

Preliminary communication

THE MECHANISM OF THE ADDITION OF TETRACHLOROMETHANE TO ALKENES IN THE PRESENCE OF $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_{10}\text{H}_8)]$

WILLIAM J. BLAND, REG DAVIS* and JIM L.A. DURRANT

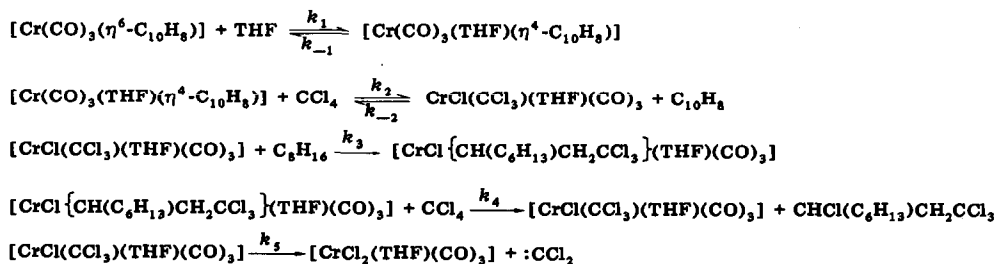
School of Chemical and Physical Sciences, Kingston Polytechnic, Penrhyn Road, Kingston upon Thames, KT1 2EE (Great Britain)

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Summary

The title reaction has been examined in detail and is shown to proceed via a non-chain catalysed mechanism involving free radical intermediates.

As part of our continuing studies of reactions of transition metal complexes that involve free radical intermediates [1], we have examined the addition of halocarbons, such as CCl_4 , across alkenic bonds in the presence of $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_{10}\text{H}_8)]$ (I). This system was first reported by Gandolfi and Cais, who proposed the mechanism shown in Scheme 1 [2]. This mechanism involves oxidative addition of CCl_4 to the metal, followed by alkene insertion. The cycle is then completed by reaction of the metal alkyl with CCl_4 , thereby forming the product by a chain sequence. In view of our findings for similar reactions in the presence of $[\text{Mo}_2(\text{CO})_6(\eta\text{-Cp})_2]$ [1], we wished to examine, in more detail, the role of the chromium complex.



SCHEME 1

Reaction of I with CCl_4 in THF showed the infrared spectral changes previously reported [2] and finally yielded a purple solution containing $[\text{CrCl}_3(\text{THF})_3]$ and $[\text{Cr}(\text{CO})_6]$. C_2Cl_6 was also identified as a product, which suggests that free radicals may play a role in the reaction, although not necessarily in the initial step. I did not show any interaction with alkenes under thermal conditions and previous studies have shown that only under UV irradiation are complexes of the type $[\text{Cr}(\text{CO})_2(\eta^2\text{-alkene})(\eta^6\text{-arene})]$ produced [3].

In order to gain further insight into the nature of these reactions, a kinetic study of the addition of CCl_4 to oct-1-ene in the presence of I was performed by the initial rate method. This yielded a rate law of the type shown in eq. 1.

$$\text{Rate} = \frac{k[\text{I}][\text{THF}][\text{CCl}_4][\text{C}_8\text{H}_{16}]}{k^1 + k^{11}[\text{C}_8\text{H}_{16}]} \quad (1)$$

The rate was markedly decreased by addition of excess naphthalene, but was unaffected when reactions were performed in solutions saturated with CO. It is thus likely that dissociation of arene, but not that of CO, is an important feature of the reaction and although we could obtain no further spectroscopic evidence than that already published [2], the first order dependence of the rate on both [I] and [THF] suggests an initial partial arene displacement by the solvent as suggested by Gandolfi and Cais [2].

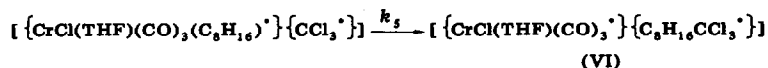
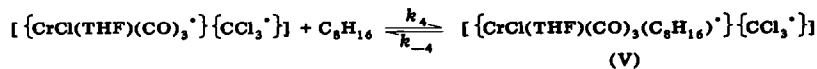
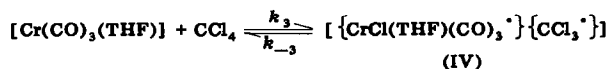
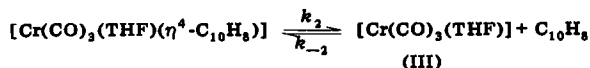
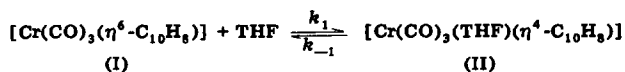
The observed kinetic orders exclude a reaction proceeding by a radical chain route in which a species such as $[\text{Cr}(\text{CO})_3(\text{THF})(\eta^4\text{-C}_{10}\text{H}_8)]$ acts simply as an initiator. Such a reaction exhibits first order dependence on $[\text{C}_8\text{H}_{16}]$ and half order dependences on [I], $[\text{CCl}_4]$ and [THF]. Furthermore, the reaction does not appear to follow a simple redox catalysed mechanism analogous to that in the presence of $[\text{Mo}_2(\text{CO})_6(\eta\text{-Cp})_2]$ [2], as in this case such a sequence yields a rate expression which is independent of alkene concentration.

The exact form of the rate law for the chain mechanism proposed by Gandolfi and Cais depends upon the nature of the reaction of $[\text{CrCl}(\text{CCl}_3)(\text{THF})(\text{CO})_3]$ leading to $[\text{CrCl}_3(\text{THF})_3]$, which is the termination sequence. If one assumes an initial step involving unimolecular decomposition to $[\text{CrCl}_2(\text{THF})(\text{CO})_3]$ and $:\text{CCl}_2$, analogous to that suggested for $[\text{Co}(\text{CCl}_3)(\text{CO})_3]$ [4], followed by reactions with CCl_4 and THF to yield $[\text{CrCl}_3(\text{THF})_3]$ and CO, which are probably fast, the rate expression (eq. 2) is not in agreement with the observed behaviour.

$$\text{Rate} = \frac{k_1 k_2 k_3 [\text{I}][\text{CCl}_4][\text{THF}][\text{C}_8\text{H}_{16}]}{k_{-1} k_{-2} [\text{C}_{10}\text{H}_8] + k_2 k_5 [\text{CCl}_4] + k_{-1} k_5} \quad (2)$$

$$\text{Rate} = \frac{K_1 K_2 k_3 k_4 k_5 [\text{I}][\text{CCl}_4][\text{THF}][\text{C}_8\text{H}_{16}]}{[\text{C}_{10}\text{H}_8] \{k_{-3} k_{-4} + k_{-3} k_{-5} + k_4 k_5 [\text{C}_8\text{H}_{16}]\}} \quad (3)$$

We are only able to assign the observed kinetic behaviour to the sequence shown in Scheme 2. Equation 3 gives the rate equation for this mechanism which involves coordination of THF, followed by dissociation of the arene yielding III as the initial steps. The reaction of III with CCl_4 could involve simple coordination or oxidative addition and both of these modes of interaction between halocarbons (although not CCl_4) and transition metal complexes have recently been reported [5,6]. However, we prefer to write IV as a radical pair and to main-



SCHEME 2

tain such structures for V and VI for the following reasons: (i) Reaction between I and CCl_4 could readily lead to C_2Cl_6 via a radical intermediate. (ii) The metal atom in IV is coordinatively unsaturated in the radical pair form, thereby allowing interaction with the alkene. (iii) A cross-over experiment in which norbornadiene was treated with a mixture of CCl_4 and CBr_4 in the presence of I at room temperature led to the addition of both halocarbons to the diene, as well as to the product arising from addition of the elements of Cl_3CBr (product ratio, $\text{CBr}_4/\text{CBr}_3\text{Cl}/\text{CCl}_4$ addition = 100/5/1). An oxidative addition-migratory insertion-reductive elimination sequence would not be expected to yield the cross-over product, which can, however, be accommodated by the sequence of Scheme 2, probably by competitive abstraction of the halogen atom from the metal or from a further CX_4 molecule by the $[\text{C}_9\text{H}_{16}\text{CCl}_3]^{\cdot}$ radical of VI. As $[\text{Cr}(\text{CO})_6]$ is a final product of the reaction and is known to initiate the addition of halocarbons to alkenes by a free radical route [7], the cross-over experiment was performed under identical conditions in the presence of this complex, however, no reaction was observed at room temperature.

We were unable to identify any free radical intermediates by ESR spectroscopy, but we [1] and others [8] have encountered similar difficulties in closely related reactions of CCl_4 with transition metal complexes.

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