Metal-assisted reactions.[1] Mechanism in Heterogeneous Catalytic Transfer Reduction

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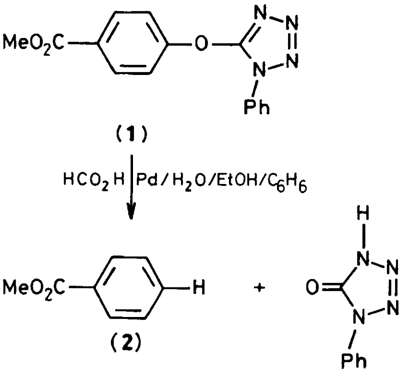
Hydrogen isotope studies have shown that heterogeneous catalytic transfer hydrogenolysis of C–O bonds in phenolic tetrazolyl ethers, under certain conditions, appears to proceed through a direct transfer of hydrogen from the donor to the substrate.

Mechanisms of heterogeneous catalytic hydrogen transfer reduction, in which a suitable hydrogen donor (other than molecular hydrogen) transfers its hydrogen to a substrate, are not nearly so well understood as are the mechanisms of homogeneous transfer reduction. Mechanisms of heterogeneous catalytic reduction using molecular hydrogen have been investigated widely.[2] There is sufficient experimental evidence to suggest that transfer of hydrogen from donor to substrate (both adjacent to each other on the catalyst surface) takes place directly;[3] production of molecular hydrogen is incidental to such a process and may actually prevent the required reduction from proceeding because the substrate cannot get to the catalyst surface. We present here evidence, from hydrogen isotope studies, that direct transfer of hydrogen can take place from a hydrogen-donor to a substrate (acceptor) molecule.

Hydrogenolysis of C–O bonds in phenols has been shown to proceed through heterogeneous catalytic transfer reduction of various phenolic ethers in which the group R, equation (1), needs to be strongly electron-withdrawing and, for convenience, is often 1-phenyltetrazolyl (see references cited in

$$\text{Ar–OR} \xrightarrow[\text{[H]}]{\text{Catalyst}} \text{Ar–H} + \text{HOR} \qquad (1)$$



(2)

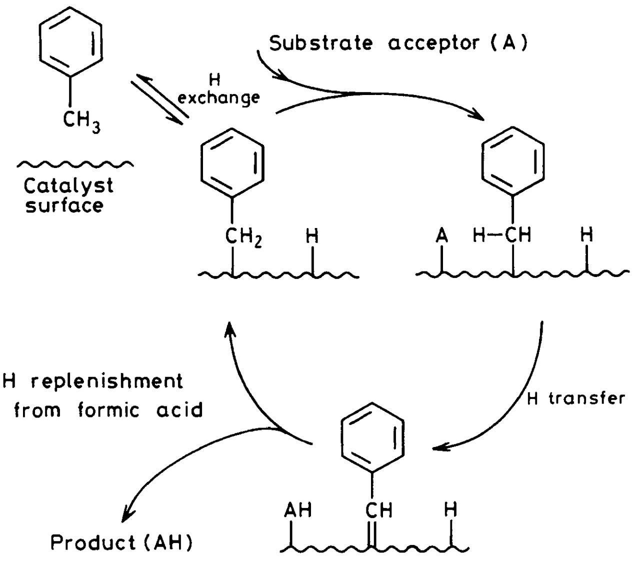
Table 1. Some hydrogen isotope labelling results for the conversion of the aryl ether (**1**) into the arene (**2**).[a]

Entry	Reaction mixture[b]	% Incorporation of hydrogen isotope into (**2**)		Expected random incorporation of hydrogen isotope into (**2**)[c]	
		H	D	H	D
1	$DCO_2D/H_2O/C_2H_5OH/C_6H_6$ (0.095)	81	19	84	16
2	$DCO_2D/D_2O/C_2H_5OD/C_6H_6$ (0.095)	12	88	0	100
3	$HCO_2H/H_2O/C_2H_5OH/C_6D_6$ (0.057)	94	6	100	0
4	$DCO_2D/D_2O/C_2D_5OD/C_7H_8$ (0.076)	86	14	59	41
5	$HCO_2H/H_2O/C_2H_5OH/C_7D_8$ (0.044)	52	48	70	30
6	$HCO_2H/H_2O/C_2H_5OD/C_6H_6$ (0.085)	97	3	84	16
7	$HCO_2H/H_2O/C_2D_5OD/C_6H_6$ (0.085)	97	3	84	16

[a] Regiospecificity of incorporation of deuterium into the *para* position of arene (**2**) was confirmed by ^1H n.m.r. The degree of deuterium incorporation was determined by mass spectrometry of arene (**2**). [b] In each case the following quantities were used: formic acid (0.03 mol), water (0.11 mol), ethanol (0.05 mol), aryl ether (**1**) (300 mg), Pd/C catalyst (10% w/w; 350 mg). The quantity of aromatic solvent (benzene or toluene) is shown in parentheses (mol). [c] Random isotope incorporations were based on two hydrogens per molecule of formic acid, two hydrogens per molecule of water, one hydrogen per molecule of ethanol (see entries 6,.7 for a comparison of C_2H_5OD and C_2D_5OD), no hydrogen per molecule of benzene, and three hydrogens per molecule of toluene. Results of mixture tests with varying quantities of the different components of the reaction system suggest that these assumptions are reasonable.

ref. 1). Under the best conditions found so far, a palladium–charcoal catalyst in a benzene–water–ethanol–formic acid system effects rapid (10 min) formation of arenes from aryl 1-phenyltetrazolyl ethers at modest temperatures (70—80 °C).[1] In experiments designed to investigate the specificity of incorporation of hydrogen into the substrate, hydrogen isotope studies were undertaken on 5-[4-(methoxycarbonyl)phenoxy]-1-phenyltetrazole (**1**), equation (2). In particular, the specific incorporation of hydrogen or deuterium into the 4-position of compound (**2**) was sought because possible mechanisms for the hydrogenolysis could involve the 3-position.[1] These hydrogen incorporation experiments were conclusive. In the presence of deuteriated formic acid, water, ethanol, or benzene, deuterium was incorporated *only* into the 4-position in the reduced product (^1H n.m.r. and mass spectroscopic results), *i.e.*, displacement of the 1-phenyltetrazolyl moiety did not involve directly any position other than that from which the 1-phenyltetrazolyl group was displaced. The experiments also revealed that formic acid was more efficient (on a molar basis) than water, ethanol, or benzene for incorporating hydrogen into the 4-position. Further, incorporation of deuterium from DCO_2D was only slightly greater than the figure expected for random incorporation (Table 1, entry 1). Incorporation of hydrogen into product (**2**) from benzene in the solvent system was small and showed a hydrogen/deuterium isotope effect of about 1.3 (Table 1, entries 2,3).

On using toluene in place of benzene in the solvent system, the situation changed dramatically. Toluene was found to be more efficient than formic acid in transferring hydrogen specifically to the substrate (**1**). Table 1 shows that, on a molar basis, toluene was about three times more efficient than formic acid and about ten times more efficient than benzene for transferring hydrogen during hydrogenolysis. When $C_6H_5CD_3$ was used in place of $C_6D_5CD_3$, there was little change in the level of incorporation, indicating that the ring hydrogens in toluene were involved to only a minor extent; this result is in keeping with the low efficiency of benzene as a source of hydrogen for the reaction, equation (2). Without formic acid in the system, no hydrogenolysis of the substrate (**1**) is observed *viz. toluene alone cannot effect hydrogenolysis* but, in the presence of formic acid, hydrogenolysis does occur with specific incorporation of hydrogen from the methyl group of toluene. Entries 4 and 5 of Table 1 show that, in reversal-experiments (DCO_2D, D_2O, C_2D_5OD, C_7H_8 *vs.* HCO_2H, H_2O, C_2H_5OH, C_7D_8), an isotope effect of about 1.3 is observed. Entry number 4 shows that, with a molar ratio of deuterium to hydrogen of 0.7 to 1, the specific incorporation of hydrogen from toluene into compound (**2**) is 86%; entry number 5 shows that, with a molar ratio of deuterium to hydrogen of 0.43 to 1, the specific incorporation of deuterium from toluene into compound (**2**) is 48%. These results suggest that incorporation of hydrogen from the methyl hydrogens of toluene is quite specific, the actual level of incorporation being considerably greater than the maximum expected for a random process. The comparative incorporations of hydrogen and deuterium indicate an overall isotope effect of about 1.3.



Scheme 1

Because the level of incorporation of hydrogen from the side-chain methyl of toluene is so specific in the presence of formic acid whereas, in the absence of formic acid, no hydrogenolysis occurs, it appears that toluene forms active sites on the catalyst surface. These active sites are able to transfer hydrogen directly to the substrate and the sites are maintained by a supply of hydrogen from the system at large when formic acid is present. A possible outline mechanism is suggested in Scheme 1.

From the isotopic labelling results, incorporation of hydrogen also occurs from the system generally into the acceptor (**1**). Either there must be more than one mechanism of hydrogenolysis under these reaction conditions or the rate of exchange of methyl hydrogens with the system is similar to the rate of hydrogenolysis (Scheme 1).† Under the latter conditions, the large molar excess of toluene over substrate (**1**) ensures that little of the hydrogen from the system (other than toluene) appears in the product (**2**).

It is interesting to note that Scheme 1 is essentially similar to the unified theory put forward to explain hydrogenation of alkenes with molecular hydrogen, in which carbonaceous sites are proposed as the active catalyst centres for transfer of hydrogen rather than direct transfer of hydrogen to the substrate from the catalyst metal itself.[4]

The authors thank the S.E.R.C. for a grant (P. J. P.).

Received, 21st March 1984; Com. 385

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† A referee has suggested that the formic acid may promote the hydrogenolysis of the C–O bond by making it more labile.