 (0.28)	0.78
(1c)	90	chpt	6.7 (1.4)	1.8 (1.0)	1.4 (1.0)	0.39
(1d)	90	chpt	10.4 (0.8)	1.8 (0.1)	*e*	0.37
(1b)	70	chd	3.4 (0.3)	11.8 (0.2)	0.29 (0.02)	0.24
(1c)	70	chd	12.5 (0.6)	4.2 (0.7)	0.92 (0.32)	0.29

[a] Reactions carried out in toluene. [b] chpt = Cycloheptatriene, chpd = cyclohepta-1,3-diene, chd = cyclohexa-1,3-diene, cot = cyclo-octatetraene, and bd = 1,4-diphenylbuta-1,3-diene. [c] Overall standard deviation (σ) = $\{\sum_{i=1}^{n}[k_{obs.}(calc.) - k_{obs.}(expt.)]_i^2)/(n-3)\}^{\frac{1}{2}}$ where n is the number of experimental observations. [d] Standard deviation in parentheses. [e] Contribution so small that accurate determination not possible.

are generally comparable with those obtained for reaction of complexes of type (1) with liquid Group 5 ligands.[25,26]

Several points may be made. (*i*) For the monoene exchange previously described, only the dissociative pathway is observed. This may be due in part to the known difference in structure of the tricarbonyl and tetracarbonyl complexes. Both in the solid state (see footnote on p. 999 for a recent structure determination) and in solution[27] the latter exhibit a trigonal-bipyramidal structure with the olefin in an equatorial position. The $[Fe(CO)_3(enone)]$ complexes are, however, square pyramidal both in the solid state[28] and in solution[29] with CO in the apical position. The availability of a vacant sixth co-ordination site may provide a pathway of lower activation energy for an associative mechanism. Although formally involving nucleophilic attack at an 18-electron metal centre, such associative pathways are well established for octahedral metal carbonyl derivatives[30] and proceed by a mechanism involving predominantly bond breaking. Conversely, such an associative process should be most favourable with ligands such as olefins which possess vacant orbitals capable of accepting d_π electron density.

(*ii*) The rapid decrease in overall $k_{obs.}$ values in the order cyclohexa-1,3-diene > cyclohepta-1,3-diene ≈ cyclo-octatetraene > cycloheptatriene ≫ 1,4-diphenylbutadiene is due predominantly to the decrease in the k_β/k_δ term, with k_α and k_γ/k_δ showing relatively little change. It has been suggested[16] that the important step in the determination of the overall rate of exchange is the process associated with k_3, *i.e.* the need to convert a possibly non-planar diene fragment in (B) into the planar η^4-diene fragment of the final product. Our results, however, do not indicate any simple relationship between overall $k_{obs.}$ and the amount of distortion required in the step associated with k_3 [as measured by the torsional angle between the ethylenic bonds of the free ligands determined by electron diffraction; cyclo-octatetraene (43°) > cycloheptatriene (40°) > cyclo-octa-1,3-diene (38°) > cyclohexa-1,3-diene (18°) > cyclohepta-1,3-diene (0°)[31]]. Particularly in the cycloalka-1,3-diene series, the rate seems to be determined by the degree of steric hindrance to co-ordination as a monoene presented by the non-bonding methylenic part of the ring. Although tub-shaped, the absence of any α- or β-methylene groups may account for the position of cyclo-octatetraene in the series. 1,4-Diphenylbuta-1,3-diene is known to have an *s-trans* geometry in the uncomplexed form;[32] severe steric hindrance by the phenyl substituent may account for its slow rate of exchange. The complexity of the rate-constant expressions makes any more quantitative interpretation difficult, and the data do not justify any simplification of the rate law or mechanism.

(*iii*) *Reaction with 1,2-bis(diphenylphosphino)ethane (dppe)*. Both (1a) and (1c) react with dppe in toluene at 34 °C to give $[Fe(CO)_3(dppe)]$ exclusively by comparison with an authentic sample prepared using $[Fe_2(CO)_9]$.[33] Kinetically, identification of an intermediate analogous to (B) is unambiguous; appearance of a band at 2 036 cm^{-1} during the reaction may be clearly associated with a $[Fe(CO)_3(\eta^2\text{-enone})(dppe)]$ species of the type observed on reaction of unidentate Group 1 ligands with (1a).[23-26] An equilibrium concentration is rapidly established and remains constant until near the end of the reaction. Identification of an analogous intermediate in the polyene exchange reactions is more difficult, although a small band observed at 2 022 cm^{-1} in the reaction of (1a) and (1d) with cycloheptatriene may be due to such a species.*

(*iv*) *Effect of added ketone*. As shown in Figure 3, for the reaction of (1a) with cycloheptatriene, $k_{obs.}$ exhibits a linear dependence on the reciprocal of the added benzylideneacetone concentration. While this has been interpreted in terms of an S_N1 mechanism for the final step associated with k_3, it is also consistent with a competition between incoming polyene and the olefinic bond of the free ketone in the steps associated with either k_2 or k_a. Qualitatively, we have observed using t.l.c. that exchange occurs on reaction of (1a)—(1d) with any of the free α,β-unsaturated ketones.

Variation of ketone. Reactions of cyclohexa-1,3-diene

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* Tricarbonylbis(methyl acrylate)iron exhibits vibrations at 2 087vw, 2 024vs, and 2 012s cm^{-1} in hexane (F. W. Grevels, D. Schulz, and E. A. K. von Gustorf, *Angew. Chem. Internat. Edn.*, 1974, **13**, 534).

with (1a)—(1c) and of cycloheptatriene with (1b)—(1d) have been studied; plots of $k_{obs.}$ *versus* cyclohexadiene concentration are shown in Figure 4, and derived rate constants obtained by the method previously described are given in Table 2. For reaction with cyclohexa-1,3-diene, k_α decreases in the order (1c) > (1b) > (1a) while the reverse order is true for k_β/k_δ. In view of the complexity of the rate-constant expressions, it is again difficult to draw any quantitative conclusions, and indeed for k_γ a different order of (1b) > (1d) > (1c) is observed for reaction with cycloheptatriene ($k_{obs.}$ data in Table 1). The variation in k_α and k_γ/k_δ values is much less marked for reaction with cycloheptatriene. Thus for the tub-shaped cycloheptatriene, steric hindrance of the polyene appears to be the determining factor, while for the less hindered cyclohexa-1,3-diene a greater influence of the ketonic substituent may be detected. The enone complex (2) exchanges at rates too slow for kinetic measurement at 70 °C. The rigid ring prevents rotation of the π-bound CO away from the metal centre, a process which may be a requirement for access to intermediate (B) *via* either an S_N1 or S_N2 process.

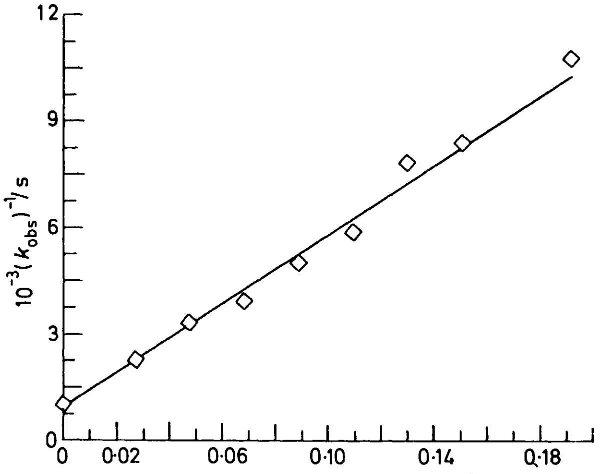


FIGURE 3 Plot of $1/k_{obs.}$ against [benzylideneacetone] for reaction of (1a) with cycloheptatriene

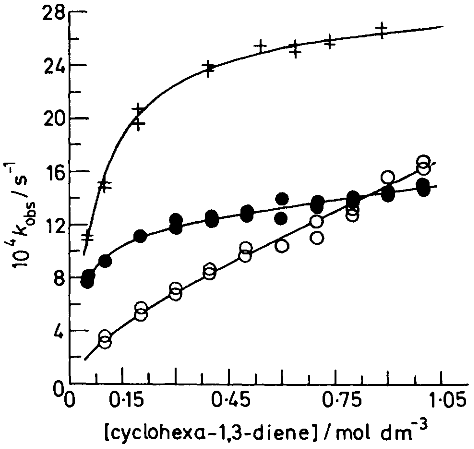
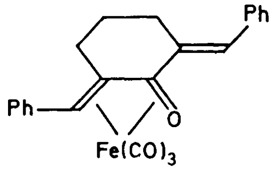


FIGURE 4 Plot of $k_{obs.}$ against [cyclohexa-1,3-diene] for reactions of (1a) (+), (1b) (●), and (1c) (○)



(2)

EXPERIMENTAL

Literature methods were used to prepare tetracarbonyl(styrene)iron [3] [ν(CO) at 2 085, 2 013, 2 006, and 1 982 cm^{-1}], tetracarbonyl(methyl acrylate)iron [ν(CO) at 2 101, 2 033, 2 019, and 1 996 cm^{-1}; light petroleum (b.p. 100—120 °C)] and complexes (1a)—(1d) and (2).[11] All olefins and polyenes used in kinetic experiments were distilled before use with the exception of 1,4-diphenylbuta-1,3-diene. Except for cyclohepta-1,3-diene,[34] all polyenes were commercial materials. All reactions were carried out under a nitrogen atmosphere. Light petroleum (b.p. 100—120 °C, AnalaR grade) and toluene were distilled and degassed before use. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer using 1 mm cells. A solvent–polyene blank of the appropriate concentration was used for the kinetic experiments.

Preparation of Tetracarbonyl(cyclo-octene)iron.—The complex [$Fe(CO)_4(PhCH{=}CH_2)$] (1.2 g, 4.4 mmol) in dry degassed light petroleum (b.p. 40—60 °C, 100 cm^3) was refluxed for 3 h with cyclo-octene (2 cm^3, 15.3 mmol). After filtration and removal of volatiles, the product was dissolved in light petroleum (b.p. 40—60 °C) and filtered through a short column of grade I alumina to remove [$Fe_3(CO)_{12}$]. Evaporation of solvent and molecular distillation gave the product as a yellow oil contaminated with traces of [$Fe_3(CO)_{12}$] (Found: C, 50.4; H, 4.85. Calc.: C, 51.8; H, 5.00%), ν(CO) at 2 072, 2 002, 1 994, and 1 982 cm^{-1} in light petroleum (b.p. 100—120 °C). Displacement is essentially quantitative, although significant loss occurs on purification.

A solution of tetracarbonyl(cycloheptene)iron was prepared in the same way [ν(CO) at 2 074, 2 000, 1 995, and 1 975 cm^{-1} in light petroleum (b.p. 100—120 °C)], but attempted purification results in decomposition to [$Fe_3(CO)_{12}$].

Kinetic Experiments.—Reactions were carried out in duplicate under nitrogen in sealed vessels in a constant-temperature bath controlled to ±0.1 °C. Aliquots were removed by syringe and the i.r. spectrum recorded. Reactions were followed over at least three half-lives to give an average of 12 absorbance–time data pairs. Rate constants ($k_{obs.}$) may be obtained from a normal least-squares analysis of plots of (*a*) $-\log A$ *vs.* time for the starting complex ($A_\infty = 0$) or (*b*) $\log (A_\infty - A_t)$ *vs.* time for the product complex. Agreement between values obtained by both methods was observed. As the small amount of decomposition observed even under strict exclusion of air prevented accurate determination of A_∞ values for product appearance, the more precise $k_{obs.}$ values obtained by method (*a*) are quoted in the text. All linear plots had correlation coefficients of greater than 0.998. Values for the standard deviation of duplicate runs, $\sigma[k_{obs.}(A) - k_{obs.}(B)]$, were in the range 0.02×10^{-4}—0.2×10^{-4} s^{-1} for reactions of (1a) with the various polyenes and 0.2×10^{-4}—0.7×10^{-4} s^{-1} for reactions of (1a)—(1d) with cyclohexadiene and cycloheptatriene and of [Fe(CO)$_4$(PhCH=CH$_2$)] with the various mono-olefins. All derived rate constants were obtained using $1/\sigma$ weighting factors, where σ is the standard deviation of the $k_{\text{obs.}}$ value. The complexes [Fe(CO)$_4$(PhCH=CH$_2$)] and (benzylideneacetone)tricarbonyliron obey the Beer–Lambert law.

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