The Hydrogenation of Hex-1-yne over Borohydride-reduced Catalysts. Evidence concerning the Mechanism of Reduction

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Summary In the hydrogenation of hex-1-yne over borohydride-reduced catalysts, hexane is formed in two distinct pathways, one not involving a free olefin intermediate.

As part of a systematic study of uses of the new borohydride-reduced catalysts,[1-3] the hydrogenation of terminal acetylenes was examined using hex-1-yne as a model compound. Of catalysts prepared from Group VIIIB metals, only borohydride-reduced platinum, palladium, and nickel catalysts were appreciably active under model preparative conditions.‡ The observed rate of hydrogen uptake was appreciably slower for hex-1-yne than for a comparable olefin, oct-1-ene. This is particularly apparent in the case of rhodium, which is nearly inactive toward the alkyne yet is highly active toward alk-1-enes. This effect is shown in Table 1.

TABLE 1

Catalyst	Initial hydrogen uptake, ml. of H_2 at s.t.p. per min.[a] Hex-1-yne	Oct-1-ene
Pt–BH_3/C[b]	22	90
Pd–BH_4/C[b]	36	90
Rh–BH_4/C[b]	2	72
P-1Ni[c]	40	72
P-2Ni[d]	62	72

[a] Separate hydrogenations of hex-1-yne and oct-1-ene.

[b] The carbon-supported borohydride reduced platinum metal catalysts.[1]

[c] Granular catalyst prepared in water.

[d] Colloidal catalyst prepared in alcohol.

TABLE 2

Catalyst	H_2 added, equiv.[a]	n-Hexane/hex-1-ene¶
Pt–BH_4/C[b]	0·0 (extrap.)	0·21
	0·2	0·22
	0·5	0·24
	1·0	0·33
Pd–BH_4/C[b]	0·5—1·0	0·03
P-1Ni[c]	0·0 (extrap.)—1·0	0·26
P-2Ni[d]	0·0 (extrap.)—1·0	0·27

[a] 2·0 equiv. required for hex-1-yne → hexane.

[b,c,d] See Table 1.

The reductions of hex-1-yne produce both hex-1-ene and hexane, even while unreacted alkyne remains; however, the proportions vary appreciably, as shown in Table 2. Only palladium is highly selective for hex-1-ene formation;

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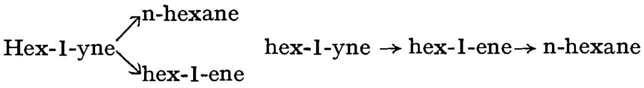
‡ Hydrogenation of 40.0 mmoles of hex-1-yne over 0·20 mmole of noble metal or 5·0 mmoles of base metal in 50 ml of ethanol solution at 25°, 1 atm. The borohydride hydrogenation[4] with *in situ* generation of catalysts was employed throughout.

¶ No isomeric hexenes were detected even over the Pd–BH_4/C catalyst which has been reported to produce considerable isomerization during hydrogenation of alk-1-enes.[1]

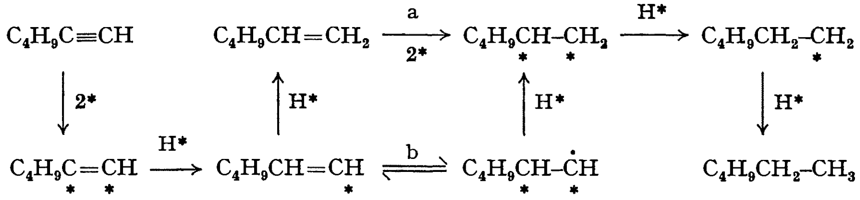
however, in general selectivity is considerably higher than might be expected from the independent hydrogenations. These results clearly suggest two pathways for the formation of hex-1-ene and n-hexane.



(I) (II)

Pathway (I) requires a constant hexane: hexene ratio, with hexane produced even at the very beginning of the reaction when little or no hex-1-ene is present. Pathway (II) requires that the hexane: hexene ratio should increase from zero as the reaction proceeds and the hexene:hexyne ratio increases.** P-1Ni, P-2Ni, and possibly Pd–BH_4/C apparently catalyse by mechanism (I). Pt–BH_4/C operates by a combination of (I) and (II); an appreciable hexane: hexene ratio is present from the beginning, yet the ratio increases as the reaction proceeds. These results are explained by the following mechanism. Pathway (I) proceeds *via* b, while (II) proceeds *via* a. A similar mechanism has been suggested for the hydrogenation of acetylene in the gas phase to account for the effects of pressure on selectivity.[6] However, the mechanism has not been investigated for the new borohydride-reduced catalysts,†† nor has the presence of two pathways been demonstrated for higher alkynes in electron-rich oxygenated solvents which might be expected to affect the nature of the surfaces considerably. Investigations into solvent effects are planned.

The results reported here clearly indicate that alkane formation in liquid-phase hydrogenation occurs predominantly directly from alkyne. In synthetic hydrogenations, a number of additives and "poisons" have been claimed to improve the selectivity of alkene formation.[7] Studies into the effects of some of these materials upon the course of alkyne hydrogenation are in progress. However, the very high selectivity of the simple Pd–BH_4/C catalysts suggests that preparative selective reductions of alkynes to alkenes may be practical without the use of detailed selective poisonings.



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** Selectivity from (I) has been termed "mechanistic selectivity"; that from (II), "thermodynamic selectivity."[5]

†† Some question still remains as to whether these materials contain boron as an occluded solid, amorphous mixture, or definite stoicheiometric boride.[8]

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[3] H. C. Brown and C. A. Brown, *J. Amer. Chem. Soc.*, 1963, **85**, 1004.

[4] C. A. Brown and H. C. Brown, *J. Org. Chem.*, 1966, **31**, 3989. A commercial model of the apparatus was obtained from Delmar Scientific Laboratories, 317 Madison St., Maywood, Illinois, U.S.A.

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[6] Ref. 5, p. 294.

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