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The addition of halogenocarbons to alkenes in the presence of $[Mo_2(CO)_4(\eta\text{-}C_5R_5)_2]$ (R = H, Me), $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and $[\{Mo(CO)_3(\eta\text{-}C_5H_4)\}_2CH_2]$

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Abstract

The addition of halogenocarbons to alkenes in the presence of $[Mo_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ (I) has been the subject of a detailed kinetic study. These results, together with the results of cross-over addition reactions of a halogenocarbon mixture and cross-over studies on catalyst mixtures of (I) and $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (IV) are interpreted in favour of a mechanism involving catalysis by an intact binuclear complex, but which also involves free radical intermediates. Studies on catalysis by $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (II) additional to those we reported earlier, suggest an analogous mechanism in this case, but also involving CO dissociation from the hexacarbonyl yielding IV as the active catalyst. A preliminary study of catalysis by $[\{Mo(CO)_3(\eta\text{-}C_5H_4)\}_2CH_2]$ (III) suggests this complex also follows a similar mechanism.

Introduction

We have previously described mechanistic studies of the addition of halogenocarbons to alkenes (Eq. 1) in the presence of $[RuCl_2(PPh_3)_3]$ [1],

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

$[Cr(CO)_3(\eta^6\text{-}C_{10}H_8)]$ [2], and $[Fe_2(CO)_4(\eta\text{-}C_5R_5)_2]$ (R = H, Me) [3]. In all cases the reactions are catalysed by a metal-containing species, but involve free radical intermediates. The reaction mechanism, common to all three systems, is shown in

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$$M + CCl_4 \longrightarrow \{MCl^{\cdot}\}\{CCl_3^{\cdot}\}$$

$$\{MCl^{\cdot}\}\{CCl_3^{\cdot}\} + RCH{=}CH_2 \longrightarrow \{MCl^{\cdot}\}\{RCHCH_2CCl_3^{\cdot}\}$$

$$\{MCl^{\cdot}\}\{RCHCH_2CCl_3^{\cdot}\} \longrightarrow RCHClCH_2CCl_3 + M$$

Scheme 1

$$Mo_2(CO)_6(\eta\text{-}C_5H_5)_2 + CCl_4 \longrightarrow MoCl(CO)_3(\eta\text{-}C_5H_5) + Mo(CO)_3(\eta\text{-}C_5H_5)^{\cdot} + CCl_3^{\cdot}$$

$$CCl_3^{\cdot} + RCH{=}CH_2 \longrightarrow RCHCH_2CCl_3^{\cdot}$$

$$RCHCH_2CCl_3^{\cdot} + MoCl(CO)_3(\eta\text{-}C_5H_5) \longrightarrow RCHClCH_2CCl_3 + Mo(CO)_3(\eta\text{-}C_5H_5)^{\cdot}$$

$$2Mo(CO)_3(C_5H_5)^{\cdot} \longrightarrow Mo_2(CO)_6(\eta\text{-}C_5H_5)_2$$

Scheme 2

Scheme 1 in which the active catalyst is represented as [M]. Catalysis by $[Fe_2(CO)_4(\eta\text{-}C_5R_5)_2]$ is of particular interest since it has been shown that the active catalyst is a binuclear species, probably $[Fe_2(CO)_3(\eta\text{-}C_5R_5)_2]$ [3]. Our studies on halogenocarbon-alkene reactions in the presence of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ [4] suggested a different mechanism (Scheme 2).

We now present studies on catalysis of the reaction between CCl_4 and oct-1-ene in the presence of $[Mo_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ (I). We also include further results concerning catalysis by $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (II) and an examination of catalysis by $[\{Mo(CO)_3(\eta\text{-}C_5H_4)\}_2CH_2]$ (III).

Results and discussion

The yields of tetrachlorononane obtained from CCl_4 and octe-1-ene in presence of I, II and III are given in Table 1, which also contains comparative data for $[Fe_2(CO)_4(\eta\text{-}C_5R_5)_2]$ (R = H, Me) taken from our earlier paper [3]. Complex I

Table 1

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

Complex	Temp (°C)	Yield of tcn (%) [b]
$[Mo_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ (I)	60	25.0
	120	88.0
$[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (II)	60	8.0
	120	56.0
$[\{Mo(CO)_3(\eta\text{-}C_5H_4)\}_2CH_2]$ (III)	60	9.0
	120	84.0
$Fe_2(CO)_4(\eta\text{-}C_5H_5)_2$	60	22.0
	120	84.0
$Fe_2(CO)_4(\eta\text{-}C_5Me_5)_2$	60	16.0
	120	72.0

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

showed moderate catalytic efficiency at 60 °C, comparable with the iron analogues, whereas II and III had low efficiency at this temperature. All three molybdenum complexes showed much improved efficiency at 120 °C, again comparable with the iron analogues. However, it is likely that free radical chain processes play a dominant role at this temperature with initiation arising from decomposition products of the metal complexes [4].

A kinetic study of the CCl_4–oct-1-ene reaction in the presence of I was carried out at 60 °C using the initial rate method. The linearity of the plots of rate versus concentration for both I and CCl_4 indicate a first order dependance on both (correlation coefficients, 0.97 and 0.98 respectively). Unlike our earlier studies of this reaction [1,2,3] the plot for I shows only a very small positive intercept, suggesting a minimal contribution from a non-catalysed reaction. However, we were unable to take advantage of this behaviour to obtain meaningful activation parameters because of the limited temperature range available for the study of the reaction. Thus, at temperature below 60 °C, the reaction rate was lowered to such an extent that the initial rate data became unreliable. Furthermore, it was not possible to accurately control the temperature of the apparatus used for these kinetic studies [1] above 70 °C. The dependence on oct-1-ene concentration is represented in the form of a plot of 1/rate versus 1/[oct-1-ene] in Fig. 1 indicating behaviour of the Michelis–Menten type. Thus the rate law for the reaction in the presence of I is of the form shown in Eq. 2. Our previous study of catalysis by $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ [3] showed the reaction rate to be retarded in the presence of CO. A similar experiment could not be performed in the case of I, since it is known that reaction between I and CO produces $[Mo_2(CO)_6(\eta\text{-}C_5Me_5)_2]$.

$$\text{Rate} = \frac{k_{obs}[\text{I}][CCl_4][\text{octene}]}{1 + [\text{octene}]} \qquad (2)$$

The rate law is similar to those obtained previously for $[RuCl_2(PPh_3)_3]$ [1], $Cr(CO)_3(\eta^6\text{-}C_{10}H_8]$ [2] and $[Fe_2(CO)_4(\eta\text{-}C_5R_5)_2]$ [3] but different to that for

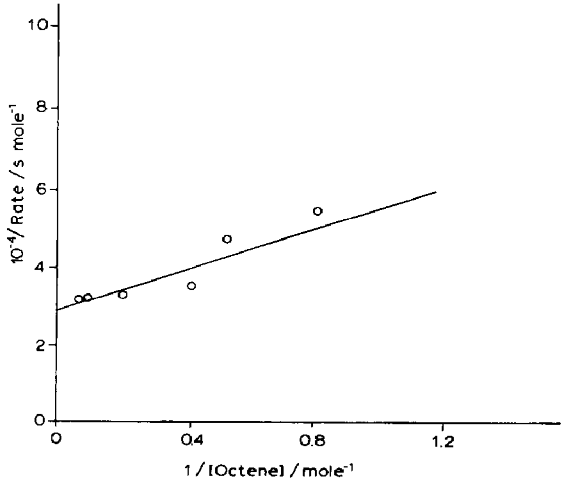


Fig. 1. Variation of the reciprocal of the rate of reaction versus the reciprocal of the oct-1-ene concentration.

Table 2

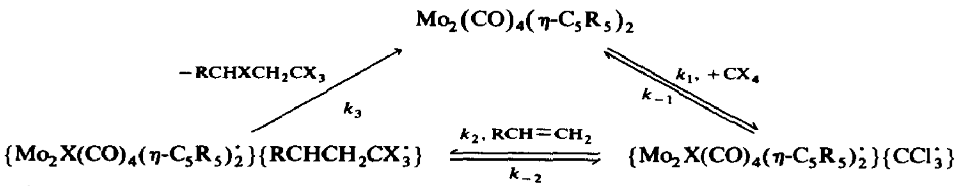
The reaction between oct-1-ene and an equimolar mixture of tetrachloromethane and tetrabromomethane [a]

Complex	Product ratios [b]			
	tcn	tcbn	tbcn	tbn
I	1	75	10	5
II	1	9	3	4
III	1	50	14	9

[a] All reactions performed at 60 °C. [b] 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.

$[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ [4] (vide infra). This is consistent with a reaction mechanism of the type outlined in Scheme 1. Further confirmation of this mechanism was obtained from a study of the cross-over reaction between a CCl_4–CBr_4 mixture and oct-1-ene in the presence of I, the results of which are shown in Table 2. The production of both homo-halogeno-products, $C_6H_{13}CHXCH_2CX_3$ (X = Cl and Br) and hetero-halogeno-cross-over products, $C_6H_{13}CHXCH_2CY_3$ (X = Cl, Y = Br; X = Br, Y = Cl) was observed. Control reactions showed that heating a mixture of the homohalogeno-products in the presence of I did not lead to cross-over. Thus the presence of radical pairs is indicated by the cross-over and kinetic data. However, the extensive nature of cross-over in the presence of I (hetero : homo products = 85 : 6) compared to the corresponding data for $[Fe_2(CO)_4(\eta\text{-}C_5R_5)_2]$ (hetero : homo products = 13 : 22 (R = H) and 16 : 41 (R = Me) suggests relatively weakly bound radical pairs in this case.

By analogy with our previous studies of catalysis by $[Fe_2(CO)_4(\eta\text{-}C_5R_5)_2]$ [3], the above data is consistent with the mechanism shown in Scheme 3, the rate expression for which is given in Eq. 3. This mechanism, which involves binuclear intermediates, was confirmed by means of a catalyst cross-over experiment, analogous to those previously reported by Slater and Muetterties [5] and by us [3]. In this experiment, the addition of CCl_4 to oct-1-ene was carried out in the presence of a mixture of I and $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (IV). Separate experiments showed that these two complexes catalyse the reaction with very similar rates (ratio of initial rates for I : IV is 1.27) and thus the cross-over approach is valid. Following catalysis by the mixture of I and IV, there was no evidence for catalyst decomposition or conversion to other carbonyl-containing products. Infrared and mass spectroscopic studies of the recovered catalyst mixture indicated the presence of I and IV only,



Scheme 3

with no evidence for formation of the cross-over product, $[Mo_2(CO)_4(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)]$.

$$\text{Rate} = \frac{k_1k_2k_3[\mathrm{I}][\mathrm{CCl_4}]\{\mathrm{RCH{=}CH_2}]}{k_{-1}k_{-2} + k_{-1}k_3[\mathrm{RCH{=}CH_2}]} \tag{3}$$

It therefore appears that catalysis of halogenocarbon-alkene addition reactions by $[Mo_2(CO)_4(\eta\text{-}C_5R_5)_2]$ proceeds by a mechanism analogous to that previously reported for $[Fe_2(CO)_4(\eta\text{-}C_5R_5)_2]$ [3]. In the case of the molybdenum, complexes, we have been unable to investigate the possibility of a CO dissociation step for the reason stated above. However, the presence of a multiple metal–metal bond in these complexes means that such a process is not strictly necessary, since halogen abstraction can occur with concomitant lowering of the metal–metal bond order. For the electronically-saturated metal centres of the diiron complexes, ligand dissociation is probably a necessary prerequisite to halogen abstraction.

Thus, on the basis of these and our previous studies, it appears that the catalysts $[RuCl_2(PPh_3)_3]$, $[Cr(CO)_3(\eta\text{-}C_{10}H_8)]$, $[Fe_2(CO)_4(\eta\text{-}C_5R_5)_2]$ and $[Mo_2(CO)_4(\eta\text{-}C_5R_5)_2]$ all operate by essentially similar mechanisms. These observations lead us to re-examine catalysis by $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (II), for which we had proposed the mechanism shown in Scheme 2 in our first mechanistic study of this reaction [4]. The rate law for this mechanism is given in Eq. 4. In our previous studies we had observed such a rate law to be followed. However, in view of the fact that the four catalysts above had all shown Michelis–Menten type behaviour for the dependence of the reaction rate upon the alkene concentration (see, for example, Fig. 1), it occurred to us that in our earlier study, we may have been performing our kinetic

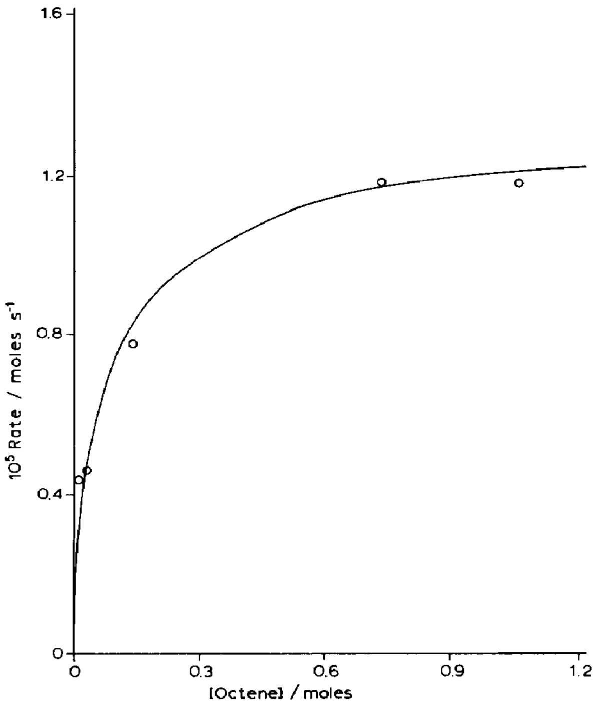


Fig. 2. The dependence of the rate of reaction upon the oct-1-ene concentration in the presence of II.

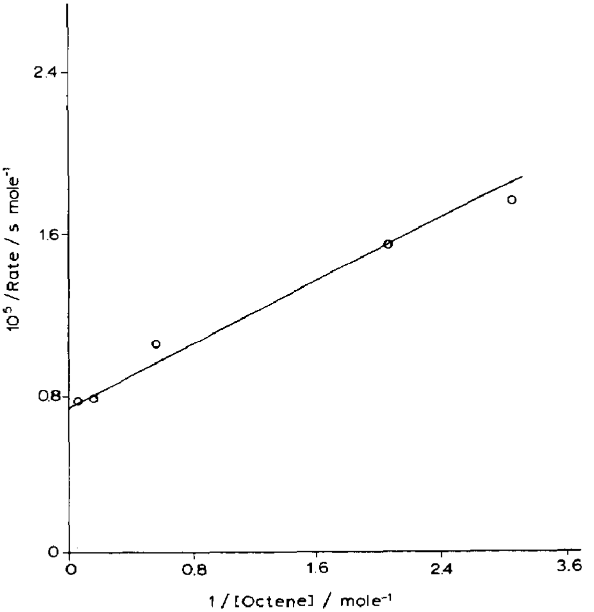


Fig. 3. Variation of the reciprocal of the rate of reaction versus the reciprocal of the oct-1-ene concentration.

measurements of the dependence on alkene at concentrations corresponding to the flat portion of such a curve.

$$\text{Rate} = k_{\text{obs}}[\text{II}][\text{CCl}_4] \tag{4}$$

A re-examination of the dependence of the rate on alkene concentration is shown in Fig. 2 and the related plot of 1/rate versus 1/[alkene] concentration is given in Fig. 3. Clearly, catalysis by II follows a rate law of the type shown in Eq. 2 and not that previously reported. We have also carried out a CCl_4/CBr_4–oct-1-ene cross-over reaction in the presence of II, the results of which (Table 2) confirm the presence of free radical intermediates. Furthermore, we have found that the rate of reaction is considerably retarded under an atmosphere of CO (rate under N_2: rate under CO = 4.85), indicating CO dissociation is occurring in the case of this catalyst. Although we did not carry out a catalyst cross-over experiment for this system, it seemed to us that a binuclear mechanism paralleling that for $[Fe_2(CO)_4(\eta\text{-}C_5R_5)_2]$ may be operating. In that case, the two likely intermediates formed by CO dissociation would seem to be $[Mo_2(CO)_5(\eta\text{-}C_5H_5)_2]$ and $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$. To investigate this, the reaction in the presence of II was followed with time and the results were compared with a second reaction involving $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (IV) run under identical conditions. The rate curves are shown in Fig. 4 which indicates that the same rate is eventually achieved for both reactions, although that in the presence of I is initially slower. We interpret this in terms of CO dissociation from I, yielding IV as the active catalyst. (Scheme 4; rate equation, equation 5).

$$\text{Rate} = \frac{K_1k_2k_3k_4[\text{II}][\text{CCl}_4][\text{RCH=CH}_2]}{k_{-2}[\text{CO}]\left[k_{-3} + k_4 + k_3k_4[\text{RCH=CH}_2]\right]} \tag{5}$$

We have also made a preliminary study of catalysis of the CCl_4–oct-1-ene reaction by $[\{Mo(CO)_3(\eta\text{-}C_5H_4)\}_2CH_2]$ (III), which contains a linked cyclopentadienyl

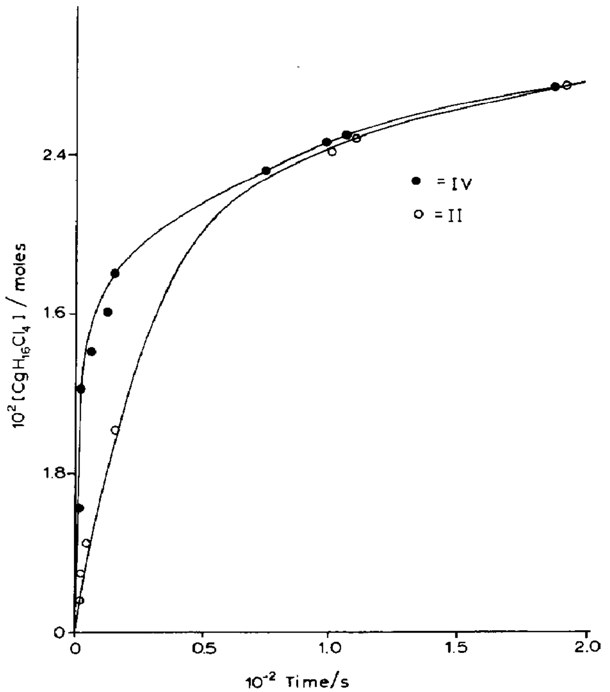


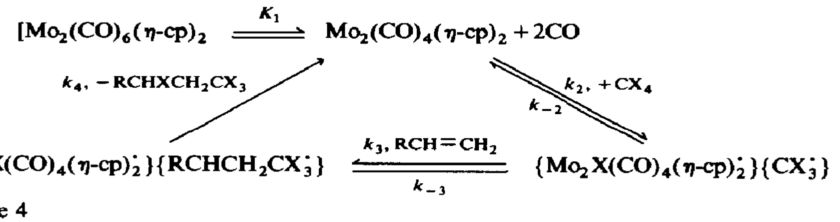
Fig. 4. Comparison of the rates of formation of 1,1,1,3-tetrachlorononane in the presence of II and IV.

ligand. Such complexes have been shown to maintain their dinuclear integrity in a range of reactions [6]. This complex shows a catalytic activity comparable to that of II (Table 1). A partial kinetic study has shown the reaction rate to have a first order dependence on III (correlation coefficient, 0.98). The results of a CCl_4/CBr_4-oct-1-ene cross-over experiment are given in Table 2.

On the basis of the above observations, catalysis by III appears to parallel that by II. However, it seems unlikely that the active catalyst in this case is $[\{Mo(CO)_2(\eta\text{-}C_5H_4)\}_2CH_2]$, since the structure of the bridging ligand would prevent tilting of CO ligands towards the other metal atom as is observed in $[Mo_2(CO)_4(\eta\text{-}C_5R_5)_2]$. Indeed, attempts to prepare $[\{Mo(CO)_2(\eta\text{-}C_5H_4)\}_2CH_2]$ have been unsuccessful [7].

Experimental

I [8]; II [9], III [10] and IV [11] were prepared by literature methods. All reactions and kinetic experiments were carried out under an atmosphere of dry nitrogen. All



Scheme 4

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 the rigorous exclusion of air.

Infrared spectra were recorded on a Perkin–Elmer 782 spectrometer and mass spectra on an AEI MS9 spectrometer. GC analyses were performed on a Pye 204 gas chromatograph using 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. Reaction conditions for the addition of halogenocarbons to alkenes have been described previously [3], as has the method employed for the kinetic studies [4].

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