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Catalytic Ionic Hydrogenation

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Data on the catalytic hydrogenation of unsaturated organic compounds in acid media are examined and discussed. A new method of catalytic hydrogenation in acid media, in which the catalyst activates hydrogen and the substrate is activated by the acid which converts it into a positively charged intermediate, is proposed. The role of catalysts as agents transferring hydride ions from molecular hydrogen to carbonium ions is considered.
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I. INTRODUCTION

Hydrogenation is one of the most general and common reactions in organic chemistry. It is widely used both in organic synthesis (among other purposes, for the preparation of important substances) and in the study of the reactivities and structures of compounds. A multiplicity of different methods for the hydrogenation of unsaturated organic compounds belonging to different classes have now been developed. Some of them, for example hydrogenation over heterogeneous catalysts, are extremely effective; they are widely used in chemistry and chemical engineering.

One of the main requirements which must be met by hydrogenation methods is selectivity, i.e. the possibility of hydrogenating some unsaturated groups in the molecule without affecting others. The majority of studies on hydrogenation have been devoted recently to the solution of this problem. The fundamental factor which determines a particular type of selectivity of the given hydrogenation method is the reaction mechanism. However, the mechanism of various hydrogenation reactions has not always been established or has been elucidated only in the very broadest outline. In particular, the determination of the mechanism of hydrogenation in the presence of heterogeneous catalysts constitutes a problem which has still not been fully solved, to a large extent because these reactions are accompanied by a number of complex physicochemical processes on the catalyst surface.

We believe that hydrogenation reactions can be classified in terms of the properties of the unsaturated substrate, which largely determine the mechanism of the given reaction, and the nature of the selectivity of the hydrogenation process can be predicted for groups of reactions based on the same property of the substrate. In this approach all the known hydrogenation processes are divided into three broad groups.

The first group comprises methods based on the ability of the unsaturated compound to be coordinated to the catalyst metal atom. It includes all hydrogenation reactions in the presence of homogeneous or heterogeneous catalysts. A common feature of the mechanism of these reactions is coordination of the unsaturated substrate to the metal or its complex, which activates hydrogen. We shall not discuss here the exact meaning of the term "coordination" and we shall only note that, whatever the mechanism of the interaction of the substrate with the catalyst, the mutual approach of the species involved in this interaction is postulated. The extensive experimental data accumulated on catalytic hydrogenation show that an increase in the number and bulk of substituents at the hydrogenated bond leads to a decrease of the rate of hydrogenation. Catalytic hydrogenation methods therefore make it possible to hydrogenate selectively less shielded multiple bonds. For example, in the series of olefins the rate of hydrogenation decreases in the sequence: terminal olefins > disubstituted ethylenes with a double bond within the chain > trisubstituted ethylenes > tetrasubstituted ethylenes.

For certain catalysts, the difference between the rates of reaction is so great that selective hydrogenation of terminal olefins is possible in the presence of olefins having a large number of substituents at the ethylenic carbon atoms. The carbonyl group and the benzene ring are hydrogenated much more slowly than the ethylenic double bond, but the shielding of the latter by bulky substituents sometimes permits the selective hydrogenation of these groups without involving the ethylenic bond. Certain catalytic systems permit the selective hydrogenation of double bonds activated by electron-accepting substituents.

One should note that catalytic hydrogenation in most cases gives rise to products of the *cis*-addition of hydrogen to the unsaturated compound.

The second large group of methods for hydrogenation processes comprises those based on the electron (or hydride ion) affinity of the unsaturated compounds. It includes methods such as reduction by active metals in alcohols, acids, and amines, reduction by complex metal hydrides, lithium tetrahydroaluminate, or sodium tetrahydroborate, boranes, or alanes, and electrochemical hydrogenation methods. A characteristic feature of the mechanisms of these reactions is initial attack on the unsaturated compound by a nucleophile—an electron or a hydride ion†; this makes it possible to combine all such reactions in a single group and to expect them to have similar selectivities in the hydrogenation of unsaturated systems.

† We believe that the hydride ion transfer process involves the overall transfer of a proton and two electrons from one molecule to another. However, the detailed mechanisms of such reactions will not be considered in the present review.

Polar groups and polarised double bonds are readily reduced by these methods. Ethylenic bonds can be reduced fairly successfully in those cases where they are conjugated to electron-accepting substituents such as carbonyl, carboxy-, nitro-, and cyano-groups, aromatic rings, and other groups. In olefins under optimum conditions there is a possibility of the selective hydrogenation of a double bond activated by an electron-accepting substituent in the presence of compounds of other types. Furthermore, the addition of aluminium and boron hydrides to olefins permits the selective hydrogenation of the terminal double bonds in the presence of double bonds within a chain or olefinic groups with branching at the ethylenic carbon atom.

The third group consists of methods for the electrophilic ionic hydrogenation‡. The reaction mechanism is based on the ability of the unsaturated compound to combine with a proton to form an active intermediate—a carbonium ion, which, by abstracting a hydride ion from a suitable donor, is converted into the hydrogenation product. For a given acidity of the medium, this reaction permits the selective hydrogenation of unsaturated compounds capable of existing in equilibrium with the corresponding carbonium ions, in the presence of other unsaturated compounds which do not form carbonium ions in the reaction medium.

For example, in acids with $H_0 \simeq -3$ (trifluoroacetic acid) the use of a hydrogen-containing silane as a hydride ion donor results in the selective hydrogenation of olefins branched at the ethylenic carbon atom. Such olefins are capable of forming tertiary alkyl cations as a result of protonation by trifluoroacetic acid; at the same time, unbranched olefins with a double bond within the chain, whose protonation might give rise to less stable secondary carbonium ions, are not hydrogenated under these conditions. The introduction of electron-donating substituents, stabilising the carbonium centre, permits the hydrogenation also of monosubstituted olefins, for example styrene, vinyl ethers, and vinyl sulphides.

The selectivity of electrophilic hydrogenation is thus fundamentally different from the selectivity of the groups of hydrogenation reactions described above, in which unsaturated substrates activated by electron-accepting substituents are hydrogenated preferentially. Yet another characteristic feature of the electrophilic ionic hydrogenation is the preferential *trans*-addition of hydrogen; in molecules with a rigid skeleton, for example, in certain steroids, *trans*-addition products are formed exclusively.

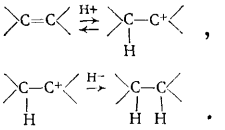
Thus all known hydrogenation methods are based on three properties of unsaturated compounds: tendency towards coordination to the catalyst metal atom, the ability to combine with a nucleophilic species (solvated electron, hydride ion, the anion of a complex hydride), and finally the tendency towards electrophilic attack—towards the initial protonation of the substrate. We believe it is difficult to imagine yet another fairly general property of unsaturated compounds which might constitute the basis of a fundamentally new hydrogenation process. It therefore appears extremely promising to combine the advantages characteristic of different groups of hydrogenation processes.

By virtue of the availability of the hydrogenating agent (molecular hydrogen), catalytic methods are greatly superior to procedures based on other hydrogenation processes. As stated above, the usual catalytic hydrogenation methods and methods based on the electron affinity of the unsaturated compound manifest similar selectivities, while the selectivity of electrophilic ionic hydrogenation is in principle unattainable when the first two methods are used. It was therefore of interest to develop a catalytic ionic hydrogenation process which would possess the advantages of catalytic methods and the selectivity of ionic hydrogenation.

‡ In contrast to this, reduction by complex metal hydrides might be called nucleophilic ionic hydrogenation.

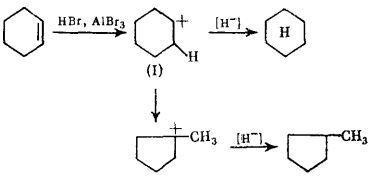
II. INTERACTION OF CARBONIUM IONS WITH HYDROGEN. HYDRIDE ION TRANSFERRING AGENTS

The mechanism of ionic hydrogenation includes two stages: protonation of the unsaturated compound with formation of an active intermediate (carbonium ion) and irreversible interaction of the latter with a hydride ion donor, leading to hydrogenation products:



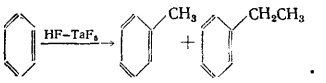
Hydrogen-containing silanes with organic substituents or hydrocarbons having a suitable structure are normally used as hydride ion donors[1]. The simplest and most readily available hydride ion donor is molecular hydrogen, but it is extremely inactive in relation to carbonium ions.

When a solution of $AlBr_3$ in cyclohexene is heated in a hydrogen atmosphere (150°C, pressure 80 atm, 26 h), only 2% of cyclohexane and 4% of its isomerisation product (methylcyclopentane) are formed[2]; the main bulk of the product consists of unidentified high-boiling hydrocarbons. The authors[2] believe that the reaction mechanism involves a stage in which a hydride ion is split off from hydrogen by a secondary carbonium ion (I), formed as an intermediate under these conditions:



A stable, i.e. relatively unreactive, cation such as triphenylcarbonium does not interact with hydrogen under the conditions indicated. A solution of $AlBr_3$ in benzene at 180°C and a hydrogen pressure of 68 atm absorbs a slight amount of hydrogen, but neither cyclohexane nor methylcyclopentane were detected in the reaction products[2].

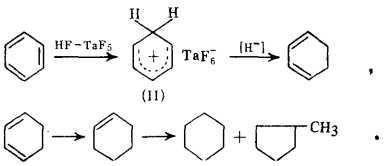
When benzene reacts with the $HF-TaF_5$ system, the main products are toluene and ethylbenzene in a yield of approximately 40% (relative to the benzene which has reacted)[3]:



The authors believe that the hydrogen required for this reaction is formed in the condensation of benzene to polycyclic compounds under the reaction conditions. When the reaction is carried out under hydrogen pressure, the yield of toluene and ethylbenzene increases by 15–25%.

The hydrogenation of benzene in the presence of the $HF-TaF_5$ system in hydrocarbons (for example in n-hexane) at 50°C leads to cyclohexane as the main product[4]. The reaction mechanism with the intermediate formation

of the carbonium ion (II) and the migration of a hydride ion towards it from hydrogen or, what is more likely, from the solvent has been proposed:



Certain cycloalkanes undergo hydrogenolysis, i.e. the cleavage of the ring with subsequent hydrogenation, in the same system at 50°C and a hydrogen pressure of approximately 15 atm.[5] Thus cyclohexane readily isomerises to methylcyclopentane, which is cleaved with formation of a mixture of t-hexyl cations. Their reduction by hydrogen leads to a mixture of isomeric hexanes. Cyclopentane gives a mixture of straight-chain pentane and isopentane. The rate of hydrogenolysis of cycloalkanes depends on the steric strain in the ring and on the nature of the carbonium ion formed during the cleavage process.

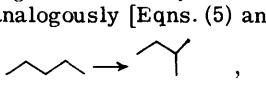
A more detailed study of the hydrogenation of benzene by hydrogen in strong acid media showed[6] that the hydrogenation proceeds at 50°C and a hydrogen pressure of approximately 30 atm in the presence of the $HF-TaF_5$, $HF-SbF_5$, $HBr-AlBr_3$, and $HCl-AlCl_3$ systems. Benzene is hydrogenated only in the presence of hydrocarbons having tertiary carbon atoms. Molecular hydrogen, unbranched alkanes, and cycloalkanes cannot serve as hydride ion donors in this reaction. Straight-chain reactions are first isomerised to isoalkanes, which are in fact the true hydride ion donors in relation to carbonium ions formed in the protonation of the benzene ring. At a hydrogen pressure >14.8 atm the reaction proceeds in the presence of catalytic amounts of isopentane, the role of hydrogen consisting in the reduction of the isopentyl cation formed from isopentane when a hydride ion is transferred to protonated benzene.

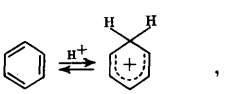
It was shown in an earlier study of the isobutane–trimethylcarbonium equilibrium in a strong acid medium[7] that this entails the reduction of the tertiary alkyl carbonium ion by hydrogen:

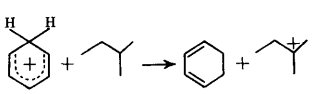
$$(CH_3)_3CH \underset{H_2}{\overset{HF,\,SbF_5}{\rightleftharpoons}} (CH_3)_3C^+SbF_6^- + H_2 .$$

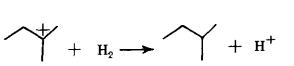
The benzyl[8], norbornyl, and methylcyclohexyl cations[9] are also reduced by hydrogen ion superacids.

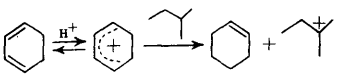
A mechanism of the hydrogenation of benzene by hydrogen in the presence of alkanes has been proposed on the basis of these data[6]: isomerisation of n-pentane to isopentane (1), protonation of benzene (2), transfer of a hydride ion from isopentane to the cationic σ-complex (3), and the reduction of the isopentyl cation by hydrogen (4). The subsequent hydrogenation of dihydrobenzene to cyclohexene takes place analogously [Eqns. (5) and (6)]:

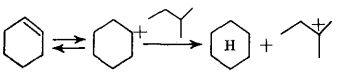

(1)


(2)


(3)

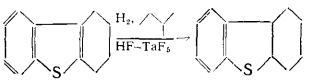

(4)


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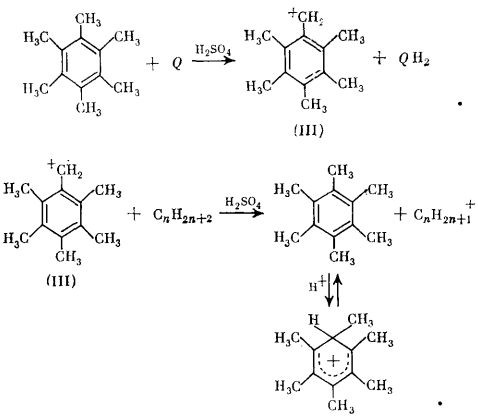

(6)

Isopentane behaves in this reaction as the catalyst—the agent which transfers a hydride ion from molecular hydrogen to carbonium ions.

It has also been shown[10] that naphthalene is hydrogenated to tetralin and the latter partly isomerises to methylindan. Anthracene is not hydrogenated under these conditions. Thiophen gives up to 40% of thiophan and dibenzothiophen is reduced to hexahydrodibenzothiophen. The same product is formed in a high yield on hydrogenation of tetrahydrodibenzothiophen in the $HF-TaF_5$ system in the presence of isopentane and hydrogen[10]:



It is of interest to note that hexamethylbenzene can serve as an agent for transferring a hydride ion from alkanes to quinones in a highly acid medium[11]. It is oxidised by the quinone to the pentamethylbenzyl cation (III), which is capable of abstracting a hydride ion from the alkane, regenerating hexamethylbenzene:



where Q = quinone.

It follows from above data that hydrogen is an extremely inactive hydride ion donor in relation to carbonium ions and, because of this, branched hydrocarbons are relatively ineffective as agents for the transfer of a hydride ion from molecular hydrogen to protonated unsaturated compounds.

III. HOMOGENEOUS HYDROGENATION CATALYSTS AS AGENTS TRANSFERRING HYDRIDE IONS FROM MOLECULAR HYDROGEN TO CARBONIUM IONS

The study of the chemistry of carbonium ions shows that one of the most characteristic reactions of these species is their ability to behave as hydride ion acceptors. The hydride mobility of hydrogen in various E–H bonds has been examined in detail in a monograph[12]. We shall only note that even strong acids such as hydrogen bromide and iodide, are capable of behaving as hydride ion donors in relation to sufficiently reactive carbonium ions.

A number of individual transition metal hydride complexes have been synthesised in recent years, many of these behaving as homogeneous hydrogenation catalysts[13,14]. Some of them are capable of transferring a coordinated hydride ion to an unsaturated substrate. Thus the isomerisation of alkyl allyl ethers to alkyl propenyl ethers catalysed by platinum hydrides[15] involves the initial addition of the platinum hydride to the double bond contrary to the Markovnikov rule, which indicates polarisation of the $Pt^{\delta+}-H^{\delta-}$ type.

It might have been expected that many transition metal hydride complexes are capable of transferring a hydride ion not only to an unsaturated compound, but also to carbonium ions; however, in the literature there are only a few isolated examples of such reactions. Thus ruthenium(IV) dihydrides reduce triphenylcarbonium, being converted into cationic complexes of ruthenium(V) [16]:

$$\underset{(IV)}{H_2RuL_3} + Ph_3C^+PF_6^- \rightarrow \underset{(V)}{(HRuL_3)^+PF_6^-} + Ph_3CH ,$$

where L = Ph_3P.

It has been asserted[17] that platinum(VI) and iridium(VII) hydride complexes reduce diphenylmethyl and triphenylmethyl cations in 60–80% sulphuric acid:

$$Ph_3C^+ \xrightarrow{(Et_3P)_2Pt(H)Cl(VI)} Ph_3CH ,$$

$$Ph_2CH^+ \xrightarrow{(Et_3PhP)_2IrH_5Cl(VII)} Ph_2CH_2 .$$

The reliability of these data[17] is open to some doubt, since a large (approximately 100-fold) excess of the metal hydride complex was used and the authors noted the decomposition of the complex in sulphuric acid. The reaction was followed solely from the change in the intensity of the band in the electronic spectrum corresponding to the absorption by the carbonium ion; the reaction products were not identified.

For the catalytic reduction of carbonium ions, the transition metal complex must be able not only to transfer a hydride ion but also to activate hydrogen with formation of a metal hydride complex in acids which are sufficiently strong to generate carbonium ions. Data demonstrating the possibility of using homogeneous catalysts to activate hydrogen in media with the required acidity for ionic hydrogenation, particularly in trifluoroacetic acid, were not available in the literature.

In 1974 the authors of the present review suggested that certain platinum-group metal complexes be used as agents for transferring a hydride ion from molecular hydrogen to stable carbonium ions[18]. The role of the catalyst in this reaction (in relation to platinum) is as follows:

(1) The platinum complex reacts with hydrogen to form the corresponding hydride complex:

$$L_2PtX_2 + H_2 \rightarrow L_2Pt(H)X + HX .$$

(2) The hydride complex then reacts with the carbonium ion, formed from the substrate in the acid medium, and converts it into the corresponding hydrocarbon:

$$L_2Pt(H)X + \diagup\!\!\diagdown C^+X^- \rightarrow L_2PtX_2 + \diagup\!\!\diagdown CH .$$

Triphenyl- and diphenyl-methanols are not reduced in trifluoroacetic acid by platinum hydride complexes, either in equimolar proportions or with a 100-fold excess of hydride, but, when the reaction is carried out under hydrogen pressure, triphenyl- or diphenyl-methanes are formed in yields exceeding 1 mole per mole of the catalyst. Consequently in trifluoroacetic acid these complexes are capable of activating molecular hydrogen and of transferring it in the form of hydride ions to stable carbonium ions.

The results of the study of the influence of the ligands and the central metal atom on the activity of catalysts in the reduction of triphenylmethanol are presented in Table 1. Comparison of data obtained for catalysts Nos. 4, 7, and 8 shows that, depending on the nature of the metal, the activity of the catalyst decreases in the sequence Pt > Pd > Ni.

Thus the possibility of using homogeneous hydrogenation catalysts (platinum, palladium, and nickel complexes of phosphine) to activate hydrogen in strong acid media and to reduce stable carbonium ions has been demonstrated.

Ruthenium salts also catalyse the reduction of triphenylmethanol by hydrogen in an acid medium[19]. In concentrated hydrochloric acid at a hydrogen pressure of 100 atm and 80°C (28 h) triphenylmethanol is converted in the presence of $RuCl_3$ into 1-(diphenylmethyl)-4-(triphenylmethyl)benzene (VIII) in 97% yield (4.2 moles per mole of the catalyst):

$$Ph_3COH \xrightarrow{HCl} Ph_3C^+ \xrightarrow{H_2,RuCl_3} Ph_3CH ,$$

$$Ph_3CH + Ph_3C^+ \rightarrow \underset{(VIII)}{Ph_2CH-C_6H_4-CPh_3} .$$

Evidently Ph_3C^+ attacks the triphenylmethane formed on reduction, giving rise to (VIII), which is stable in hydrochloric acid.

Table 1. Reduction of Ph_3CCH (0.3–0.4 g) in CF_3COOH (3 ml) (amount of catalyst 0.04–0.05 g, p_{H_2} = 100 atm, 20°C, 150 h).[18]

No.	Catalyst	Yield of Ph_3CH, mole/mole of catalyst
1	*cis*-$(Ph_3P)_2Pt(OCOCF_3)_2$	39
2	*cis*-$(Et_3P)_2Pt(OCOCF_3)_2$	27
3	*trans*-$(Ph_3P)_2Pt(H)Cl$	23
4	*cis*-$(Ph_3P)_2PtCl_2$	19
5	*cis*-$(Et_3P)_2PtCl_2$	19
6	*cis*-$(n\text{-}Bu_3P)_2PtCl_2$	14
7	*cis*-$(Ph_3P)_2PdCl_2$	15
8	*cis*-$(Ph_3P)_2NiCl_2$	10
9	*trans*-$(n\text{-}Bu_3P)_2PtCl_2$	5

The interaction between triphenylmethanol and hydrogen in trifluoroacetic acid in the presence of $RuCl_3$ leads to triphenylmethane in 96% yield. Other ruthenium salts, such as the acetate and trifluoroacetate, also catalyse the hydrogenolysis of triphenylmethanol, and are more active than $RuCl_3$. Thus under identical conditions $RuCl_3$, ruthenium acetate, and ruthenium trifluoroacetate give rise to 68, 87, and 97% of triphenylmethane. Among ruthenium salts, the trifluoroacetate is the most active. When this catalyst is used, the reduction of Ph_3C^+ is accelerated with increase of temperature. The yield of triphenylmethane was 26% (5 moles per mole of the catalyst) at 20°C, 78% (14 moles per mole of catalyst) at 50°C, and 96% (18 moles per mole of the catalyst) at 80°C. At a hydrogen pressure of approximately 1 atm, there is no reduction but, when the pressure is raised from 5 to 90 atm, the yield of triphenylmethane increases from 35 to 98%. The results show that the ruthenium salts investigated are capable of catalysing the transfer of a hydride ion from hydrogen to the carbonium ion.

The authors of the present review showed recently[20] that certain phosphine complexes of iridium (IX) also catalyse the reduction of triphenylmethanol in an acid medium, the iridium trihydride complex being the most active:

$$Ph_3COH \xrightarrow[70^\circ C,\ p_{H_2}=100\ atm]{L_3IrH_nX_{3-n}(IX),\ CF_3COOH} Ph_3CH ,$$

$$L = Ph_3P;\ X = Cl;\ n = 1-3 .$$

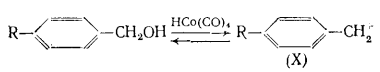
The ability of certain hydrogenation catalysts to activate hydrogen in an acid medium and to transfer it in the form of hydride ions to carbonium ions made it possible to propose a new mechanism for catalytic hydrogenation, in which the catalyst activates hydrogen and the unsaturated substrate is activated by the solvent—an acid, which converts it into the active intermediate (the carbonium ion). This permits catalytic hydrogenation with a selectivity characteristic of electrophilic ionic hydrogenation.

1. Catalytic Ionic Reduction of Alcohols

The relative rate of homogeneous reduction of substituted benzyl alcohols under hydroformylation conditions in the presence of cobalt tetracarbonyl hydride decreases in the following sequence of substituents[21]:

$$p\text{-}OCH_3 > p\text{-}CH_3 > m\text{-}CH_3 > p\text{-}C(CH_3)_3 > H > p\text{-}Cl > m\text{-}OCH_3 > m\text{-}CF_3.$$

This sequence corresponds to that expected for reactions with the intermediate participation of carbonium ions (X): it is suggested that they are formed from benzyl alcohols under the influence of the acid $HCo(CO)_4$:



(X)

The mechanism of the reduction of carbonium ions was not established in the above investigation.

It has been found[22] that, in trifluoroacetic acid under hydrogen pressure and in the presence of phosphine complexes of platinum, a primary alcohol (2-ethylhexanol) and a secondary alcohol (cyclohexanol) are not reduced, while tertiary alcohols (tri-n-butylmethanol and 1-methylcyclohexanol) are converted under these conditions into the corresponding hydrocarbons. The yield of 5-n-butylnonane and methylcyclohexane were 56 and 80% respectively under identical conditions. Thus, when hydrogen is used as the hydride ion donor and phosphine complexes of platinum are used as hydride ion transferring agents, there is a possibility of the selective catalytic ionic hydrogenolysis of tertiary alcohols.

The influence of certain factors on the reduction of tertiary alcohols has been studied[22] in relation to 1-methylcyclohexanol. Methylcyclohexane is formed only when the reaction mixture contains simultaneously an alochol, trifluoroacetic acid, hydrogen, and the catalyst. Methylcyclohexane is the only product of the reduction of methylcyclohexanol; skeletal isomerisation products were never detected. After the reaction, the mixture remains homogeneous and metallic platinum is not formed. This reaction is catalytic. When bistriphenylphosphineplatinum bistrifluoroacetate is used as the catalyst in trifluoroacetic acid (hydrogen pressure 200 atm, 50°C, 35 h), the catalytic yield of methylcyclohexane is 103 moles per mole of the catalyst. After the removal of volatile mixture components, the reuse of the catalyst gives rise to similar results: the yield after 25 h under analogous conditions is 73 moles per mole of the catalyst.

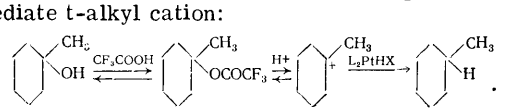
In the reduction of methylcyclohexanol, as in the reduction of triphenylmethanol, $(Ph_3P)_2Pt(OCOCF_3)_2$ is the most active of the catalysts investigated. The platinum hydride chloride and dichloride complexes exhibit similar but smaller activities. The phosphine complexes of palladium and nickel are almost inactive in the hydrogenolysis of both tertiary and secondary aliphatic alcohols.

The reduction of 1-methylcyclohexanol is greatly influenced by the solvent (Table 2). In neutral and weakly acid media (tetrahydrofuran, acetic acid, and formic acid) the reduction of 1-methylcyclohexanol is not observed. The increase of the polarity of the medium on passing from benzene to nitrobenzene and the increase of the concentration of trifluoroacetic acid appreciably increase the yield of methylcyclohexane.

Table 2. Reduction of 1-methylcyclohexanol (0.2 g) in the presence of trifluoroacetic acid (0.4 ml), the solvent (2 ml), and the $(PPh_3)_2PtCl_2$ catalyst (0.05 g) (p_{H_2} = 100 atm, 27 h, 50°C).[22]

Solvent	Yield of methylcyclohexane, %
Tetrahydrofuran	0
Acetic acid	0
Formic acid	0
Benzene	5
Toluene	6
Chloroform	14
Nitrobenzene	32
Trifluoroacetic acid–toluene (1:1)	35
Trifluoroacetic acid	96

The results permit the conclusion that the reduction of tertiary alcohols under these conditions involves hydride ion transfer from the platinum hydride complex to the intermediate t-alkyl cation:



The reduction of tertiary alcohols alone in the presence of secondary and primary alcohols confirms the ionic reaction mechanism, since in trifluoroacetic acid only tertiary alcohols are in equilibrium with the corresponding alkyl carbonium ions. In the above reaction mechanism the function of the catalyst is restricted to the activation of hydrogen, while the substrate is activated by being converted into a carbonium ion.

Ruthenium salts activate via an analogous mechanism the selective reduction of a tertiary alcohol (methylcyclohexanol) in the presence of a secondary alcohol (cyclohexanol)[19].

Thus many homogeneous hydrogenation catalysts are capable of catalysing the reduction of tertiary alcohols, and the same selectivity is observed as in the ionic hydrogenation by the silane–trifluoroacetic acid system.

2. Catalytic Ionic Hydrogenation of Olefins

Protic or Lewis acids are usually employed in homogeneous hydrogenation processes to rupture the carbon–metal σ-bond. They also facilitate the dissociation of the

ligand with liberation of a vacant site in the coordination sphere of the metal as a result of the coordination of the acid to the ligand or to the metal atom. Even in those cases where there is a possibility, in principle, of the formation of carbonium ions in the reaction [for example, in the homogeneous hydrogenation of cyclohexene with the aid of $RhCl(PPh_3)_3$ in the presence of aluminium bromide[23] or in the homogeneous hydrogenation of a series of olefins catalysed by $Rh(OCOCH_3)(PPh_3)_3$ in the presence of toluene-*p*-sulphonic acid[24]], their involvement in the reaction has not so far been discussed.

The homogeneous hydrogenation of olefins via an ionic mechanism has been described[25]. Data for the homogeneous hydrogenation of olefins in the presence of ruthenium trifluoroacetate are presented in Table 3. Evidently, when the reaction is carried out in toluene, a disubstituted ethylene (cyclohexene) is hydrogenated, while a trisubstituted ethylene (1-methylcyclohexene) does not react; the relative reactivities of these olefins in trifluoroacetic acid are reversed. Consequently, the hydrogenation of olefins in the solvents investigated proceeds via different mechanisms.

Table 3. Hydrogenation of olefins (0.1 g) in the presence of the $Ru(OCOCF_3)_3$ catalyst (0.05 g) (p_{H_2} = 85 atm, 50°C, 20 h).[25]

Olefin	Yield of saturated hydrogenation products			
	%	mole/mole of catalyst	%	mole/mole of catalyst
	in CH_3COOH		in toluene	
Cyclohexene	0	0	55	9
1-Methylcyclohexene	46	6	0	0
1,2-Dimethylcyclohexane	14	1.5	—	—
Tetramethylethylene	13	2	—	—

When the reaction takes place in toluene, the usual homogeneous hydrogenation, involving the coordination of the olefin to the ruthenium atom, occurs. Ruthenium homogeneous hydrogenation catalysts are known to be capable of the selective hydrogenation of terminal double bonds in compounds containing double bonds also within the chain or branches at ethylenic carbon atoms[26]. In trifluoroacetic acid methylcyclohexene is hydrogenated, while cyclohexene is not, which conflicts with the above rule and, in order to explain it, another hydrogenation mechanism, an ionic mechanism, must be resorted to. Since only tertiary alkyl carbonium ions are capable of existing in trifluoroacetic acid, the selectivity observed in this case can be readily accounted for from the standpoint of an ionic hydrogenation mechanism, involving the transfer of a hydride ion from the reduced form of the catalyst to the carbonium ion. One should note that even tetrastituted olefins—tetramethylethylene and 1,2-dimethylcyclohexene—are hydrogenated under these conditions. This is the first instance of the homogeneous hydrogenation of tetrasubstituted olefins catalysed by ruthenium compounds.

As in the reduction of alcohols, it was found that the hydrogenation of olefins occurs only when the reaction mixture contains all the components: the olefin, trifluoroacetic acid, the catalyst, and hydrogen. One should also note that the mixture remains homogeneous during hydrogenation and that the catalysts are insensitive to oxygen and atmospheric moisture.

The use of phosphine complexes of platinum as catalysts also permits the catalytic ionic hydrogenation of olefins. This reaction occurs only in trifluoroacetic acid; in toluene, in acetic and formic acids, in the benzene–methanol mixture, and in nitrobenzene with added hydrochloric acid the formation of alkanes is not observed.

As in the reduction of triphenylmethanol, in the hydrogenation of olefins bistriphenylphosphineplatinum bistrifluoroacetate is the more active catalyst. The results for the hydrogenation of a series of olefins in its presence are presented in Table 4. Evidently substitution of hydrogen atoms at the ethylenic bond by methyl groups has a small influence on the hydrogenation process. It is noteworthy that, in contrast to the data in Table 3, in this case the cyclohexene is also hydrogenated. Presumably the hydrogenation of cyclohexene occurs at the instant of the protonation of the substrate and some of the cyclohexyl carbonium ions have sufficient time to split off a hydride ion from the platinum hydride and to be converted into cyclohexane, while others combine irreversibly with the trifluoroacetate anion, forming cyclohexyl trifluoroacetate, which is incapable of further reduction. Indeed, with increase of the reaction time under the conditions indicated in Table 4, the yield of cyclohexane does not increase, while in the reaction of olefins branched at an ethylenic carbon atom the yield of the hydrogenation products continues to rise.

Table 4. Hydrogenation of olefins (0.1 g) in the presence of the $(Ph_3P)_2Pt(OCOCF_3)_2$ catalyst (0.02 g) and CF_3COOH (1 ml) (p_{H_2} = 100 atm, 50°C, 20 h).[25]

No.	Olefin	Yield of alkane	
		%	mole/mole of catalyst
1	Tetramethylethylene	84	50
2	1,2-Dimethylcyclopentane	56	30
3	1,2-Dimethylcyclohexene	41	22
4	1-Methylcyclohexene	45	23
5	Cyclohexene	35	20

The above data confirm the homogeneous catalytic ionic hydrogenation mechanism which involves a transfer of a hydride ion from the metal hydride complex to the carbonium ion. The ease of hydrogenation of unsaturated compounds is in this case determined by the stability of the corresponding carbonium ions and not by their tendency to coordinate to the metal atom. This leads to easier hydrogenation of trisubstituted olefins compared with olefins containing a terminal double bond or a double bond within the chain without a branch at the ethylenic carbon atom. This type of selectivity of hydrogenation is not attainable, in principle, when any other catalytic hydrogenation method is used.

3. Catalytic Ionic Hydrogenation of Carbonyl Compounds

The homogeneous hydrogenation of carbonyl compounds has been developed to a much lesser extent than the hydrogenation of olefins. The phosphine complexes of cobalt,

iridium, and rhodium may be mentioned as catalysts for the homogeneous hydrogenation of carbonyl compounds [27]. All these catalysts are capable of initiating the reduction of other functional groups as well. The following substrate activity series is then observed: olefins with a terminal double bond > disubstituted ethylenes with a double bond within the chain > trisubstituted ethylenes > aldehydes > ketones.

When homogeneous hydrogenation catalysts are used, the carbonyl group must be activated. Thus $H_3Ir(PPh_3)_3$ is an effective catalyst for the hydrogenation of aldehydes to alcohols only in acetic acid [28]. The cationic hydrides $RhH_2L_2S_2^+$ [L = PPh_3, PPh_2CH_3, $PPh(CH_3)_2$, or $P(CH_3)_3$; S is the solvent], in the presence of small amounts of water as a promoting agent, are capable of hydrogenating the carbonyl group of ketones under mild conditions [29]. It has been shown [29] that the neutral complexes $RhHL_2S_2$ do not reduce carbonyl compounds. Hydrogenation occurs only when HBF_4 is added to these catalysts, i.e. when the carbonyl group is activated either by an excess of acid or by the complex itself.

The above data show that the catalytic hydrogenation of the carbonyl group under mild conditions requires its activation by protic or Lewis acids.

Carbonyl compounds are readily reduced by hydrogen-containing silanes in trifluoroacetic acid and the mechanism of this reaction involves a stage in which the hydride ion is transferred from the silane to the intermediate carboxonium ion (XI): [1]

$$R_2C{=}O \xrightleftharpoons{CF_3COOH} \underset{(XI)}{[R_2C{=}OH]^+} \xrightarrow{R_3SiH} R_2CH{-}OH\ .$$

Table 5. Dependence of the yield of isopropyl trifluoroacetate on the catalyst (~0.1 g of acetone, ~0.02 g of catalyst, 3 ml of CF_3COOH, p_{H_2} = 85 atm, 30 h, 50°C). [30]

Catalyst*	Yield	
	%	mole/mole of catalyst
$(PPh_3)_2PtCl_2$	80	63
$(PPh_3)_2Pt(OCOCF_3)_2$	34	27
$(PPh_3)_2PdCl_2$	⩽1	—
$(PPh_3)_2NiCl_2$	⩽1	—

*There is no hydrogenation in the absence of the catalyst.

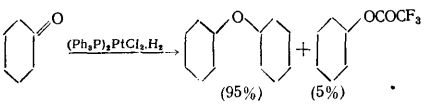
It has been shown [30] that phosphine complexes of platinum, which do not catalyse the homogeneous hydrogenation of carbonyl compounds, acquire this capacity in trifluoroacetic acid. In the ionic hydrogenation of acetone by silane and trifluoroacetic acid a mixture of 60% of isopropyl alcohol (in the form of isopropyl trifluoroacetate) and 25% of di-isopropyl ether is formed. The catalytic ionic hydrogenation of acetone gives rise to only one product–isopropyl trifluoroacetate. Data for the dependence of the yield on the nature of the catalyst are presented in Table 5. An increase of the acidity of the medium leads to an increase of the yield of the hydrogenation product (Table 6); in the absence of acid there is no hydrogenation. When trifluoroacetic acid is replaced by formic or acetic acid, the hydrogenation of acetone slows down. Under the same conditions, the yields of isopropyl trifluoroacetate, formate, and acetate, are 45, 32, and about 10% respectively.

Thus, in the homogeneous catalytic ionic hydrogenation of acetone the highest yields of product (isopropyl trifluoroacetate) were obtained when trifluoroacetic acid was used as the proton donor and solvent and the catalyst and hydride ion transferring agent was bistriphenylphosphine-platinum dichloride. The rate of ionic hydrogenation increases with increase of temperature, hydrogen pressure, duration of heating, and acidity with the medium.

Table 6. Dependence of the yield of isopropyl trifluoroacetate on the amount of trifluoroacetic acid [~0.1 g of acetone, 0.02 g of $(Ph_3P)_2PtCl_2$, p_{H_2} = 85 atm, 55°C, 23 g]. [30]

Composition of solvent, ml		Yield, %	Composition of solvent, ml		Yield, %
CF_3COOH	benzene		CF_3COOH	benzene	
0	3	0	1	2	31
0.3	2.7	5	3	0	45

As in ionic hydrogenation by the $R_2SiH-CF_3COOH$ system, in the catalytic ionic hydrogenation cyclohexanone is reduced much faster than acetone. Thus the complete reduction of cyclohexanone at 50°C and a hydrogen pressure of 85 atm takes place over a period of 21 h, whereas acetone is hydrogenated over a period of 40 h under the same conditions. The reaction gives rise to a mixture of dicyclohexyl ether (95%) and cyclohexyl trifluoroacetate (5%):

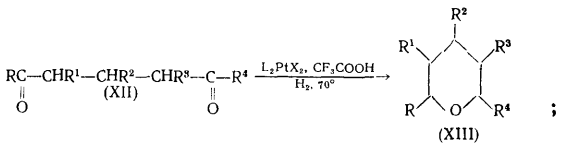


Catalytic homogeneous ionic hydrogenation of cyclohexanone can serve as a preparative method for the synthesis of dicyclohexyl ether, while other methods for its formation give low yields. For example, one of the known methods for the synthesis of this ether, from cyclohexanol and cyclohexene in hydrofluoric acid, gives only 12% of dicyclohexyl ether [31], while the yield in ionic hydrogenation by the $Et_3SiH-CF_3COOH$ system is 15%. [1]

The catalytic ionic hydrogenation of n-butyraldehyde results in the formation of only one product—n-butyl trifluoroacetate [30]. A mixture of 33% of dibutyl ether and 60% of n-butyl trifluoroacetate is obtained in the ionic hydrogenation of n-butyraldehyde by the $Et_3SiH-CF_3COOH$ system [1]. n-Butyraldehyde is hydrogenated faster than acetone. At 50°C and a hydrogen pressure of 85 atm the yields of isopropyl and n-butyl trifluoroacetates after 22 h are 42 and 67% respectively. The catalytic ionic hydrogenation of benzaldehyde gave benzyl trifluoroacetate in approximately 70% yield [30]. The yield of dibenzyl ether in the reduction of benzaldehyde by silane was 80%. [1]

The catalytic ionic hydrogenation of aromatic ketones, like their ionic hydrogenation by silanes, involves the more far-reaching reduction of the carbonyl group to the methylene group, which can be accounted for by the stability of carbonium ions in which a benzene ring adjoins the carbonium centre [30]. When benzophenone was reduced under a hydrogen pressure of 150 atm at 60°C over a period of 135 h, diphenylmethane was isolated in 93% yield. It was found [32] that, in the catalytic ionic

hydrogenation of acyclic and bicyclic 1,5-dicarbonyl compounds (XII), the corresponding tetrahydropyrans (XIII) are formed in high yields:



(XIII)

$RR^1=R^3R^4=(CH_2)_4$, $R^2=H$ (85%);

$R=R^4=C_6H_5$, $R^1=R^3=H$, $R^2=CH_3$ (97%);

$R=R^4=C_6H_5$, $R^1=R^3=CH_3$, $R^2=H$ (80%);

$R=R^2=R^4=C_6H_5$, $R^1=R^3=H$ (82%) .

The above method for the hydrogenation of 1,5-diketones is suitable also for the synthesis of tetrahydropyrans, which are of interest as plasticisers and solvents. The methods described previously for their synthesis are preparatively difficult, because in most cases they involve the addition of various compounds to the double bond of dihydropyrans, which are relatively difficult to obtain.

IV. HETEROGENECUS CATALYSTS AS HYDRIDE ICN TRANSFERRING AGENTS

Hydrogenation in the presence of heterogeneous catalysts still remains the most widely used hydrogenation procedure in industry and laboratory practice. It is highly efficient and usually presents no difficulties. The determination of the mechanism of hydrogenation in the presence of heterogeneous catalysts is extremely difficult, largely because hydrogenation is accompanied by phenomena occurring on the surface of the catalyst.

The main role of the catalysts consists in the activation of molecular hydrogen and the substrate. According to the generally accepted theory of Horiuchi and Polanyi [33], the process can be divided into the following stages:

(a) $Cat + H_2 \rightleftharpoons Cat.HH$ (adsorption of hydrogen);

(b) $Cat.HH + S \rightleftharpoons Cat.HH.S$ (adsorption of substrate);

(c) $Cat.HH.S \rightleftharpoons Cat.H.SH$ (hydrogenation);

(d) $Cat.H.SH \rightleftharpoons Cat.SH_2$;

(e) $Cat.SH_2 \rightleftharpoons Cat + SH_2$ (desorption of product).

(Here Cat is the catalyst and S the substrate). It follows from the above scheme that the hydrogen activated by the catalyst adds in steps to the adsorbed substrate via the stage with a semihydrogenated state. As a rule stage (c) or (d) is rate-limiting.

The nature of the activation of hydrogen on the surface of the transition metal is still not clear, although its investigation has remained in the centre of attention of many investigators [34-36]. Without going into the details of this complex field, we shall only note that it has now come to be regarded as established than an M–H bond is formed on the metal surface [37]. The removal of hydrogen from the metal takes place via both homolytic and heterolytic mechanisms, depending on the nature of the substrate. If the substrate is a positively charged species, for example, a carbonium ion, then chemisorbed hydrogen can be transferred to the substrate in the form of a hydride ion. The reaction can then be represented by the usual scheme for ionic hydrogenation, as in the homogeneous catalytic hydrogenation in acid media (see Section III):

$$S + H^+ \rightleftarrows SH^+ \ ;$$

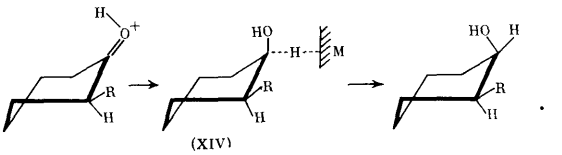
$$Cat + H_2 \rightleftarrows Cat \cdot HH \ ;$$

$$Cat \cdot HH + SH^+ \rightleftarrows CatH^+ + SH_2 \ ;$$

$$CatH^+ \rightleftarrows Cat + H^+ \ .$$

Under these conditions hydrogen is activated by the catalyst and the substrate by the acid, which converts it into a cation. The catalyst behaves as an agent transferring a hydride ion from molecular hydrogen to the substrate.

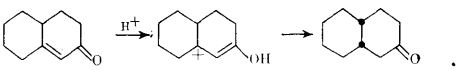
This section deals with hydrogenation reactions occurring on heterogeneous catalysts in acid media, for which an ionic mechanism has been suggested. The hypothesis of a possible ionic hydrogenation mechanism on heterogeneous catalysts was first put forward by Brewster [38] in 1954. In order to explain the influence of the medium on the stereochemistry of the hydrogenation of α-substituted cyclohexanones, he suggested that a protonated form of the ketone (XIV), coordinated in such a way that the bulky substituent (the metal) occupies a sterically less hindered equatorial position, exists in an acid medium on the catalyst surface. The hydride transfer from the catalyst to the protonated form of the ketone leads to axial alcohols:



(XIV)

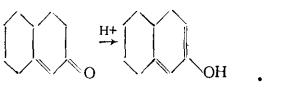
McQuillin [39,40], who studied the hydrogenation of cholestenone and testosterone over Pd/C and PtC_2 in various solvents, also found that the stereochemistry of the reaction product (the formation of 5α- or 5β-steroids) depends on the polarity of the medium. In order to account for the stereochemical results in an acid medium, he adopted Brewster's hypothesis of an ionic hydrogenation mechanism.

The concept of hydride transfer from the catalyst surface was used to interpret data obtained in the hydrogenation of a series of unsaturated cyclopropanes [41]. When $\Delta^{1,9}$-2-octalinone is hydrogenated over Pt/C or Pt/C in media with pH < 2, mainly *cis*-2-decalinone (XV) is obtained [42-44]. It is suggested that at the above pH values the protonated form (XVI) is formed as an intermediate and is more effectively adsorbed on the catalyst surface than the initial ketone:



(XVI) (XV)

Coordination of the metal from the sterically less hindered side of the carbocycle ensures a direction of attack by the hydride ion on the adsorbed carbonium ion which leads to (XV). It has been noted [42-44], however, that a similar stereochemical result can be obtained in the hydrogenation of the homoannular dienol (XVII), which can isomerise in an acid medium:



(XVII)

At low concentrations of ketones the rate of their hydrogenation over PtO_2 greatly increases on passing from acetic to trifluoroacetic acid or when strong acids (for example, $HClO_4$) are added to acetic acid [45]. Assuming the possibility that the reaction in strong acids proceeds via either one of the two mechanisms mentioned above, i.e. with formation of carboxonium ions or homoannular enols, Peterson and Casey [45] gave preference to the reaction mechanism involving the enol. They believe that this view is confirmed by the hydrogenolysis of t-butyl alcohol

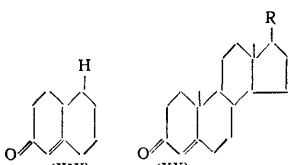
over PtO_2 in trifluoroacetic acid, which proceeds, in their view, via the hydrogenation of the isobutene in equilibrium with the initial alcohol. The equilibrium involves the intermediate formation of the t-alkyl cation (XVIII), but the possibility of the transfer of a hydride ion from the catalyst to the carbonium ion is not considered:

$$(CH_3)_3COH \overset{CF_3COOH}{\rightleftharpoons} (CH_3)_3COCOCF_3 \rightleftarrows (CH_3)_3C^+ \rightleftarrows (CH_3)_2C{=}CH_2 \quad .$$
(XVIII)

The hydrogenation of $\Delta^{8,9}$-dihydropimaric acid over PtO_2 in acetic acid with formation of *trans,anti,trans*-tetrahydropimaric acid (instead of the expected *trans,anti,cis*-acid) was explained by a carbonium ion reaction mechanism [46].

The accelerating effect of the addition of acids (HCl and $HClO_4$) to aqueous solutions of methanol and acetic acid in the hydrogenation of nitrobenzene, acetophenone, and cyclohexene over Pt/C was explained by the formation of protonated species [47].

The ideas developed in the studies quoted above are hypothetical and are open to many objections. Firstly, the acidity of the solvents employed is insufficient for the formation of carbonium ions in the absence of the catalyst, which, however, does not rule out the possibility of the protonation of the unsaturated compound already coordinated to the catalyst. It may be that the acid has an activating effect on the catalyst, altering its properties, and not on the substrate [46]. Secondly, on the basis of the stereochemistry of the hydrogenation products, one cannot decide whether the reaction proceeds via an ionic mechanism, since the stereochemical result of heterogeneous hydrogenation is a consequence of several factors: the adsorption of the unsaturated substrate alters its geometry, which therefore entails a change in the torsional strain and intramolecular interactions; there is a possibility of the isomerisation of the substrate on the catalyst; furthermore, the surface of the catalyst is not planar, as assumed in the classical theory [49]. For example, in the study of the hydrogenation of the enones (XIX) and (XX) in acids a very large difference was observed between the stereoselectivities (i.e. between the ratios of the *cis*- and *trans*-products) when the catalyst and hydrogenation conditions were altered [50]. This effect for similar compounds cannot be accounted for solely by the formation of protonated species.

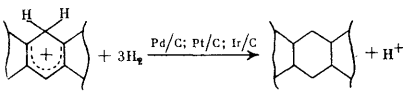


(XIX) (XX)

The reduction of stable carbonium ions can serve as direct evidence for the possibility of an ionic hydrogenation mechanism. It was observed in 1975 [51] that the hydrogenation of the triphenylcarbonium cation formed from triphenylmethanol in trifluoroacetic acid over Pt/C at 50 atm leads to triphenylmethane. This reaction can take place also over other catalysts, namely PtO_2 and Pd/C. In non-polar solvents, for example, in ether, there is no hydrogenation of triphenylmethanol.

It was later shown [52] that the catalytic hydrogenation of the triphenylcarbonium ion can take place not only in acids, but also in aprotic solvents, for example, in acetic anhydride over Pt/C, Pd/C, Ir/C, and Rh/C at 27 atm. Subsequently several more studies were published in which convincing data are presented concerning the possibility of an ionic hydrogenation mechanism on heterogeneous catalysts.

Wristers [52] observed a very large increase in the rate of hydrogenation of aromatic compounds, for example, benzene, mesitylene, hexamethylbenzene, *p*-di-(t-butyl)-benzene, and ethyl phenyl ether over Pt/C, Ir/C, and Pd/C in the presence of superacids $HF-BF_3$ or $HF-TaF_5$ (Table 7). It was found that the main product of the hydrogenation of mesitylene is 1,3,5-trimethylcyclohexane; other trimethylcyclohexane isomers are also formed, as well as insignificant amounts of alkanes with nine carbon atoms. In the hydrogenation of different aromatic hydrocarbons the rate increases with increasing concentration of the protonated aromatic compound (XXI):



(XXI)

It has been suggested [52] that the catalyst initially activates hydrogen. The subsequent interaction of the activated hydrogen with the carbonium ion, i.e. with the cationic σ-complex (XXI), leads to the formation of a hydrocarbon and a positively charged metal. The interaction of the latter with molecular hydrogen regenerates the species with an M–H bond and the proton.

Table 7. Hydrogenation of mesitylene (0.1 mole) in acid [52].

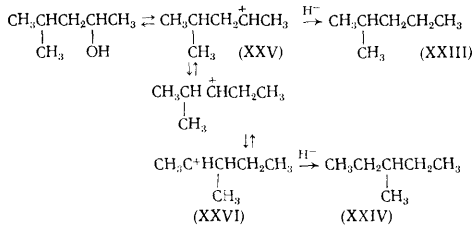
Acid (moles)	Catalyst (5% on charcoal), g	$t_{1/2}$, min	Relative increase of rate for acid-catalysed reaction
Without acid	Pd; 1.0	12 720	1
HF (2,2)	Pd; 1.0	88	144
HF (2,3) + BF_3 (0,23)	Pd, 1.0	3.5	3630
HF (2,3) + TaF_5 (0,20)	Pd, 1.0	4.5	2830
Without acid	Ir; 1.8	1 300	1
HF (2,2) + TaF_5 (0,20)	Ir; 1.8	8.5	153
Without acid	Pt; 1.83	299	1
HF (2,4) + TaF_5 (0,20)	Pt; 1.83	22	14

The formation of saturated products characteristic of reactions occurring with participation of carbonium ions, particularly alkylation and isomerisation reactions [53], was observed in the hydrogenation of a number of aromatic hydrocarbons over PtO_2 and RuO_2 in anhydrous hydrogen fluoride [53]. For example, the hydrogenation of benzene leads to 92% of cyclohexane as well as a small amount of cyclohexylbenzene and bicyclohexyl; the hydrogenation of *m*- and *p*-xylenes gives rise to six isomeric dimethylcyclohexanes, etc. It has also been shown [53] that PtO_2 catalyses the hydrogenation of 4-methylpentan-2-one to the corresponding alcohol (XXII) in a mixture of HF with ether:

$$CH_3{-}\underset{\displaystyle CH_3}{\overset{}{C}}{-}CH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3 \rightarrow CH_3{-}\underset{\displaystyle CH_3}{\overset{}{C}}{-}CH_2{-}\underset{\displaystyle OH}{\overset{}{CH}}{-}CH_3 \quad .$$
(XXII)

In a highly acid medium (anhydrous HF) the alcohol (XXII) undergoes further reduction to a mixture of hydrocarbons (XXIII) and (XXIV). This result may be expected for the

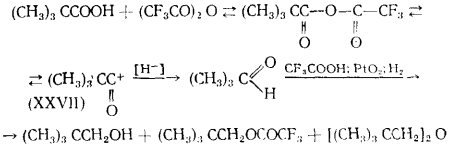
intermediate involvement of the carbonium ions (XXV) and (XXVI) in the reaction



Under the conditions indicated, cyclohexanone is reduced to a mixture of cyclohexane and methylcyclopentane. Electronegative substituents suppress hydrogenation. On the basis of these data, the author[53] believes that hydrogenation proceeds via hydride ion transfer from hydrogen on the surface of the catalyst to the intermediate carbonium ion.

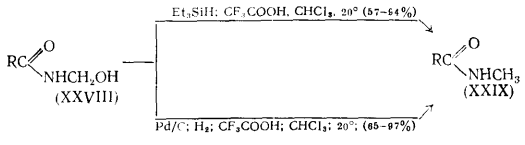
The use of anhydrous HF as the solvent, in which there is a possibility of ionic processes, permits the hydrogenation of even carboxylic acids—the class of compounds which are most difficult to hydrogenate. However, the reaction requires fairly severe conditions (300 atm) and a considerable amount of PtO_2. Dodecanecarboxylic acid is hydrogenated to a mixture of 21% of dodecane, 42% of dodecyl ether, and 6% of dodecyl dodecanoate. Acetic anhydride gives rise to ethyl acetate and diethyl ether. Succinic anhydride and oxalic acids are not reduced. It has been suggested[53] that acylium ions behave in this instance as hydride ion acceptors.

In trifluoroacetic acid, which is a weaker acid than anhydrous HF, carboxylic acids are not reduced over PtO_2. Acylium ions cannot apparently be formed in this solvent. However, the authors of the present review found[54] that, in the presence of equimolar amounts of trifluoroacetic anhydride, pivalic acid is reduced to a mixture of neopentyl alcohol, dineopentyl ether, and neopentyl trifluoroacetate in trifluoroacetic acid over PtO_2. The products of the reaction of the CF_3CO group are not formed under these conditions. The reaction evidently proceeds via the mixed anhydride of pivalic and trifluoroacetic acids, which dissociates with formation of the pivaloyl cation[53] (XXVII). The latter is reduced with abstraction of a hydride ion from the hydrogen activated by the catalyst:



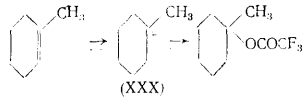
The reduction of pivalic acid in mixtures with trifluoroacetic anhydride by the triethylsilane–CF_3COOH system proceeds analogously[56]. As stated above, this system is widely used in ionic hydrogenation reactions.

N-Hydroxymethylamides of carboxylic acids (XXVIII) are converted into *N*-methylamides (XXIX) just as readily under the influence of triethylsilane as in hydrogenation in the presence of the Pd/C heterogeneous catalyst in trifluoroacetic acid[57]:



The ease of reduction of the amides (XXVIII) can be explained by the fact that the corresponding cations $RCONHCH_2^+$ are stabilised by conjugation with the free electron pair of the nitrogen atom.

A study of the competing hydrogenation of cyclohexene and 1-methylcyclohexene over Pd/C revealed[58] a change in the hydrogenation selectivity as a function of the acidity of the medium. In acetic acid both olefins are quantitatively hydrogenated, the hydrogenation of methylcyclohexene beginning only after all the cyclohexene has reacted. In trifluoroacetic acid only cyclohexene is hydrogenated, while methylcyclohexane was not detected in the reaction products. An increase of the acidity of the medium by the addition of 10% of toluene-*p*-sulphonic acid to trifluoroacetic acid leads to the quantitative hydrogenation of methylcyclohexene, while cyclohexene is hydrogenated only to the extent of 43%. These data are consistent with the ionic mechanism of the hydrogenation of methylcyclohexene under the conditions indicated. Indeed in trifluoroacetic acid methylcyclohexene combines with the acid almost quantitatively, being converted into the corresponding trifluoroacetate:



The equilibrium concentration of the carbonium ion (XXX) is low, and the adduct of hydrogen and palladium is probably a less active hydride ion donor than triethylsilane or ruthenium and platinum complexes (see Section III), and is incapable of reducing methylcyclohexene under these conditions. The addition of toluene-*p*-sulphonic acid increases sharply the concentration of carbonium (XXX) and promotes ionic hydrogenation. Under these conditions, cyclohexene combines irreversibly with CF_3COOH to form cyclohexyl trifluoroacetate, which entails a decrease of the yield of the hydrogenation product (cyclohexane).

On the basis of the foregoing, one may conclude that hydrogenation on heterogeneous catalysts in fairly acid media can proceed via an ionic mechanism, the catalysts behaving as hydride ion transferring agents.

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Catalytic ionic hydrogenation constitutes a new procedure for catalytic hydrogenation in which the unsaturated substrate is activated by the solvent (acid), which converts it into a protonated form (a carbonium ion), while the catalyst activates hydrogen and transfers it in the form of a hydride ion to the cation formed. This process permits catalytic hydrogenation with a selectivity characteristic of ionic hydrogenation reactions. There is reason to believe that many of the known hydrogenation catalysts can undergo a change in the mechanism of their action in media where there is a possibility of the formation of active protonated forms of unsaturated substrates and can behave as ionic hydrogenation catalysts.

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