Heterogeneous transfer hydrogenation involves pairwise hydrogen transfer from the same position of two molecules of formic acid

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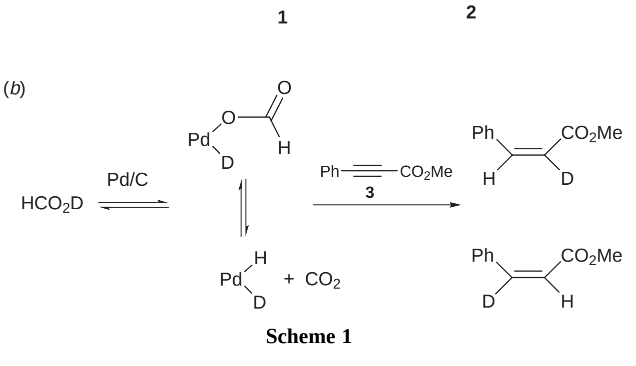
Using the reduction of an alkyne to *cis*-alkene as a hydrogen trap, differentially deuterium labelled formic acid is shown to deliver a pair of hydrogen atoms either from the formyl or the carboxy position, which suggests that palladium diformate is a key intermediate in heterogeneous transfer hydrogenation.

The oxidation of formic acid to carbon dioxide has been widely used as a source of hydrogen for the reduction of organic compounds.[1–3] This reaction has been shown to be one of the most effective methods for transfer hydrogenation that could potentially replace traditional hydrogenation conditions, such as asymmetric reduction where high pressure is often required.[4] The reverse reaction involving conversion of carbon dioxide to formic acid using catalytic hydrogenation has attracted much interest in recent years because it offers an environmentally friendly approach to the use of carbon resources as a raw material for the chemical industry.[5–8] The advantage of using heterogeneous catalysts in industrial processes has prompted us to investigate the mechanism of this reversible reaction catalysed by palladium on carbon.

A major effort has already been directed to the understanding of the mechanism of this reaction in homogeneous systems with the formato-(hydrido) metal complex proposed as a key intermediate **1** [Scheme 1(*a*)], based on deuterium labelling studies and *ab initio* calculations.[9–11] Recent studies using NMR spectroscopy have provided evidence for the existence of this intermediate,[12,13] however, as discussed by Halpern,[14] such thermodynamically stable compounds may not be the active species on hydrogenation pathways.

It has been proposed that the formato-(hydrido) metal complex **1** collapses to give a metal dihydrido species **2** [Scheme 1(*a*)] which can then carry out the reduction.[9] If this mechanism is operating in heterogeneous systems then the two hydrogen atoms from the same formic acid molecule will always be transferred as a pair in one catalytic cycle. Correspondingly, when the catalytic cycle proceeds from carbon dioxide to formic acid, one hydrogen molecule will provide both hydrogen atoms for the reduction of one molecule of carbon dioxide to give the same intermediate **1**.



Scheme 1

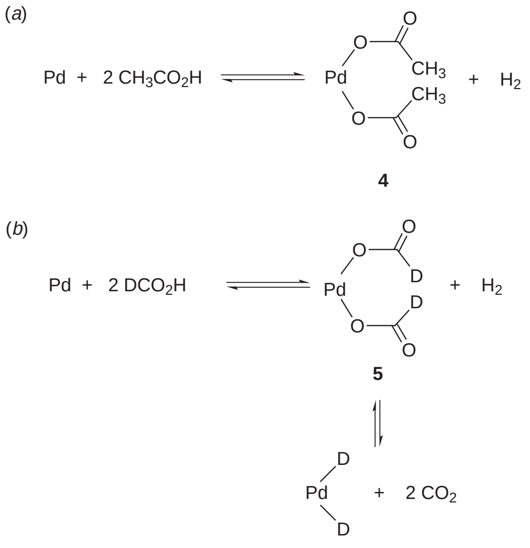
To investigate whether **1** is the active intermediate that provides the hydrogen on the catalytic cycle, the reduction of the triple bond of phenylpropiolate to the *cis*-double bond was employed to trap the hydrogen liberated by the collapse of **1** [Scheme 1(*b*)]. If differentially deuterium labelled formic acid (HCO_2D or DCO_2H) is used then the distribution of deuterium across the *cis*-double bond can determine the origin of the hydrogen transferred to the triple bond. The reduction of a double bond was not used as a reporter molecule for the hydrogen transfer because of the possible additional incorporation of deuterium through isomerization of the double bond before saturation occurs.[15,16]

When the reduction was carried out with HCO_2D the results show that the major product is the *cis*-double bond containing two hydrogen atoms (Table 1), rather than mono-deuterated *cis*-double bond which would be predicted to dominate if both hydrogen atoms came from the same molecule of formic acid as proposed previously for the homogeneous system.[9] It is possible that the major product containing two hydrogen atoms on the double bond could be formed by the preferential donation of hydrogen from the metal surface (H–Pd–D, intermediate **2,** Scheme 1) owing to a favourable kinetic isotope effect. However, when **3** was reduced with an equal mixture of hydrogen and deuterium the results show that there is no

Table 1 Reduction of methyl phenylpropiolate

	Product distribution (%)[a]		
Hydrogen source	H + H	H(D) + D(H)	D + D
HCO_2D[b]	72	10	18
DCO_2H[b]	25	18	57
XCO_2D[c]	28	37	35
$H_2 + D_2$[d]	25	51	24

[a] Errors for the data are ±5%. [b] Labelled formic acids were prepared by treating sodium formate (either DCO_2Na or HCO_2Na) with 1 M HCl or DCl, extracted with Et_2O and dried over anhydrous Na_2SO_4. Distillation of the extracts gave DCO_2H or HCO_2D (99% atom excess as determined by ^1H NMR analysis and mass spectrometry). Pd/C (10%, 38 mg) was added to a mixture of HCO_2D or DCO_2H (235 mg, 5.0 mmol), Et_3N (2.8 g) and phenylpropiolate **3** (80 mg, 0.5 mmol) and vigorously stirred under a blanket of argon. The progress of the reaction was monitored by TLC and stopped at approximately 40% conversion to avoid formation of the fully saturated product. This precaution was taken because the protons α to the carbonyl group of the saturated product can exchange under these conditions and could potentially lead to scrambling of the label. The reaction mixture was filtered to remove the catalyst and evaporated to give residue (81 mg) which was purified by column chromatography (eluted with hexane–Et_2O, 50:1) to afford 25 mg of *cis*-alkene. The distribution of deuterium across the double bond of the *cis*-alkene was determined by ^1H NMR analysis and mass spectrometry. [c] X = a mixture of D and H (2:1). [d] Pd/C (10%, 19 mg) was added to a mixture of Et_3N (2.8 g) and phenylpropiolate **3** (80 mg, 0.5 mmol) and purged with hydrogen and deuterium (1:1). The reaction mixture was stirred at room temperature and stopped at approximately 40% conversion. The isolation and analysis of the *cis*-alkene was carried out as detailed above.

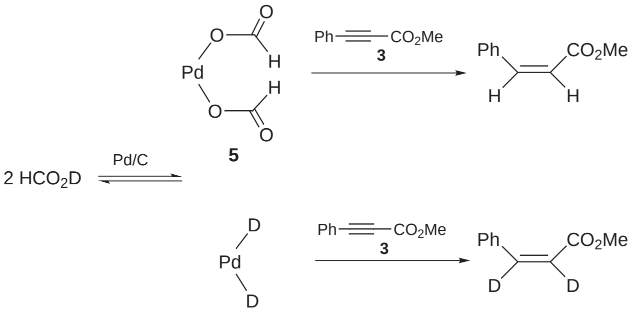


Scheme 2

substantial isotope effect (Table 1), which was also found in an earlier study using a homogeneous catalyst.[17] Furthermore, this mechanism cannot account for the fact that more double deuterated than mono-deuterated *cis*-double bond is formed.

These results would be consistent with a direct pairwise hydrogen transfer from either the formyl or the carboxy position of two different formic acid molecules. It is feasible that two hydro-formato species **1** on the surface of the metal could line up in such a way that the two adjacent formyl groups can donate hydrogen in a pairwise manner. However, palladium is known to react with acetic acid to form palladium diacetate **4** with the liberation of hydrogen from the carboxy position [Scheme 2(*a*)][18] which has prompted us to propose that palladium diformate **5** is formed in a similar manner and is reponsible for pairwise transfer of two formyl hydrogens [Scheme 2(*b*)]. Although palladium diformate has not been isolated, maybe owing to its instability, other metal diformate species have been characterised, such as vanadyl diformate,[19] triarylbismuth diformate[20] and ruthenium diformate.[21] This last example is particularly important because it was identified during the hydrogenation of carbon dioxide using a homogeneous ruthenium catalyst.

The formation of the palladium diformate would give one molecule of hydrogen solely from the carboxy end of the two formic acid molecules that can be used for the reduction of the triple bond (Scheme 3). The palladium diformate can then transfer another pair of hydrogen atoms from the formyl positions to another triple bond. The results with DCO_2H also show that the major *cis*-alkene produced from the alkyne contains two deuterium atoms on the double bond (Table 1). The minor monodeuterated product is probably formed by scrambling of the deuterium label. This could occur either *via* reduction of the carbon dioxide to give formic acid[9] or by collapse of intermediate **5** [Scheme 2(*b*)], if not immediately trapped by the triple bond, to give deuterium which can then mix with the hydrogen from the carboxy end to form HD. The formation of HD from hydrogen and deuterium on the surface of the metal has been shown to readily occur in a control experiment (Table 1).



Scheme 3

The combined results with HCO_2D and DCO_2H strongly suggests that the hydrogen comes directly from the palladium diformate intermediate **5** rather than intermediate **1**, since this latter species would give the same distribution of deuterium on the double bond in both cases. The high level of pairwise addition of hydrogen from HCO_2D or deuterium from DCO_2H demonstrates the greater reactivity of the formyl position. It is noteworthy that there is a higher incorporation of hydrogen from the formyl position of HCO_2D than deuterium from the same position of DCO_2H, suggesting an isotope effect is involved in the cleavage of the carbon–hydrogen bond of the palladium diformate (Table 1).

The theory was further tested by using a mixture of DCO_2D and HCO_2D in a ratio of 2:1 to reduce the triple bond. The results show that there is a large increase in product containing one hydrogen and one deuterium compared to the product obtained using soley HCO_2D (Table 1). The increase in monodeuterated *cis*-alkene can only be accounted for by pairwise transfer from the formyl position rather than from the formato-hydride intermediate **1** which would be predicted to produce less of the monodeuterated product with the addition of DCO_2D.

The results clearly show that heterogeneous transfer hydrogenation involves the transfer of a pair of hydrogen atoms either from the formyl or the carboxy position of two molecules of formic acid. This provides evidence that palladium diformate is a key intermediate in this reaction and suggests that the reduction of carbon dioxide must also proceed through the diformate intermediate.

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Notes and References

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