Kinetic Hydrogen Isotope Effects in the Catalytic Hydrogenation of Alkenes

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Summary Observed kinetic hydrogen isotope effects in catalytic hydrogenation reactions are functions of the apparent order of the reaction with respect to hydrogen; the range of values to be expected is governed by the equilibrium constant for the exchange reaction involving hydrogen and the deuteriated catalyst.

We have measured the kinetic hydrogen isotope effect for the hydrogenation of cyclohexene catalysed by chlorotris(triphenylphosphine)rhodium(I) (**1**) in benzene as part of a broader study of catalysis by transition metal complexes. We find the effect is small although normal (k_H/k_D, 1·17 ± 0·09 and 1·10 ± 0·09 for the apparent first and zero order rate constants at 30° and 1 atm of hydrogen) rather than inverse, $k_H/k_D = 0{\cdot}9$, as previously reported.[1]† In contrast, for the hydrogenation of 1-hexene catalysed by hydridocarbonyltris(triphenylphosphine)rhodium(I) (**2**), O'Connor and Wilkinson report an appreciable normal kinetic isotope effect, $k_H/k_D = 1{\cdot}47$.[2] We suggest that the observed hydrogen isotope effect is related to the kinetic order with respect to hydrogen or deuterium and this must be considered when the isotope effect in clearly different mechanisms such as those which typify catalysis by (**1**) and (**2**) are compared.[1–3] The development of this argument is as follows.

Suppose hydrogen combines rapidly and reversibly with the catalyst (A) to form a hydrido-species (AH_2) and that the rate determining step is the combination of the latter with the alkene (S).

$$A + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AH_2;\ K_1 = k_1/k_{-1}$$

$$AH_2 + S \xrightarrow{k_2} \text{Product}$$

Scheme 1

The rate law is given by equation 1. The apparent order

$$-d[S]/dt = k_2K_1[S][A][H_2]/(1 + K_1[H_2]) \qquad (1)$$

with respect to hydrogen changes from first at low pressures to zero at high and accordingly the observed rate constant changes from k_2K_1 to k_2. Similarly the kinetic isotope effects range from $(k_2K_1)_H/(k_2K_1)_D$ to $(k_2)_H/(k_2)_D$ and the ratio of these extreme values is $(K_1)_H/(K_1)_D$, the equilibrium constant for exchange reaction (2).

$$H_2 + AD_2 \rightleftharpoons AH_2 + D_2 \qquad (2)$$

Although the above mechanism is an oversimplification of that which applies to the hydrogenation of alkenes catalysed by (**1**),[1,3] it can guide our analysis of the kinetic isotope effect in the real situation. The equilibrium constant for the exchange reaction involving $RhH_2Cl(PPh_3)_3$ (**3**) can be computed from the Bigeleisen and *Mayer* equations[4] using the recorded i.r. absorption frequencies associated with the stretching modes (2066 and 2035 cm^{-1}) and the bending mode (829 cm^{-1}) of the rhodium hydrogen bonds[1,5] (the frequencies involving deuterium are assumed to be smaller by a factor of 0·707) and the vibrational frequencies, for D_2 and H_2, 3118·8 and 4405·3 cm^{-1} respec-

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† At a fixed pressure of hydrogen, the reaction follows accurately a first order rate law (with respect to alkene) at low concentrations of alkene and approximates a zero order rate at high concentrations of alkene. Our results are not strictly comparable to those given by Osborn *et al.*, because of differences in the design of the experiments and the method of analysis of the results (to be reported elsewhere).

tively[6] The value computed is 1 38 Therefore the observed kinetic isotope effect will decrease by this factor as the apparent order of the reaction changes from first to zero When the concentration of cyclohexene is small, and near 1 atm of hydrogen, the apparent order with respect to hydrogen is small, but not zero (*ca* 0 2) in agreement with the reported stability of (**3**) [1,5] Thus the measured kinetic isotope effect corresponds to the change in the bonding to hydrogen on going from hydridocomplex to the transition state of the rate controlling step *e g* $(k_2)_H/(k_2)_D$ Apparently this change is small The isotope effect will be greater if it is measured under conditions in which the reaction is first order in hydrogen

However, if the rate controlling reaction is simply the oxidative addition of hydrogen to a transition metal complex and if the bonding of hydrogen to the metal in the transition state is comparable to that found in the rhodium hydride (**3**) then the kinetic isotope effect should be the same as that computed for the exchange reaction (1 38) For comparison we cite the isotope effect reported for the oxidative addition of hydrogen to *trans*-$IrCl(CO)(PPh_3)_2$ (k_H/k_D = 1 22) which is first order in hydrogen[7] Similarly the rate of hydrogenation of 1-hexene catalysed by (**2**) (k_H/k_D = 1 47) is also first order in hydrogen and in this instance the rate controlling step appears to be the oxidative addition of hydrogen[2] It is curious that the value of these isotope effects is close to the maximum we would predict for the catalysis of alkene hydrogenation by (**1**) in which the transfer of hydrogen to the rhodium atom precedes the rate controlling step [1,3]

The arguments given here should apply equally to heterogeneous catalytic hydrogenations, the hydrogenation of ethylene over cobalt oxide at about room temperature, has a rate law which is first order in hydrogen, zero order in ethylene, and the kinetic isotope effect is k_H/k_D = 1 4[7] Other examples are cited in the same paper

Although the equilibrium constant computed for reaction (2) may be in error, we expect to observe a significant change in the kinetic isotope effect for hydrogenations catalysed by (**1**) as changes in reaction conditions shift the apparent order from zero to one Experiments to obtain the required information are in progress

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