

An Inverse Kinetic Isotope Effect for the Hydrogenation of Norbornadiene by the $[\text{Ir}(\text{PPh}_3)_2(\text{OCMe}_2)_2\text{H}_2]^+$ Ion and its Dideuterio-analogue

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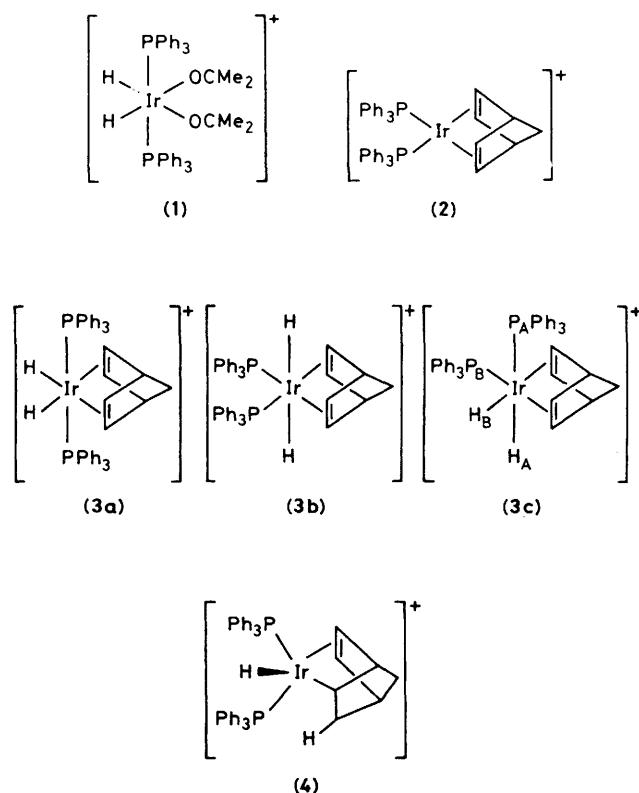
A stopped-flow kinetic study reveals a marked inverse kinetic isotope effect for the hydrogenation of bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, nbd) by the $[\text{Ir}(\text{PPh}_3)_2(\text{OCMe}_2)_2\text{H}_2]^+$ ion (1), and its dideuterio-analogue, and a detailed mechanism is proposed.

The cation (1) is known to be an isomerisation and hydrogenation catalyst¹ and has been shown to activate cycloalkanes.² We have described previously how allyl-hydride species are formed between (1) and conjugated dienes, and demonstrated that the reversible hydrogen transfer between metal and hydrocarbon ligand occurs *via* a C–H . . . Ir^{III} interaction.³ We now report kinetic evidence for the interchange between the iridium(III) diene-hydrides (3a)–(3c) and the alkyl-hydride (4) *via* reversible hydrogen transfer, and a subsequent reaction of (4) with a further diene molecule during the hydrogenation of norbornadiene (nbd). Iridium(III) diene-dihydride isomers, structurally analogous to (3a) and (3c), have previously been characterised during the hydrogenation of cycloocta-1,5-diene (cod).⁴

¹H and ¹³C n.m.r. spectroscopy reveal that the formation of (2), from (1) and excess of nbd (Scheme 1), occurs by both

hydrogenation (k_1, k_2) and H₂ elimination (k_E) pathways, since less monoene[†] is formed than (2). Further, two diene-dihydrides (3a) and (3b) may be detected at 233 K in CD₂Cl₂ [molar ratio (3a):(3b) *ca.* 3:1], whose hydride shifts and couplings (²J_{PH}/Hz) are: (3a) δ –15.9 (t, 16.5) and (3b) δ –7.7 (t, 17.6); ³¹P n.m.r. shifts (3a) δ 4.2 and (3b) δ 13.0 p.p.m. The third isomer (3c) may be obtained by flushing a CD₂Cl₂ solution of (2) with H₂ at 213 K; for (3c) the hydride shift and couplings are H_A δ –10.1 (84.7 *trans*, 21.5 *cis*) and H_B δ –14.2 (22.3, 13.4), ²J_{HH} 5.5 Hz; ³¹P n.m.r. data: P_A δ –5.1 and P_B δ 13.1 p.p.m. (²J_{PP} 17.6 Hz). Unlike its cod analogue,⁴ the (3c) nbd isomer will partially interconvert into (3a) and (3b)

[†] The use of the dideuteride of (1) gave the *endo,endo*-5,6-dideuteriobicyclo[2.2.1]hept-2-ene product exclusively, as determined by ¹H and ¹³C n.m.r. spectroscopy.



Scheme 1

on warming, before H_2 elimination occurs to reform (2). Isomer interchange *via* an alkyl-hydride intermediate (4) is a likely mechanism, although pseudorotation will equally explain these findings.

Solvent lability at (1) and its dideuterio-analogue have been measured⁵ (for both the rate constant is 395 s^{-1} at 298 K), whilst nbd binding to (1) is known to be rapid, especially when compared with cod.⁶ A u.v.-visible stopped-flow kinetic study was used to monitor the formation of (2) in CH_2Cl_2 (+ 2% v/v Me_2CO) at 510 and 605 nm (298 K). Using a fixed concentration of (1) ($5 \times 10^{-4} \text{ mol dm}^{-3}$) with the concentration of nbd varied from 4×10^{-4} to 1.25 mol dm^{-3} , the formation of (2) was found to be first-order over this entire concentration range. The observed rate constants (k_{obs}) for the formation of (2) are larger for the deuteride than for the hydride of (1) over the range studied (Figure 1). This apparent anomaly may be

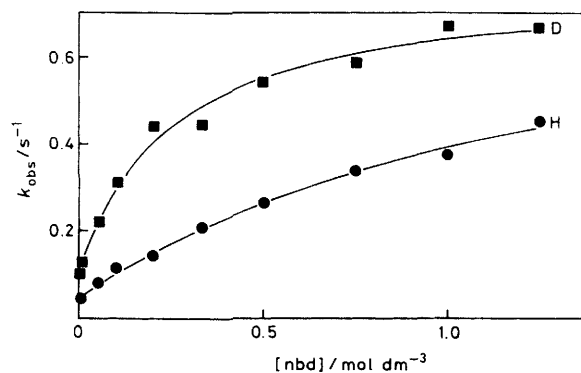
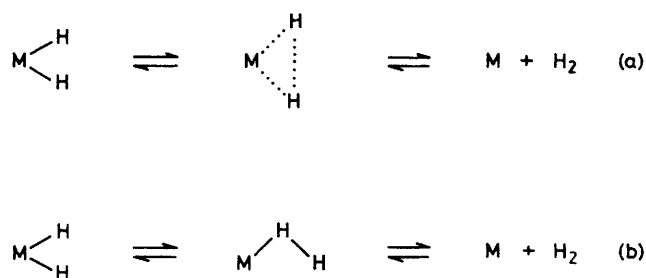


Figure 1. Observed rate constants for the formation of (2) (Scheme 1) starting from (1) (circles) and its dideuterio-analogue (squares). The solid lines are computer calculated curves fitting data to the equation in the text.



Scheme 2

rationalised by proposing the intermediate (4) (Scheme 1) in the hydrogenation pathway. A steady-state treatment gives

$$k_{\text{obs}} = k_E + \frac{k_1 k_2 [\text{nbd}]}{k_{-1} + k_2 [\text{nbd}]}$$

Using non linear least-squares analysis to fit values of k_{obs} to this equation gives ‡

$$\begin{aligned} k_1^{\text{H}} &= (0.889 \pm 0.129) \text{ s}^{-1} \\ (k_{-1}^{\text{H}}/k_2^{\text{H}}) &= (1.54 \pm 0.38) \text{ mol}^{-1} \\ 10^2 k_E^{\text{H}} &= (4.60 \pm 0.74) \text{ s}^{-1} \\ k_1^{\text{D}} &= (0.675 \pm 0.039) \text{ s}^{-1} \\ (k_{-1}^{\text{D}}/k_2^{\text{D}}) &= (0.268 \pm 0.054) \text{ mol}^{-1} \\ 10^2 k_E^{\text{D}} &= (11.4 \pm 1.6) \text{ s}^{-1}. \end{aligned}$$

If one assumes the interception of (4) by nbd is approximately isotope independent (i.e. $k_2^{\text{H}} \approx k_2^{\text{D}}$), then this analysis gives the following isotope ratios.

$$\begin{aligned} (k_1^{\text{H}}/k_1^{\text{D}}) &= 1.32 \pm 0.16 \\ (k_{-1}^{\text{H}}/k_{-1}^{\text{D}}) &= 5.73 \pm 0.32 \\ (k_E^{\text{H}}/k_E^{\text{D}}) &= 0.405 \pm 0.215 \end{aligned}$$

The observed inverse kinetic isotope effect is attributed to the large isotope ratio for the k_{-1} step in the equilibrium

‡ Superscripts H and D refer to hydride and deuteride respectively. At low [nbd], $[\text{nbd}] = [\text{nbd}]_{\text{total}} - [(1)]$.

between (3) and (4). Inverse kinetic isotope effects have been noted in other metal catalysed alkene hydrogenations,⁷ although saturation kinetics were not observed as in the present case. The dependence of the k_2 step on [nbd] indicates that in a catalytic cycle, increasing the concentration of free substrate will assist the rate of hydrogenation of bound substrate. The species X in Scheme 1 may have a number of structures from which the rapid reductive-elimination of the monoene occurs to form (2), and since loss of X is rapid we believe that its structure is of minor importance in the overall reaction scheme.

Although prone to greater error, there would also appear to be an inverse kinetic isotope effect for H₂ loss ($k_E^H/k_E^D = 0.41 \pm 0.22$). This is in direct contrast to a previous report on a related iridium system.⁸ Two possible mechanisms for this reaction are shown in Scheme 2. Should zero-point energy isotope differences be greater for the symmetrical three-centre transition-state compared to the ground-state [Scheme 2(a)], then an inverse isotope effect might be expected. However, the brief existence of an end-on M-H-H intermediate [Scheme 2(b)] with a large kinetic isotope effect for a rapid back reaction (as observed for k_{-1}) could also account for this observation.

Unfortunately, we have no further supporting evidence for either mechanism.

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