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Preliminary Communication

Nature of the Transient Intermediate Involved in the Reactions between Tricarbonyl(tropylium)tungsten(0) and molybdenum(0) Fluoroborate and Iodide Ion

Paul Powell, Leslie J. Russell and Elizabeth Styles
Dept. of Chemistry, Royal Holloway College, Egham, Surrey TW20 0EX
Alan J. Brown, Oliver W. Howarth and Peter Moore*
Dept. of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

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Summary. - The reactions between iodide ion and $[M(C_7H_7)(CO)_3]BF_4$ (M = Mo, W; $C_7H_7^+$ = tropylium ion) have been investigated kinetically by flow ^1H n.m.r. and by stopped-flow spectrophotometry, and the n.m.r. method shows that two fluxional intermediates are formed in each reaction by transfer of the iodide ion to the tropylium ring, from an initial rapidly formed intermediate probably involving a metal-iodide bond.

A brown intermediate is reported to form during the course of reaction (1) (M = Mo, W; $C_7H_7^+$ = tropylium ion):[1]

$$[M(C_7H_7)(CO)_3]^+ + I^- \longrightarrow [M(C_7H_7)(CO)_2I] + CO \qquad (1)$$

The structure of the intermediate has not been established previously and could arise from attack of iodide ion at the tropylium ion, at the metal or even at one of the carbonyl groups. Previous studies have shown that nucleophiles such as HS^-, MeO^- and H^- react at the tropylium ion,[2] and phosphines and phosphites are also known to be involved in attack at aromatic rings.[3] In other cases nucleophilic attack at the carbonyl groups has been established, as in the reactions with amines or hydrazines,[4] and in the reactions of dienyl(tricarbonyl)iron(0) where there is infra-red evidence for the formation of an acyl derivative.[5] Nucleophilic attack at the metal centre is also known to occur during the reaction of $[M(C_7H_7)(CO)_3]^+$ (M = Cr, Mo and W) with acetonitrile, where displacement of the tropylium ion takes place and $[M(MeCN)_3(CO)_3]$ is eventually formed.[6]

In the present study reactions (1) have been studied in acetone solution by stopped-flow spectrophotometry, and by stopped-flow Fourier transform ^1H n.m.r. (SFFTNMR).[7] A mechanism consistent with the observed rate laws is shown in the scheme.

SCHEME

$$[M(C_7H_7)(CO)_3]^+ + I^- \underset{}{\overset{K}{\rightleftharpoons}} [IM(C_7H_7)(CO)_3]\ (\underline{I}^1),\ \text{rapid} \qquad (2)$$

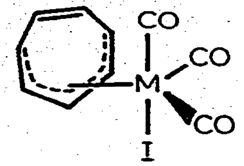
$$\underline{I}^1 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [M(C_7H_7I)(CO)_3]\ (\underline{I}^2) \qquad (3)$$

$$\text{acetone} + \underline{I}^2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [M(C_7H_7I)(CO)_2\,(\text{acetone})] + CO \qquad (4)$$

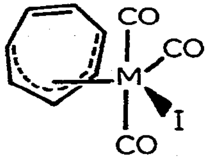
$$[M(C_7H_7I)(CO)_2(\text{acetone})] \xrightarrow{k_3} [M(C_7H_7)(CO)_2I] + \text{acetone} \qquad (5)$$

When M = W, the spectrophotometric results show that formation of the brown intermediate $\underline{I}^2$ follows the rate law: $d[\underline{I}^2]/dt = \{\underline{a}/(1 + K[I^-])\}[I^-][W(C_7H_7)(CO)_3^+]$. At 297.2 K, $\underline{a} = k_1K = 771 \pm 45$ dm^3 mol^{-1} s^{-1}, $K = 61 \pm 7$ dm^3 mol^{-1} and hence the limiting value of k_1 at high $[I^-]$ is 12.7 ± 0.8 s^{-1}. Formation of $\underline{I}^2$ was also followed between 219 and 258 K by SFFTNMR under the limiting condition of high $[I^-]$, and the activation parameters associated with k_1 are $\Delta H^\ddagger$/kJ mol^{-1} = 89.4 ± 8.2 and 60.3 ± 2.4, $\Delta S^\ddagger$/J K^{-1} mol^{-1} = 75 ± 32 and -23 ± 10 for M = W and Mo respectively.

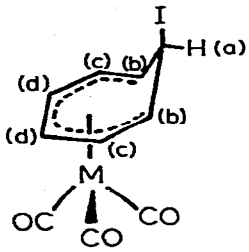
Intermediate $\underline{I}^1$ which forms rapidly upon mixing the complexes with excess iodide ion could either be an ion-pair, or more likely a complex in which the iodide ion is co-ordinated at the metal centre. We favour either structure $\underline{A}$ or structure $\underline{B}$ for intermediate $\underline{I}^1$, $\underline{A}$ being more likely since conversion to $\underline{I}^2$ (structures $\underline{C}$ or $\underline{D}$) is facilitated by the *cis*-geometry. There are two pieces of evidence in favour of initial attack at the metal centre rather than ion-pair formation. Firstly, the significantly different enthalpies of activation associated with k_1 fits with the greater strength of W-I compared with Mo-I bonds, and we would not expect such a difference if $\underline{I}^1$ was an ion-pair. Secondly, we observe in our SFFTNMR experiments with the less reactive tungsten complex at 237 K, that upon first mixing with excess I^- (and before any of the brown intermediate $\underline{I}^2$ has formed) there is a significant broadening (but negligible shift) of the singlet C_7H_7 resonance at $\delta = 6.56$ p.p.m. from $\Delta\nu_{\frac{1}{2}} = 1.36$ Hz in the starting material to $\Delta\nu_{\frac{1}{2}} = 2.85$ Hz for $\underline{I}^1$. Furthermore, as the resonance at $\delta = 6.56$ p.p.m. decays, it is replaced by two new C_7H_7 resonances from $\underline{I}^2$ at $\delta = 5.47$ p.p.m.



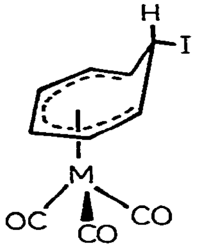
(A)



(B)



(C)



(D)

[*ca.* 93%, probably (C)] and at $\delta = 5.19$ p.p.m. [*ca.* 7%, probably (D)] and the height of the resonance from the major I^2 species ($\delta = 5.47$ p.p.m., $\Delta\nu_{\frac{1}{2}} = 1.86$ Hz at 237 K) when completely formed is nearly twice as large as that observed initially for I^1. This fits with structures A or B for I^1 which would be expected to be fluxional and therefore have a broadened C_7H_7 resonance. It proved impossible to freeze out the broad resonance associated with I^1 owing to the low solubility at greatly reduced temperatures, but the resonance at $\delta = 5.47$ p.p.m. from (C) did collapse upon cooling, as shown in the figure. The spectral assigments shown for (C) are consistent with some closely related structures. The unique hydrogen atom (a) has a resonance at high field as in C_7H_8, $[(C_7H_8)M(CO)_3]$,[8] and the adduct between $[W(C_7H_7)(CO)_3]^+$ and Bu^n_3P,[3] whereas in $[(C_5H_7)Fe(CO)_3]^+$ which has a different structure the unique hydrogen has a resonance at low field.[9] The complex between $[W(C_7H_7)(CO)_3]^+$ and Bu^n_3P is reported to have a structure the same as that postulated for the brown intermediate (C) with I^- replaced by Bu^n_3P, and this is confirmed by the low temperature spectrum of (C) where the chemical shifts are very similar to those observed at room temperature for the stable adduct with Bu^n_3P (figure).

Studies of the rate of loss of the brown intermediate I^2 to give the final product

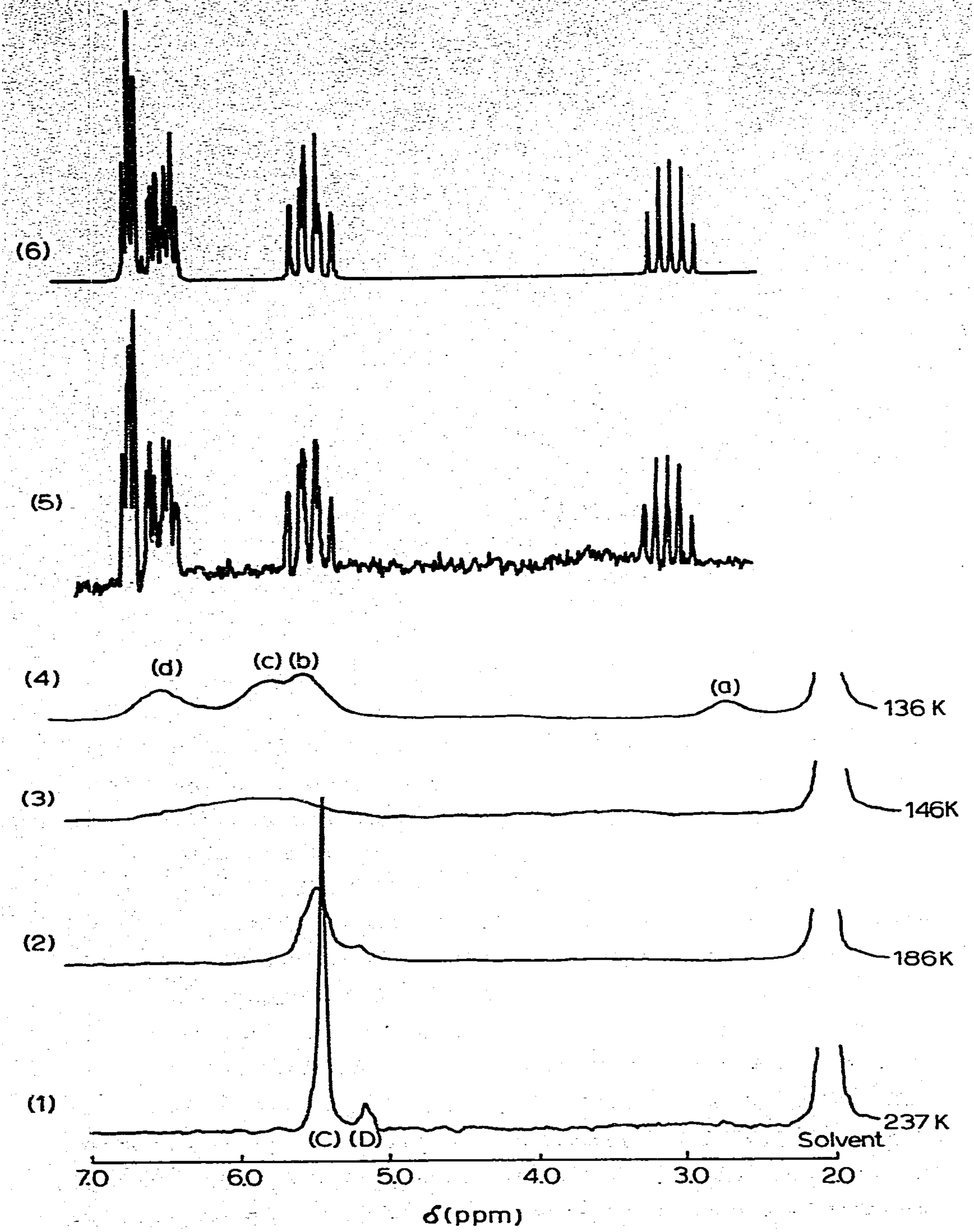


Fig. 1. (1) - (4). Variable temperature ^{1}H n.m.r. spectra of ($\underline{I}^2$). (5). Room temperature ^{1}H n.m.r. spectrum of the Bu^n_3P adduct of $[(C_7H_7)W(CO)_3]^+$ [simulation is (6)].

indicate an initial rapid reaction followed by a slower step. The rate constants observed for the slow step vary approximately inversely with the initial complex concentration, varying from $1.9 \times 10^{-2}\ s^{-1}$ when [complex] = 5×10^{-4} mol dm^{-3}, to $4.6 \times 10^{-3}\ s^{-1}$ when [complex] = 5×10^{-3} mol dm^{-3}. Furthermore, if solutions are pre-saturated with CO before the addition of iodide ion, the brown intermediate can be stabilised for quite a long period of time. This behaviour is consistent with reactions (4) - (5): application of the steady-state approximation to the postulated solvento-complex gives $k(\text{observed}) = k'_2k_3/(k_{-2}[CO] + k_3)$; ($k'_2 = k_2$[acetone]). Initially when $[CO] \simeq 0$, $k(\text{observed}) = k'_2$, but as [CO] increases in solution the rate decreases until finally $k(\text{observed}) \simeq k'_2k_3/k_{-2}[CO]$. Since [CO] is directly related to [complex], the final rate is inversely dependent on [complex] as observed. Reactions (4) - (5) are also consistent with the observation that the final product is not in a reversible equilibrium with $\underline{I}^2$, since there is no brown intermediate reformed when the final product is reacted with excess CO.

The possibility that the minor intermediate species observed in these reactions (tentatively assigned the *endo*-structure, $\underline{D}$) is, in fact, the solvento-complex postulated in reactions (4) - (5) is unlikely since the concentration of $\underline{D}$ is not significantly reduced when the reaction (M = W) is carried out in the presence of an excess of CO. On the basis of the reversible reaction (4), the concentration of the minor species would be expected to be reduced to zero under these conditions.

The mechanism postulated here for the formation of the intermediate ($\underline{I}^2$) is very similar to that reported recently for the reactions between $[(C_7H_9)Fe(CO)_3]^+$ and nucleophiles (*e.g.* N_3^-, OEt^-, Bu^n_3P), attack occurring first at the metal centre followed by transfer of the nucleophile to the C_7H_9 ring.[10]

Acknowledgement

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