A SIMPLE FLOW REACTOR FOR TRANSFER HYDROGENATION OF OLEFINS

Babiker Elamin, Jeen-Woo Park and Gary E. Means* Department of Biochemistry, The Ohio State University Columbus, Ohio 43210, USA

Abstract: A simple column reactor containing a small amount of palladium catalyst, in the form of palladium black, and formic acid as a hydrogen donor can be used to hydrogenate several types of olefins.

Transfer hydrogenation using various organic liquids as hydrogen donors is of interest because it avoids some of the inconvenient aspects of conventional hydrogenation procedures. Until recently, however, the low reactivity of the commonly used hydrogen donors usually necessitated long reaction times and/or high temperatures which of course leads to some loss in selectivity and $convenience^{1-3}$

Table I shows that several types of olefins can be readily hydrogenated at room temperature and ambient pressure by passage through a simple column reactor containing a small amount of palladium catalyst in the presence of formic acid. In a typical procedure, a freshly prepared batch of palladium black (5.6 mmol or 0.6 g)⁴ suspended in water or methanol-water was poured into a column (0.9 x 15 cm) containing a small plug of glass wool. Transfer hydrogenation in the presence of formic acid was accomplished by allowing the starting material (1 mmol), dissolved in appropriate solvents plus 1% formic acid, to pass slowly (normally 0.5 ml/min) through the column. The optimal flow rate can be readily attained by adjusting the stopcock. Effluents containing products plus a few additional column volumes of solvent as a rinse were collected in a round bottom flask and evaporated to dryness on a rotary evaporator. We have observed no need to protect the reactors access to air during use or storage.

The reaction is very fast such that complete reaction is usually obtained upon a single pass through the reactor. Under the indicated conditions, for example, we have observed the hydrogenation of several simple olefins at rates exceeding 0.1 mmol/min. The procedure is extremely simple and convenient. It involves no cylinder of hydrogen, flow or pressure regulators, heating, shaking or stirring devices. The catalyst is separated from products in the normal course without filtering or otherwise handling and can apparently be used indefinitely.

Starting Material	Product		Melting Points		TLC (Rf)	
		% Yield	Starting Material	Product	Starting Material	Product
Cinnamic Acid	3-Phenylprop- ionic Acid ^a	100	134°	47°	0.87 ^b	0.79 ^b
Coumarin	Dihydrocoumarin ^a	100	69°	liquid	-	-
Oleic Acid	Stearic Acid	86	liquid	69°	0.29 ^C	0.65 ^C
Fumaric Acid	Succinic Acid ^a	98	286°	183°	-	-
Cholesterol	Cholestanol	88	147°	140°	0.60 ^d	0.32 ^d

Table I. Hydrogenation of Olefins by Formic Acid and Palladium Black in a Column Reactor.

a) Identical to an authentic sample by mass spectrum. TLC systems were as follows: b) toluene/chloroform/acetone (40:25:35); c) hexane/diethyl ether/ acetic acid (50:50:1); d) benzene/ethyl acetate/bromine (100:5:0.005 (v/v)) on silica gel G.

As compared to hydrogen, formic acid is very soluble in most common solvents. It reacts rapidly with palladium black at room temperature even without the presence of a hydrogen acceptor to give a hydrogenated palladium black, Pd_nH, and carbon dioxide. Transfer hydrogenation with formic acid and palladium black thus appears to proceed in two separate and distinct steps as follows:

Both reactions occur rapidly in the column reactor such that all of the compounds listed in Table I were completely reduced upon a single passage of less than 5 min in duration.

References

- 1. G. Brieger and T.J. Nestrick, <u>Chem. Rev.</u> <u>74</u>, 567 (1974).
- 2. A.E. Jackson and R.A.W. Johnstone, Synthesis, 785 (1976).
- G.M. Anantharamaiah and K.M. Sivanandaiah, J. <u>Chem. Soc. Perkin Trans. I</u>, 490 (1977).
- J.P. Greenstein and M. Winitz, "Chemistry of the Amino Acids" vol 3 (1961) Wiley, new York, p 1223.

(Received in USA 8 June 1988)