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The addition of halogenocarbons to alkenes in the presence of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and related complexes

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Abstract

A kinetic study has been made of the addition of halogenocarbons to alkenes in the presence of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (I). The results, together with the results of cross-over addition reactions of a halogenocarbon mixture and cross-over studies on catalyst mixtures of I and $[Fe_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ (II) have been interpreted in terms of a mechanism which involves catalysis by an intact dinuclear species, probably $[Fe_2(CO)_3(\eta\text{-}C_5R_5)_2]$, but which also involves free radical intermediates.

Introduction

We have previously reported on the addition of halogenocarbons to alkenes in the presence of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (I) [1], and suggested that the reaction follows a non-radical pathway in which a dinuclear species, probably $[Fe_2(CO)_3(\eta\text{-}C_5H_5)_2]$, is the active catalyst. We now report that we have been unable to repeat some of the work reported in this paper. This led us to reexamine all of the work presented previously, to add further results, and to formulate a slightly different mechanism.

We previously studied the mechanism of the reaction of halogenocarbons with alkenes (eq. 1) in the presence of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ [2], $[RuCl_2(PPh_3)_3]$ [3] and

$$RCH{=}CH_2 + CX_4 \rightarrow RCHXCH_2CX_3 \qquad (1)$$

$[Cr(CO)_3(\eta^6\text{-}C_{10}H_8)]$ [4]. In all cases we showed that the reactions are catalysed by a metal-containing species, but that free radical intermediates are involved. The

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$RuCl_2(PPh_3)_3 \rightleftharpoons RuCl_2(PPh_3)_2 + PPh_3$

$RuCl_2(PPh_3)_2 + CX_4 \rightleftharpoons [RuCl_2X(PPh_3)_2^{\cdot}\}\{CX_3^{\cdot}\}$

$\{RuCl_2X(PPh_3)_2^{\cdot}\}\{CX_3^{\cdot}\} + RCH{=}CH_2 \rightleftharpoons [RuCl_2X(PPh_3)_2^{\cdot}\}\{RCHCH_2CX_3^{\cdot}\}$

$\{RuCl_2X(PPh_3)_2^{\cdot}\}\{RCHCH_2CX_3^{\cdot}] \rightarrow RuCl_2(PPh_3)_2 + RCHXCH_2CX_3$

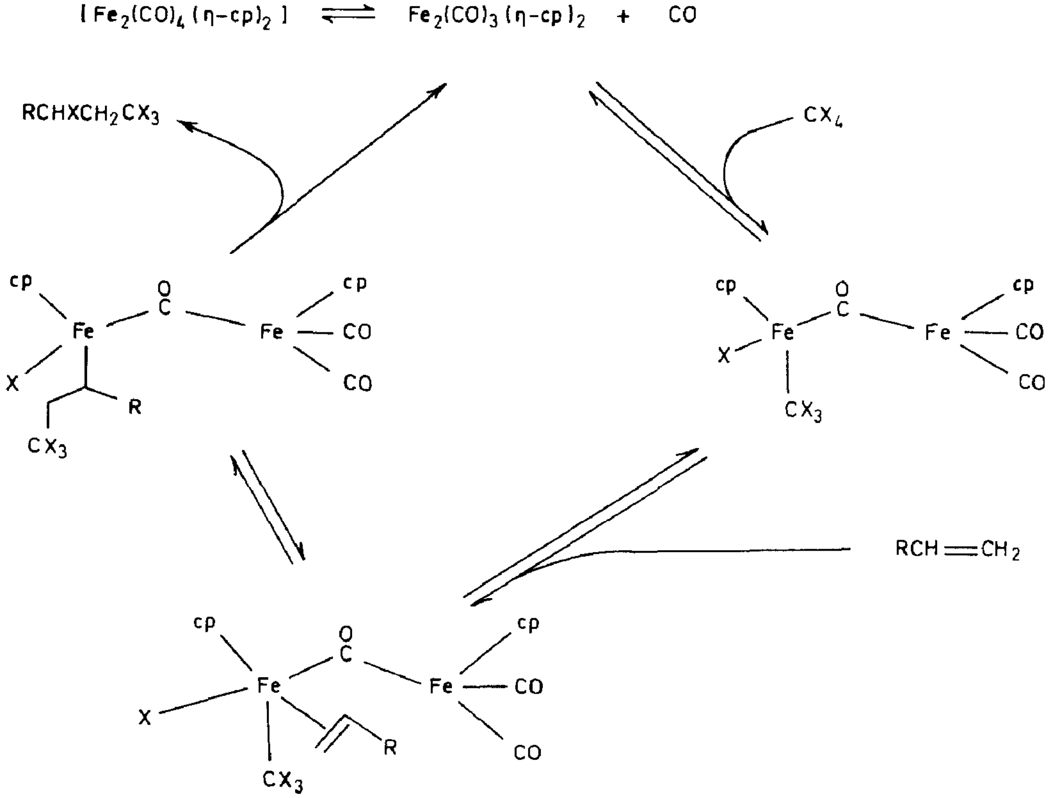
Scheme 1

$Fe_2(CO)_4(\eta\text{-cp})_2 + CCl_4 \rightarrow FeCl(CO)_n(\eta\text{-cp}) + FeCCl_3(CO)_n(\eta\text{-cp})$

$FeCCl_3(CO)_n(\eta\text{-cp}) + RCH{=}CH_2 \rightarrow Fe(CHRCH_2CCl_3)(CO)_n(\eta\text{-cp})$

$Fe(CHRCH_2CCl_3)(CO)_n(\eta\text{-cp}) + CCl_4 \rightarrow FeCCl_3(CO)_n(\eta\text{-cp}) + RCHClCH_2CCl_3$

Scheme 2



Scheme 3

mechanism operating in the presence of $[RuCl_2(PPh_3)_3]$ is shown in Scheme 1. Susuki and Tsuji have previously shown I to be an effective promoter for reaction 1 [5]; although they did not make a detailed mechanistic study of this system, they postulated a non-radical catalysed process (Scheme 2) in the light of the fact that the presence of a free radical inhibitor, hydroquinone, did not lower the reaction rate. Our original mechanistic proposal is shown in Scheme 3 and was based on the following evidence: (i) A complete kinetic study revealed the rate equation shown in eq. 2. (ii) The rate was lower in the presence of CO. (iii) The reaction between

$$\text{Rate} = \frac{k[\text{I}][\text{CX}_4][\text{RCH=CH}_2]}{\{k' + k''[\text{RCH=CH}_2]\}[\text{CO}]} \tag{2}$$

alkene and a mixture of CCl_4 and CBr_4 in the presence of I gave no cross-over products, $C_6H_{13}CHClCH_2CBr_3$ and $C_6H_{13}CHBrCH_2CCl_3$. (iv) Cyclohexene underwent slow hydrogenation in the presence of I. (v) Following reactions leading to both the addition of CCl_4 to oct-1-ene and the hydrogenation of cyclohexene in the presence of a mixture of I and $[Fe_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ (II), these two complexes were recovered unchanged and there was no evidence for formation of the cross-over product $[Fe_2(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$. The interpretation of these findings in terms of the mechanism shown in Scheme 3 was given in our earlier publication [1].

Results and discussion

Our initial concern over the findings outlined above arose because we were unable to repeat the reactions leading to the hydrogenation of cyclohexene in the presence of either I or II. This led us to carry out a new investigation of all aspects of the title reaction. The yields of tetrachlorononane from reactions between CCl_4 and oct-1-ene in the presence of I, II and $[Fe_2(CO)_4(\eta\text{-}C_5H_4Me)_2]$ are shown in Table 1. The reactions show a moderate efficiency in the temperature range 25–60 °C. Although much higher yields are obtained at 120 °, it is likely that free radical chain processes play a dominant role under these conditions with initiation involving decomposition products of the metal complexes [2].

A kinetic study of the CCl_4-oct-1-ene reaction in the presence of I was carried out at 60 °C by use of the initial rate method. Figures 1, 2 and 3 show the rate versus concentration plots for I, CCl_4 and oct-1-ene respectively. The linearity of

Table 1

Yield of tetrachlorononane from the reaction of oct-1-ene and tetrachloromethane [a]

Complex	Temperature (°C)	Yield of tcn (%) [b]
$Fe_2(CO)_4(\eta\text{-}C_5H_5)_2$	25	9.0
(I)	30	12.3
	60	22.0
	120	61.0
$Fe_2(CO)_4(\eta\text{-}C_5Me_5)_2$	30	7.0
(II)	60	16.0
	120	72.0
$Fe_2(CO)_4(\eta\text{-}C_5H_4Me)_2$	60	21.0
$\{Fe(CO)_2(\eta\text{-}C_5H_4)\}_2CH_2$	60	25.0
(III)	120	91.0
$Ru_2(CO)_4(\eta\text{-}C_5H_5)_2$	80	2.0
(IV)	100	6.3
	120	49.6
	160	74.3

[a] Yields based on alkene charged rather than consumed. All reactions for 18 h. [b] tcn = 1,1,1,3-tetrachlorononane.

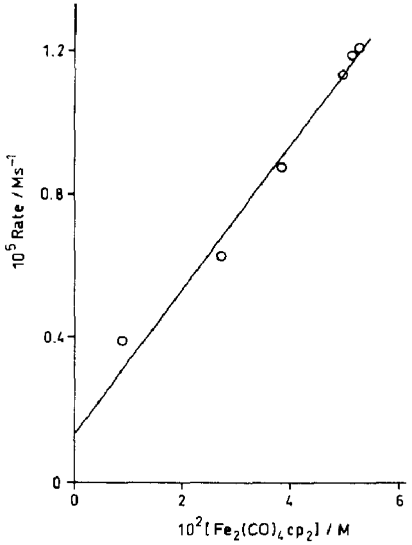


Fig. 1. Dependence of the rate of reaction upon concentration of [$Fe_2(CO)_4(\eta$-$C_5H_5)_2$].

the plots for I and CCl_4 indicates a first order dependance on both. It is to be noted that the plot for I has a small positive intercept, suggesting a minor contribution from a reaction not involving I. For this reason, no attempt was made to obtain activation parameters. [6] Similar behaviour was observed in our previous studies.

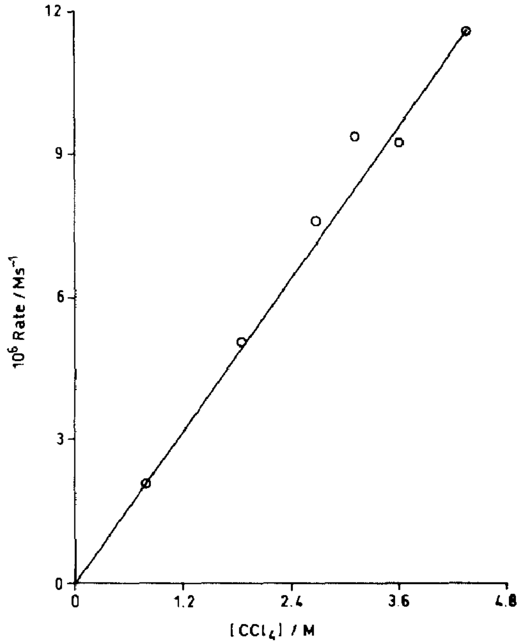


Fig. 2. The dependence of the rate of reaction upon CCl_4 concentration.

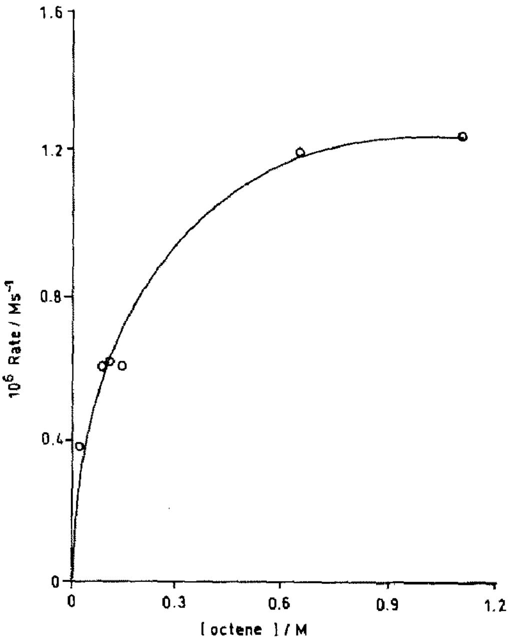


Fig. 3. Dependence of the rate upon oct-1-ene concentration.

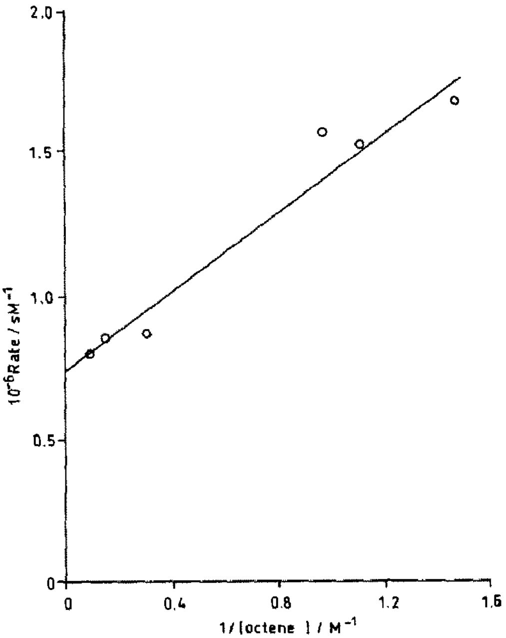


Fig. 4. Variation of the reciprocal of the rate of reaction versus the reciprocal of oct-1-ene concentration.

[3,4] The dependance on oct-1-ene concentration is more complex. A plot of the reciprocal of the rate versus the reciprocal of the alkene concentration is shown in Fig. 4, and this is in accord with a dependance of the type given in eq. 3. Figure 5 shows that there is a reduction in the rate in the presence of CO (1 bar). Thus an

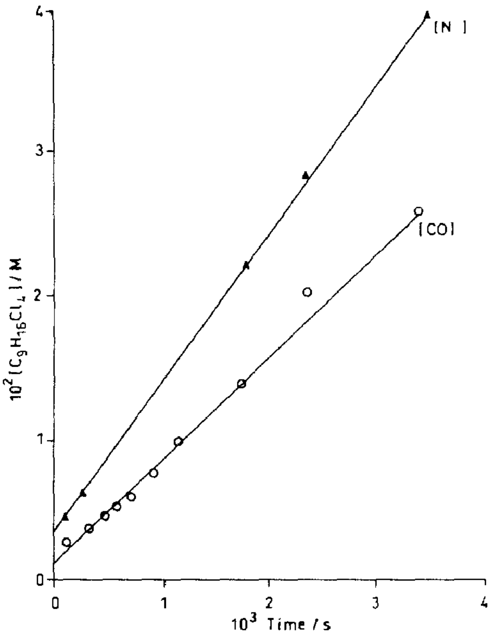


Fig. 5. The effect of added (CO) on the initial rate of reaction.

overall rate equation of the type given in eq. 2 is confirmed.

$$\text{Rate} = \frac{k_{\text{obs}}[\text{RCH=CH}_2]}{1 + [\text{RCH=CH}_2]} \tag{3}$$

This rate law is not consistent with a free radical chain mechanism in which I acts solely as an initiator. Such a mechanism would give rise to the rate expression shown in eq. 4. Neither is it consistent with a mechanism in which cleavage of I to give an active mononuclear catalyst is the rate-determining step, since this would also be expected to be half-order in I. Furthermore, a simple redox process similar to that proposed for CCl_4-alkene addition reactions in the presence of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (Scheme 4) would give rise to an alternative rate equation (eq. 5).

$$\text{Rate} = k_{\text{obs}}[\text{I}]^{1/2}[\text{CX}_4]^{1/2}[\text{RCH=CH}_2] \tag{4}$$

$$\text{Rate} = k_{\text{obs}}[\text{I}][\text{CX}_4] \tag{5}$$

The observed kinetic behaviour parallels that previously reported for catalysis of this reaction by $[RuCl_2(PPh_3)_3]$ [3]. This mechanism (Scheme 1) involves radical pair formation.

In order to investigate whether such radical pairs are produced in the reaction between halogenocarbons and oct-1-ene in the presence of I, a reaction involving an

$$[\text{Fe}_2(\text{CO})_4(\eta\text{-cp})_2] + \text{CX}_4 \rightarrow \text{FeX(CO)}_2(\eta\text{-cp}) + \text{CX}_3^{\cdot} + \text{Fe(CO)}_2(\eta\text{-cp})^{\cdot}$$

$$\text{CX}_3^{\cdot} + \text{RCH=CH}_2 \rightarrow \text{RCHCH}_2\text{CX}_3^{\cdot}$$

$$\text{RCHCH}_2\text{CX}_3 + \text{FeX(CO)}_2(\eta\text{-cp}) \rightarrow \text{RCHXCH}_2\text{CX}_3 + \text{Fe(CO)}_2(\eta\text{-cp})^{\cdot}$$

$$2\text{Fe(CO)}_2(\eta\text{-cp})^{\cdot} \rightarrow \text{Fe}_2(\text{CO})_4(\eta\text{-cp})_2$$

Scheme 4

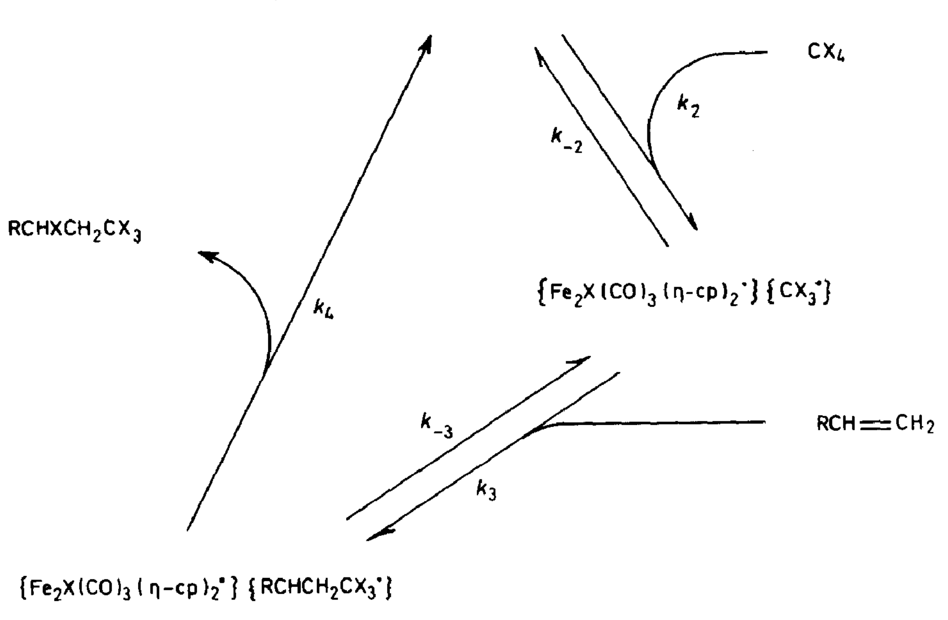
Table 2

The reaction between oct-1-ene and an equimolar mixture of tetrachloromethane and tetrabromomethane

Complex	Temperature (°C)	Product ratios [a]			
		tcn	tcbn	tbcn	tbn
I	60	1	10	3	21
II	60	1	10	6	40
III	60	1	30	12	10
IV	80	1	7	2	3

[a] tcn = 1,1,1,3-tetrachlorononane, tcbn = 1,1,1-trichloro-3-bromononane, tbcn = 1,1,1-tribromo-3-chlorononane, tbn = 1,1,1,3-tetrabromononane.

equimolar mixture of CCl_4 and CBr_4 was carried out, and the results obtained in the presence of both I and II are shown in Table 2. Both the homohalogeno products, $C_6H_{13}CHXCH_2CX_3$ ($X = Cl$ and Br) and the hetero-halogeno-cross-over products, $C_6H_{13}CHXCH_2CY_3$ ($X = Cl$, $Y = Br$ and $X = Br$, $Y = Cl$) were observed. Control experiments showed that heating a mixture of the homohalogeno products in the presence of I did not lead to cross-over. The results of the cross-over and kinetic experiments are in accord with the mechanism shown in Scheme 5, the rate expression for which is given in eq. 6. However, a related mechanism (Scheme 6), involving mononuclear intermediates, gives rise to a rate expression (eq. 7) which is also in accord with the above kinetic and cross-over data. However, it is to be noted



Scheme 5

$$Fe_2(CO)_4(\eta\text{-cp})_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe_2(CO)_3(\eta\text{-cp})_2 + CO$$

$$Fe_2(CO)_3(\eta\text{-cp})_2 + CX_4 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} FeX(CO)_2(\eta\text{-cp}) + \{Fe(CO)(\eta\text{-cp})^{\cdot}\}\{CX_3^{\cdot}\}$$

$$\{Fe(CO)(\eta\text{-cp})^{\cdot}\}\{CX_3^{\cdot}\} + RCH{=}CH_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \{Fe(CO)(\eta\text{-cp})^{\cdot}\}\{RCHCH_2CX_3^{\cdot}\}$$

$$\{Fe(CO)(\eta\text{-cp})^{\cdot}\}\{RCHCH_2CX_3^{\cdot}\} + FeX(CO)_2(\eta\text{-cp}) \overset{k_4}{\rightleftharpoons} Fe_2(CO)_3(\eta\text{-cp})_2 + RCHXCH_2CX_3$$

Scheme 6

that eq. 7 contains the term $[FeCl(CO)_2(\eta\text{-}C_5H_5)]$ in the denominator. Thus, if such

$$\text{Rate} = \frac{k_1k_2k_3k_4[\text{I}][CX_4][RCH{=}CH_2]}{k_{-1}[CO]\{k_{-3} + k_4 + k_3k_4[RCH{=}CH_2]\}} \tag{6}$$

$$\text{Rate} = \frac{k_1k_2k_3[\text{I}][CX_4][RCH{=}CH_2]}{k_{-1}[CO]\{k_{-2}[FeCl(CO)_2(\eta\text{-cp})] + k_3[RCH{=}CH_2]\}} \tag{7}$$

a mechanism did operate the rate should be reduced in the presence of added chloro complex. Figure 6 compares the reaction rate in the presence and absence of added $[FeCl(CO)_2(\eta\text{-}C_5H_5)]$; no inhibition of the reaction was observed, although the concentration of chloro complex was nine times that of I. Surprisingly the rate of reaction increased slightly in the presence of the chloro complex. This may be a consequence conversion of some $[FeCl(CO)_2(\eta\text{-}C_5H_5)]$ into I under the reaction conditions. $[FeCl(CO)_2(\eta\text{-}C_5H_5)]$ showed no activity as a catalyst for the reaction.

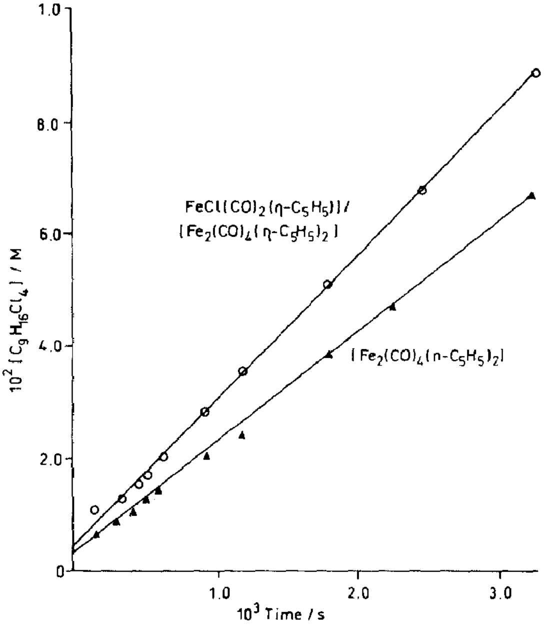


Fig. 6. A comparison of the reaction rate in the presence of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and a mixture of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[FeCl(CO)_2(\eta\text{-}C_5H_5)]$.

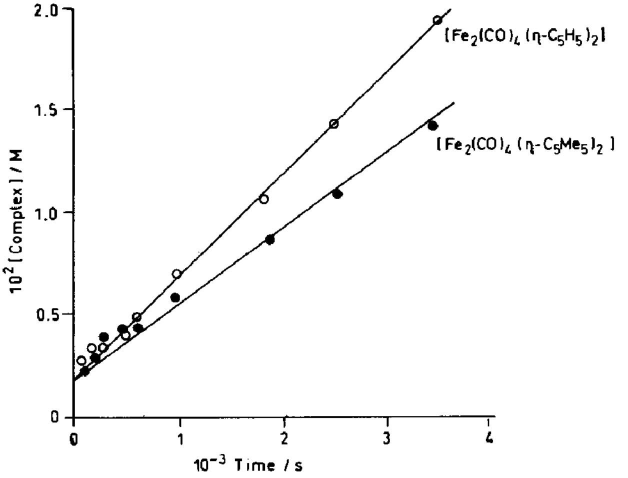
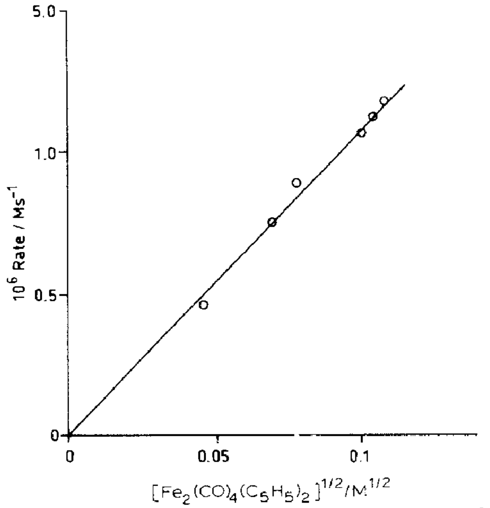


Fig. 7. Comparison plots for the rate of reaction for $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[Fe_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ at 40 °C.

The above findings favour the mechanism shown in Scheme 5, which involves a binuclear intermediate. In order to gain further information on this aspect, a catalyst cross-over experiment was undertaken. Such an approach was previously used by Muetterties et al. [7] in their study of catalysed hydrogenation of alkynes in the presence of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ as a test for catalysis by a dinuclear species. It was argued that provided $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[Mo_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ were of approximately equal efficiency, then catalysis in the presence of a mixture of the two would be informative. Thus, catalysis by intact dinuclear species would not give rise to the cross-over complex, $[Mo_2(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ among the recovered catalysts at the end of the reaction. However, if mononuclear intermediates are formed which recombine at the end of the reaction, then the cross-over complex should be formed. In the event, they observed no cross-over complex and, thus, postulated catalysis by a dinuclear species.

In the present work catalysis by I and II proceeded with comparable efficiencies (Fig. 7) and so the cross-over approach was employed. A reaction between CCl_4 and oct-1-ene in the presence of a mixture of I and II was stopped after 60 min and the volatile reactants and products removed under vacuum. There was no evidence for decomposition of the catalysts and the infrared and mass spectra of the residue indicated the presence of only I, II, and the chloro complexes $[FeCl(CO)_2(\eta\text{-}C_5R_5)]$ (R = H, Me). The cross-over complex $[Fe_2(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ was not observed. Notwithstanding these observations, it was necessary to identify the route by which the chloro complexes were formed, otherwise it might be convincingly argued that catalysis involves only that proportion of I and II which is ultimately converted into the chloro complexes, thereby negating the cross-over experiment.

The formation of $[FeCl(CO)_2(\eta\text{-}C_5H_5)]$ from the reaction of I with CCl_4 in the presence of oct-1-ene was the subject of a kinetic study. Figure 8 shows a plot of the initial rate of formation of $[FeCl(CO)_2(\eta\text{-}C_5H_5)]$ versus $[I]^{1/2}$. Clearly, the chloro complex is formed in a half-order process which is different from that leading to reaction between CCl_4 and oct-1-ene, which is first order in I. On the basis of these findings, the catalyst cross-over experiment appears to be valid and to support the



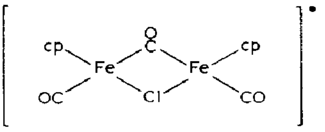


Fig. 8. Initial rate of formation of $Fe(CO)_2Cl(\eta^5\text{-}C_5H_5)$ vs. $[I]^{1/2}$.

Fig. 9. Proposed structure for the $[Fe_2Cl(CO)_3(\eta\text{-}C_5H_5)_2]^{\bullet}$ radical.

catalysis by a dinuclear species. We thus, propose that addition of halogenocarbons to alkenes in the presence of I proceeds by the mechanism outlined in Scheme 5.

We have been unable to obtain direct evidence for the formation of $[Fe_2(CO)_3(\eta\text{-}C_5R_5)_2]$, but this species has been shown by others to be formed upon photolysis of I [8]. Furthermore, photolysis of II allowed isolation of $[Fe_2(CO)_3(\eta\text{-}C_5Me_5)_2]$ [9]. An X-ray crystallographic study of this complex showed it to contain 3 bridging carbonyl groups, and magnetic measurements showed it to be paramagnetic, containing two unpaired electrons. Thus, the tricarbonyl may be viewed as a diradical, and so it is not surprising that it readily enters into free radical reactions.

We have no direct evidence for the structure of the metal-containing unit in the radical pair $\{Fe_2Cl(CO)_3(\eta\text{-cp})_2^{\bullet}\}\{CCl_3^{\bullet}\}$. It may be represented as containing a bridging chlorine atom (Fig. 9), making it a 35 electron system. This structure bears a clear relationship to those of the stable 33 electron systems $\{Fe_2(CO)_7(\mu\text{-}PR_2)^{\bullet}\}$ [10] and $[Co_2(CO)_6(\mu\text{-}P\{CH(SiMe_3)_2\}_2)^{\bullet}]$ [11], and the 35 electron systems $[Fe_2(CO)_6L_2(\mu\text{-}PPh_2)^{\bullet}]$ ($L = PMe_3$, PEt_3, $P(OMe)_3$) [10].

Complexes such as $[\{Fe(CO)_2(\eta\text{-}C_5H_4)\}_2CH_2]$ (III), containing a linked cyclopentadienyl ligand, have been shown to maintain their dinuclear integrity in range of reactions [12]. In view of the above findings, this complex was examined as a catalyst for the reaction of CCl_4 with oct-1-ene. The results given in Table 1 show it to be comparable in activity to I and II. Furthermore, reaction of a mixture of CCl_4 and CBr_4 with oct-1-ene in the presence of III gives both homo- and hetero-halogeno products (Table 2). These preliminary findings suggest a mechanism for catalysis by III which is analogous to that given in Scheme 5.

A preliminary study of reaction 1 in the presence of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$, (IV) showed this complex to be a much less efficient catalyst than the iron analogues (Table 1). The low activity precluded a kinetic study, but the reaction is certainly free radical in nature, as evidenced by the results of a CCl_4-CBr_4 cross-over experiment (Table 2).

Experimental

Complex I was supplied by the Aldrich Chemical Co. Ltd., and II by Strem Chemicals Inc. [$FeCl(CO)_2(\eta$-cp)] [13], III [12] and IV [14] were prepared by published methods. All reactions and kinetic experiments were carried out under dry nitrogen. All solvents and reagents were purified by standard techniques and all solvents thoroughly degassed by three freeze-pump-thaw cycles immediately prior to use. Transfer of solvents and solutions between vessels and all other manipulations were carried out with rigorous exclusion of air.

Infrared spectra were recorded on a Perkin Elmer 782 spectrometer and mass spectra were recorded on an AE1 MS9 spectrometer. GC analyses were performed on a Pye 204 gas chromatograph fitted with a 2 m, $\frac{1}{4}$ inch column packed with 5% OV17 on Chromosorb (80/100 mesh), with a column temperature of 180 °C, an injector temperature of 200 °C, and a detector temperature of 250 °C.

Typical reaction conditions for the addition of halogenocarbons to alkenes

Oct-1-ene (2.1 g, 0.02 mol), the halogenocarbon (0.05 mol), and the catalyst (2.3×10^{-4} mol) were placed in a glass tube with a restriction at the neck to facilitate sealing. The mixture was degassed three times by the freeze-pump-thaw method and the tube was sealed under vacuum, then kept in an oven at the chosen temperature for 18 h. The products were analysed by GC.

Kinetic studies

The procedures were as described previously [2].

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