Noble Metal Catalysed Hydrogenation of Carbocations: a Key Step in the Rapid Hydrogenation of Aromatic Hydrocarbons with HF–, HF–TaF_5–, and HF–BF_3–Noble Metal Catalysts

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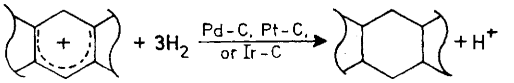
Summary Pd–C, Pt–C, and Ir–C catalyse the rapid and complete hydrogenation of carbocations formed through the protonation of aromatic hydrocarbons in super acid media and of stabilised carbocations in aprotic media.

The hydrogenation of localized carbocations proceeds easily in super acid media to produce a saturated hydrocarbon and a proton.[1] Conversely, delocalized carbocations, for instance those formed by the protonation of an aromatic hydrocarbon, do not react with hydrogen directly,[2] but are only hydrogenated if a hydrocarbon capable of donating a tertiary hydride ion is present.[3]

It has been found that noble metals will also catalyse the hydrogenation of these stable delocalized carbocations; see equation (1). Although cations have been proposed as fleeting intermediates in the noble metal catalysed hydrogenations of ketones,[4] α,β-unsaturated ketones,[5] and tosylates,[6] all in acidic media, this is the first case in which this reaction has been unambiguously observed and studied.† One source of the delocalized carbocations used has been aromatic hydrocarbons which are known to be essentially completely protonated in super acids.[7] For instance the 1,3,5-trimethylcyclohexadienyl carbocation, formed by protonating mesitylene with anhydrous HF–TaF_5 [7b] is rapidly hydrogenated at room temperature if Pd–C is present. No reaction occurs in the absence of either the Pd or the acid.‡ Thus, when 2·3 mol of HF, 0·200 mol of TaF_5, 0·100 mol of mesitylene, and 1·00 g of 5% Pd–C are stirred in the presence of 27 atm of H_2, the time to convert one half of the 1,3,5-trimethylcyclohexadienyl carbocation into completely hydrogenated products is 4·5 min at 30 °C. The major products, recovered after quenching the reaction mixture with water and diethyl ether extraction are 1,3,5-trimethylcyclohexane and its cyclic isomers. A small amount of completely saturated acyclic C_9-compounds is also formed. The isomers and acyclic compounds are formed through the expected acid catalysed reactions of 1,3,5-trimethylcyclohexane under these conditions.[3b] The hydrogenation is zero-order in the aromatic hydrocarbon and in hydrogen at pressures > *ca.* 3 atm. ESCA of the recovered Pd indicates that it has not been altered.



(1)

The noble metal catalysed hydrogenation of carbocations is not limited to super acid media but also occurs in aprotic media. Thus the triphenylmethyl carbocation is hydrogenated readily in acetic anhydride if Pd–C, Pt–C, Ir–C, or Rh–C is present. In the absence of noble metals no reaction occurs. For example, 0·0125 mol of $Ph_3C^+BF_4^-$ stirred in 75 cm^3 of acetic anhydride containing a dispersion of 1·0 g of 5% Pt–C and kept under 27 atm of H_2 was hydrogenated to produce >90% yield of triphenylmethane in <1 h.

The hydrogenation of delocalized carbocations formed by the protonation of aromatic hydrocarbons results in the rapid and complete reduction of a class of organic compounds that is traditionally one of the most difficult to hydrogenate. For instance, the anhydrous acids HF, HF–TaF_5, or HF–BF_3 in combination with either Pd–C, Ir–C, or Pt–C have been found to be very active aromatic hydrogenation catalysts at room temperature, HF–BF_3–Pd–C being the most active. In all these cases no reduction occurred in the absence of the noble metal. Other anhydrous acids used in the same quantities, such as HCl, HBr, HCl-$AlCl_3$, and H_2SO_4, in combination with these noble metals, or other metals and metal complexes such as Rh–C, Ru–C, Ni, $PdCl_2$, or $Pd(PPh_3)_4$§ in combination with HF, HF–TaF_5 or HF–BF_3 were found to be inactive.¶ The Table lists the conditions and the rate enhancements for the active catalysts when mesitylene is the aromatic hydrocarbon. These HF, HF–TaF_5, and HF–BF_3 catalysed noble metal hydrogenations were also observed for other aromatic compounds such as benzene, hexamethylbenzene, anthracene, *p*-di-t-butylbenzene, and phenyl ethyl ether. In all cases the acid catalysed rate enhancements were greatest under conditions which ensured the greatest proportion of protonated aromatic hydrocarbon.**

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† The concept of the noble metal catalysed hydrogenation (or the reverse reaction) of carbocations generated from hydrocarbons appears to be novel. For instance, acidic support–noble metal catalysts are thought to have two functions; the support catalyses the carbocation reactions and the noble metal catalyses the hydrogenations and dehydrogenations of the hydrocarbons. These results suggest that the noble metal may be catalysing the carbocation hydrogenations (dehydrogenations). See also ref. 6.

‡ In the absence of a noble metal no hydrogenation occurs even at 130 °C. In the presence of a tertiary hydride ion source the hydrogenation rate is not appreciable until at least 80 °C.

§ Pd complexes were used in an attempt to prepare a homogeneous aromatic hydrogenation catalyst. Few such catalysts exist. E. L. Muetterties and F. J. Hirsekorn, *J. Amer. Chem. Soc.*, 1974, **96**, 4063.

¶ Although the lack of activity in these systems has not been thoroughly studied, it appears as if reactions between the noble metal and the acid or with impurities in the acid render the noble metal inactive.

** There are differences between the present work and earlier work in which other acids were found to catalyse noble metal hydrogenations [see: E. Aristoff, R. W. Rieve, and H. Shalit, U.S. P. 3,409,684 (1968); J. H. Brown, H. W. Durand, and C. S. Marvel, *J. Amer. Chem. Soc.*, 1936, **58**, 1594; J. R. Lewis and C. W. Shoppee, *J. Chem. Soc.*, 1955, **1365**; T. J. Kealy and R. E. Benson, *J. Org. Chem.*, 1961, **26**, 3162; and ref. 6]: i, most of these other acids demonstrated no promoting effect in quantities and under conditions similar to those here; ii, the present rate enhancements are an order of magnitude higher; iii, the earlier work mainly involved relatively weak acids, in the presence of heteroatoms, thus minimizing carbocation formation.

TABLE
Acid catalysis of mesitylene hydrogenation[a]

Acid (mol)	Metal 5% on C, g	$t_{\frac{1}{2}}$/min[b]	Rate increase[e] for acid catalysed reaction
None	Pd, 1·0	12,720[c]	—
HF (2·2)[d]	„	88	144
HF (2·3)–BF_3 (0·23)	„	3·5	3630
HF (2·3)–TaF_5 (0·20)	„	4·5	2830
None	Ir, 1·8	1300[c]	—
HF (2·2)–TaF_5 (0·20)	„	8·5	153
None	Pt, 1·83	299	
HF (2·4)–TaF_5 (0·20)	„	22	41

[a] All experiments used 0·100 mol of mesitylene; hydrogen partial pressures were kept at 20–27 atm. [b] Time taken to hydrogenate half mesitylene at 30 °C. [c] Owing to the slowness of the reaction at 30 °C, the time to hydrogenate half of mesitylene was estimated to be twice that found at 50 °C. [d] The product also contained 12% of saturated hydrocarbons in the C_{15}—C_{18} range, formed through the reaction of unprotonated mesitylene with protonated mesitylene followed by hydrogenation. [e] Time to hydrogenate completely one half of mesitylene in the presence of the acid divided by the time to hydrogenate the same amount of mesitylene in the absence of the acid using the same metal catalyst.

The mechanism for the noble metal catalysed hydrogenations of carbocations is not completely known. However, the noble metal probably first activates the molecular hydrogen as in the first step of the Horiuti–Polanyi hydrogenation mechanism.[9] This may then be followed by reaction of the carbocation with the hydrogen–metal species to form a neutral reduced hydrocarbon and a positively charged metal. Reaction of the positively charged metal with molecular hydrogen would regenerate the hydrogen–metal species and a proton. It is not known if the hydrocarbon intermediates are π-bonded to the noble metal. This situation is possible in light of the ample evidence for such positively charged unsaturated hydrocarbon–metal hydrogen species in homogeneous organometallic chemistry.[10] The rate enhancements are observed in the aromatic hydrogenations probably because protonation of the aromatic hydrocarbon removes the *ca.* 20 kcal mol^{-1} of aromatic resonance stabilization energy that must be overcome before hydrogenation can begin.

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