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Preliminary communication

HYDROGENATION OF FERROCENE

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Summary

Ferrocene and derivatives can be hydrogenated in acidic medium at ambien temperature and atmospheric hydrogen pressure using supported palladium as the catalyst.

The unreactivity of ferrocene towards hydrogenation is well-known. Woodward et al. [1] and Fischer [2] have reported that ferrocene resists catalytic hydrogenation over platinum. Attempts by Trifan and Nicholas [3] and by Balandin et al. [4] to hydrogenate ferrocene over a rhodium catalyst in acetic acid were also unsuccessful. The same holds for the use of a Raney nickel catalyst (at 150° and 150 atm hydrogen pressure) by Fischer [5], while Nesmeyanov et al. [6] achieved partial hydrogenation but only using severe cond tions (340° and 280 atm hydrogen pressure).

We have achieved complete hydrogenation of ferrocene using palladium (10% on carbon) as the catalyst in an acidic medium under mild conditions (20-50° and 1 atm hydrogen pressure). As shown by the hydrogen uptake and the analysis of the reaction products, the following overall reaction is involved:

$$Fe(C_5H_5)_2 + 4\ H_2 + 2\ H^+ \rightarrow Fe^{2+} + 2\ \text{cyclo-}C_5H_{10}$$

The reaction was found to be first order in catalyst and zero order in ferrocene. Autoretardation was observed, which is apparently due to adsorption of reaction products (e.g. acetates when using acetic acid as the solvent) onto the palladium surface.

Results obtained with several media are listed in Table 1.

With non-acidic media as ethanol or tetrahydrofuran only low conversions of ferrocene were obtained. Apparently, the palladium surface is poisoned rapidly due to adsorption of iron species generated during the hydrogenation. Similar poisoning effects might have played a role in some earlier attempts [2, 5, 6

Complete and facile hydrogenation of ferrocene on palladium is achieved

TABLE 1

HYDROGENATION OF FERROCENE[a] OVER Pd—C

Solvent	Acid added	Relative rate[b]
100% CH_3COOH	—	0.44
95% CH_3COOH	—	0.55
80% CH_3COOH	—	1.0
100% CF_3COOH	—	4.5
80% CF_3COOH	—	2.4
99% CH_3COOH	$HClO_4$	15.0
95% CH_3COOH	$HClO_4$	8.7
80% CH_3COOH	$HClO_4$	4.7
99% CH_3COOH	HBF_4	7.1
95% CH_3COOH	HBF_4	5.0
80% CH_3COOH	HBF_4	1.9
95% CH_3COOH	H_2SO_4	2.9
80% CH_3COOH	H_2SO_4	4.1
80% CH_3COOH	HBr	< 0.01
80% CH_3COOH	HCl	< 0.01
80% C_2H_5OH	H_2SO_4	0.80
80% $(CH_2)_4O$	H_2SO_4	0.36
80% $(CH_3)_2CO$	H_2SO_4	0.41

[a] Ferrocene, 0.57 mmol; solvent, 20 ml; acid, 4.8 mmol; catalyst, Pd (10% on C); 50°; 1 atm H_2. [b] Rates are relative to the rate of hydrogenation of ferrocene in 80% aqueous acetic acid using 100 mg of 10% Pd—C ($t_{1/2}$ 4 min).

when an organic acid or a solution of a mineral acid is used as the reaction medium. The data show that raising the degree of acidity increases the rate of the hydrogenation. Other relevant factors include the solubility of the products formed, e.g. a solution of sulfuric acid in acetic acid requires dilution in order to keep the ferrous sulfate in solution. Furthermore, solutions of hydrochloric and hydrobromic acid in acetic acid are not suitable as hydrogenation media, probably because of the good coordination ability of halogen anions towards palladium [7].

A particularly useful medium is an aqueous solution of perchloric acid in acetic acid. It combines a good solubility for ferrocene with strong acidity, and it also protonates acetate, thus reducing coadsorption of anionic ligands, perchlorate being a very weak ligand.

The hydrogenation of substituted ferrocenes over palladium in an acidic medium is also under investigation. The following order of reactivity was observed as the substituents were varied: H > Me > t-Bu > COOMe > 1,1'-t-Bu_2, 1,3-t-Bu_2. Steric as well as electronic effects appear to be involved in determining this order. It should be noted that hydrogenation of substituted ferrocenes can be used as a synthesis of cyclopentane derivatives, providing an alternative to metal—ammonia reduction [3].

The hydrogenation of ferrocene and derivatives is clearly wholly practicable using palladium on carbon as the catalyst, but it requires a careful choice of solvent and acidity. Detailed investigations concerning the mechanism of the hydrogenation are in progress.

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