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Ionic Hydrogenation

D.N.Kursanov and Z.N.Parnes

Papers on the ionic hydrogenation of a double bond, consisting in the successive addition of a proton and a hydride ion, are surveyed. The use of trifluoroacetic acid as donor of the proton and of triethylsilane as donor of the hydride ion has permitted the hydrogenation of alkenes, dienes, cyclopropane hydrocarbons, saturated and unsaturated ketones, aldehydes, quinones, and anils. Each class of compounds shows selectivity on ionic hydrogenation with the above pair of hydrogenating agents. The reaction extends to single bonds in the case of disulphides and ethers, which undergo ionic hydrogenolysis. Ideas on the mechanism of ionic hydrogenation are examined.

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I. INTRODUCTION

Interest in the hydrogenation of unsaturated organic compounds arose in an early stage of the development of organic chemistry. The outstanding event in this field was the discovery of hydrogenation on heterogeneous catalysts. This discovery led to the founding of new branches of organic and physical chemistry, and also acquired important industrial applications.

Intense study of hydrogenation reactions continues at the present time, the reason being the great practical and theoretical interest of hydrogenation. Each of the proposed methods of hydrogenation has fundamental limitations as well as its own merits. In particular, such methods frequently do not possess the required selectivity.

Reactions involving hydrogenation in the presence of complex organometallic catalysts under homogeneous conditions are being comprehensively investigated at the present time. Complex metal hydrides are being widely used in practical hydrogenation.

A special place among methods of hydrogenation is occupied by reactions involving stages of successive addition of a proton and of a hydride ion to the substance to be hydrogenated:

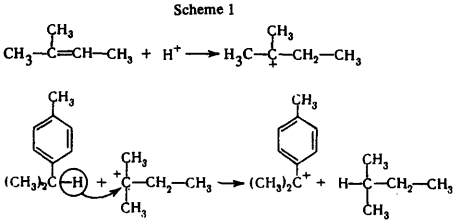
$$A{=}E + H^+ \rightleftarrows AH{-}E^+ \xrightarrow{+H^-} AH{-}EH\ .$$

The above is not the only possible path of ionic hydrogenation. A different sequence of stages can be imagined, the first stage being addition of the hydride ion, and addition of a proton to the resulting carbanion the second stage. Ionic hydrogenation reactions are also possible involving the transfer of two electrons and two protons. However, the present Review will be confined to reactions of ionic hydrogenation taking place solely by the first route, which for brevity we shall term reactions of ionic hydrogenation.

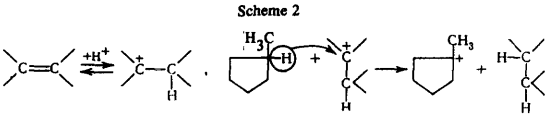
Several investigators have observed ionic hydrogenation as a side reaction in the study of the alkylation and the polymerisation of alkenes [1-3]. Nametkin and Abakumovskaya [4] as early as 1932 probably observed ionic hydrogenation by the action of sulphuric acid on cyclohexene. From the reaction products they isolated a hydrogenated dimer, obviously formed by interaction between the carbonium ion (formed by protonation of cyclohexene) and another cyclohexene molecule acting as a donor of a hydride ion.

Ipatieff and Pines [5-7], in an attempt to alkylate alkylbenzenes with alkenes in sulphuric or hydrofluoric acid, obtained good yields of alkanes (Scheme 1). In the above cases and in the work of Haaf and Koch [8] (Scheme 2) the proton donor was sulphuric or hydrofluoric acid, while the donor of a hydride ion was an alkane or an alkylbenzene.

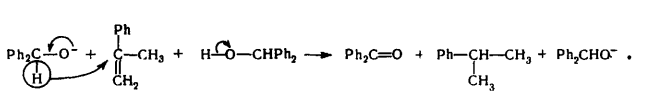
Scheme 1



Scheme 2



Vitt and Martinkova [9] effected a reaction closely similar to ionic hydrogenation on reducing the activated double bond in methylstyrene with diphenylmethanol and its alkoxide:



In contrast to the reactions considered earlier, in which the intermediate formation of carbonium ions is either demonstrable or extremely probable, it is difficult to assume such formation in the present reaction. Hydrogenation apparently takes place by a different mechanism in this case.

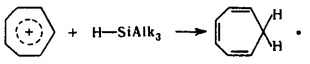
In ionic hydrogenation it is necessary that the proton donor should be sufficiently active to form a carbonium ion, but its activity should be limited, since it must not react with the hydride-ion donor to form molecular hydrogen. Besides, the carbonium ion should possess a certain stability, so that its lifetime is sufficient for

reaction with the hydride-ion donor. Yet increase in stability of the carbonium ion diminishes its rate of interaction also with the hydride donor, so that a more active source of hydride ions may be required in conducting the reaction. Ionic hydrogenation will yield only one product provided that the rate of interaction of the carbonium ion with the hydride-ion donor exceeds the rates of isomerisation and polymerisation of the carbonium ion.

It follows from the above that the choice of pair of hydrogenating agents is of decisive significance. Kursanov, Parnes, and their coworkers proposed trifluoroacetic acid and a trialkylsilane as a hydrogenating pair. These compounds hardly interact at all. Trifluoroacetic acid is a strong acid ($H_0 = -3.2$) having strong ionising and solvating properties [10]. The ability of alkyl- and aryl-silanes to split off a hydride ion has now been proved. The hydride activity of the hydrogen in a silane was already evident from the work of Whitmore, Pietrusza, and Sommer [11], who found that neopentyl chloride reacts with triethylsilane in the presence of aluminium chloride, being converted into isopentane:

$$(CH_3)_3CCH_2Cl + H{-}SiEt_3 \xrightarrow{AlCl_3} (CH_3)_3CHCH_2CH_3 .$$

More recent work has shown that a trialkylsilane transforms the tropylium ion into cycloheptatriene [12]:



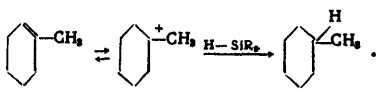
Corey and West [13] studied the exchange of hydrogen for halogen in a silane–triphenylmethyl halide system, and showed that the reaction occurs in those polar solvents in which the carbon–halogen bond undergoes dissociation (nitromethane, nitrobenzene, and dichloroethane), but not in non-polar solvents, in which dissociation is not observed. Diphenylmethyl halides and t-butyl chloride do not react with a silane. On the addition of boron tribromide to the reaction mixture, however, reaction takes place, in conformity with results for the dissociation of t-butyl chloride in the presence of boron tribromide [14].

Kursanov, Setkina, and Novikov [15] have established that phenylsilanes are capable of the ionic exchange of hydrogen with lithium tetradeuterioaluminate. Since lithium tetrahydroaluminate is a strong hydride-ion donor, the occurrence of hydrogen exchange is evidence of the hydride activity of the hydrogen in silanes.

II. IONIC HYDROGENATION OF HYDROCARBONS

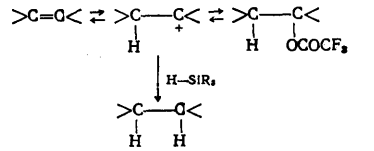
1. Alkenes

(*a*) Monoalkenes. Investigations have shown [16,17] that, with relative proportions of the components—alkene, triethylsilane, and trifluoroacetic acid—of 1 : 1 : 2 at 20–50°C, selective hydrogenation takes place of those alkenes in which branching occurs at the ethylenic carbon (such as methylcyclohexene, methylcyclopentene, 2-methylbut-2-ene, 2-methylpent-1-ene, etc.), saturated hydrocarbons being formed in 80% yield:



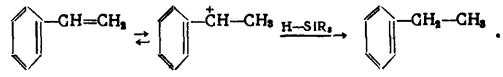
Unbranched alkenes and cycloalkenes, as well as alkenes in which there is no branching at the ethylenic carbon, are not hydrogenated.

This reaction was explained on the basis that ionic hydrogenation is undergone only by alkenes which, as a result of the protonation or dissociation of the corresponding trifluoroacetate, are able to form a sufficiently stable carbonium ion:

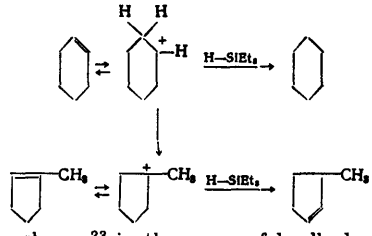


In a study of the isotopic exchange of hydrogen Setkina and Kursanov showed [18–21] that trifluoroacetates of secondary alcohols, unlike those of tertiary alcohols, do not form carbonium ions in trifluoroacetic acid. It was found, in full agreement with this, that, under the conditions of ionic hydrogenation, the trifluoroacetate of a tertiary alcohol reacts with a silane in trifluoroacetic acid (with equimolecular proportions of the components) to form a saturated hydrocarbon [16]. The trifluoroacetate of a secondary alcohol does not react with the silane under these conditions.

The fact that styrene, in which there is no branching at an ethylenic carbon atom, is hydrogenated to ethylbenzene is formally inconsistent with the above scheme. However, such behaviour of styrene is apparently due to the formation by its protonation of a carbonium ion which is stabilised by conjugation with the benzene ring †:



Similar behaviour is shown by indene ‡ and vinylcyclopropane [22], which on protonation also give carbonium ions, stabilised by the benzene ring and by the cyclopropane ring respectively. Further support for the scheme is provided by the slow ionic hydrogenation of unbranched alkenes and cycloalkenes when the acidity (the relative quantity of trifluoroacetic acid) is increased or when the reaction is conducted under more severe conditions (heating in sealed tubes at 140°C). Under these conditions, however, isomerisation products are also formed, and the yield of saturated hydrocarbons is very low.



It has been shown [23] in the case of 1-alkylcyclohexenes that the yield and the rate of ionic hydrogenation are independent of the number of atoms in the alkyl group.

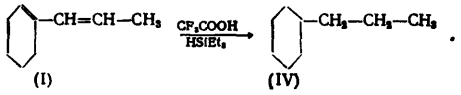
The fact that unbranched alkenes and cycloalkenes undergo ionic hydrogenation with increase in the acidity of the medium agrees well with results obtained by Setkina, Kursanov, and their coworkers [21], who have shown that the formation of a carbonium ion from trifluoroacetates depends on the acidity of the medium.

† It must be noted that the yield of ethylbenzene is small (~ 30%) in the case of styrene, probably because of the competitive effect of polymerisation.

‡ Indene polymerises under the reaction conditions, so that its yield is small.

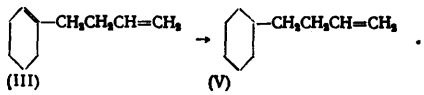
(*b*) Dienes. Various 1-alkenylcyclohexenes—1-propenylcyclohexene (I), 1-allylcyclohexene (II), and 1-but-3′-enylcyclohexene (III)—have been investigated[23] in studying the behaviour of dienes under conditions of ionic hydrogenation, when only one of the ethylenic bonds is able to yield a tertiary carbonium ion on protonation.

Propenylcyclohexene, which contains conjugated double bonds, is completely hydrogenated to propylcyclohexane (IV):



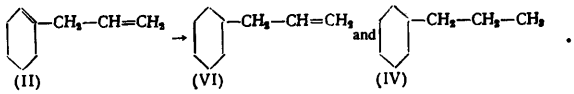
(I) (IV)

In 1-but-3′-enylcyclohexene (III), in which the multiple bonds are separated by two carbon atoms, only the branched ethylenic bond is hydrogenated, with the formation of but-3-enylcyclohexane (V):



(III) (V)

In the case of 1-allylcyclohexene (II), where the multiple bonds are separated by a single carbon atom, two hydrogenation products—allylcyclohexane (VI) and propylcyclohexane (IV)—are formed in the proportions 4 : 1 (see Table 1):



(II) (VI) (IV)

Table 1. Ionic hydrogenation of dienes (at 50°C for 10 h).

Initial alkene	Reaction product	Yield (%) with proportions of alkene : silane : acid	
		1:1:2	1:2:3
1-Propenylcyclohexene	propylcyclohexane	35	70
1-Allylcyclohexene	allylcyclohexane,	28	55
	propylcyclohexane	7	15
1-But-3′-enylcyclohexene	but-3-enylcyclohexane	30	65
Cyclohexadiene	cyclohexene	<2	

The formation of propylcyclohexane from allylcyclohexene may, perhaps, be explained by partial isomerisation of the latter, in the presence of trifluoroacetic acid, into propenylcyclohexene, which has been shown to be completely hydrogenated to propylcyclohexane.

Conjugated dienes containing no branchings undergo hardly any ionic hydrogenation. Under the reaction conditions cyclohexa-1,3-diene gives cyclohexene in less than 2% yield.

2. Aromatic Hydrocarbons

Trifluoroacetic acid and triethylsilane convert anthracene into 9,10-dihydroanthracene[24]. In benzene solution, with the hydrocarbon, silane, and acid in the proportions 1 : 1 : 3.5, the yield of dihydroanthracene at 50°C is 80% after 10 h. Benzene and naphthalene do not react even under considerably more severe conditions.

3. Cyclopropane Hydrocarbons

Cyclopropanes behave similarly to alkenes in many reactions[25]. In particular, they are able to form salts of carbonium ions on treatment with acids. They might therefore be expected to undergo ionic hydrogenation, and obey the same rules as alkenes.

It has in fact been shown[22] that *gem*-dimethylcyclopropanes are hydrogenated with cleavage of the ring to form saturated hydrocarbons (in yields up to 80%). Ethylcyclopropane does not undergo ionic hydrogenation. Phenylcyclopropane is hydrogenated to n-propylbenzene (in 70% yield) (see Table 2).

Table 2. Ionic hydrogenation of cyclopropane hydrocarbons.

Substituents in cyclopropane	Hydrocarbons obtained	Yield, %
1,1,2-Trimethyl	2,3-dimethylbutane,	75
	2-methylpentane	25
Phenyl	propylbenzene	70
Isopropyl	2-methylpentane	40

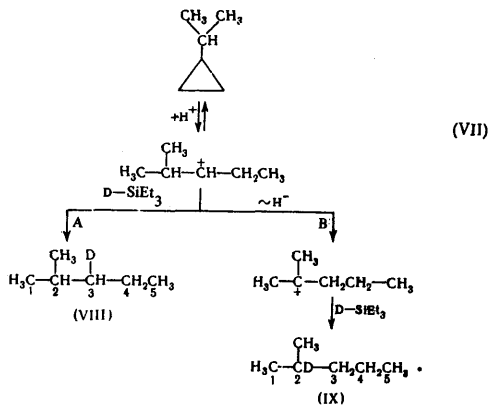
First of all it was necessary to establish the site of ring cleavage during ionic hydrogenation. It was found that the bond between the most and the least hydrogenated carbon atoms ruptures preferentially, as occurs in the action of mercury acetate and inorganic acids[26,27].

It is interesting that, in heterogeneous hydrogenation on palladium, the bond between the two most hydrogenated carbon atoms breaks[28], which leads to the formation of hydrocarbons isomeric with those obtained by ionic hydrogenation.

Isopropylcyclopropane also can be hydrogenated under these conditions, although protonation cannot lead directly to the formation of a tertiary carbonium ion. The capacity of isopropylcyclopropane for ionic hydrogenation may be due to the formation in this case, as an exception to the general rule, of a secondary carbonium ion, which reacts with the silicon hydride to give an alkane. However, the reaction could also occur in a different way, intramolecular hydride transfer producing isomerisation with formation of a tertiary carbonium ion, which reacts with the silane.

To settle this question a study has been made[29] of the reaction of isopropylcyclopropane (VII) with trifluoroacetic acid and deuteriotriethylsilane. If the secondary carbonium ion reacts with the silane, the 2-methylpentane formed by the reaction should contain deuterium in position 3 (VIII) (path A). If, however, a tertiary carbonium

ion reacts with the silane, the deuterium should be located in position 2 (IX) (path B):



(VII)

(VIII)

(IX)

Analysis of the proton magnetic resonance spectra has shown unambiguously that the deuterium is in position 2, which indicates that hydrogenation takes place by path B.

The ionic hydrogenation of isopropylcyclopropane is peculiar in occurring approximately to the extent of 40%, this yield not increasing with the duration of the experiment[30]. The formation of 2-methylpentane is accompanied by that of 1-ethyl-2-methylpropyl trifluoroacetate $CH_3CH(CH_3)CH(C_2H_5)OCOCF_3$. These results can be understood on the assumption that the cyclopropane ring is not opened in the first act of protonation, but a protonated cyclopropane is formed, the possibility of which in the first stage is widely accepted at the present time[31-33]. The protonated cyclopropane then undergoes cleavage, with the irreversible formation of the trifluoroacetate of the secondary alcohol. Partial isomerisation occurs at the same time as ring cleavage, and yields a tertiary carbonium ion, which reacts with the silane to give 2-methylpentane.

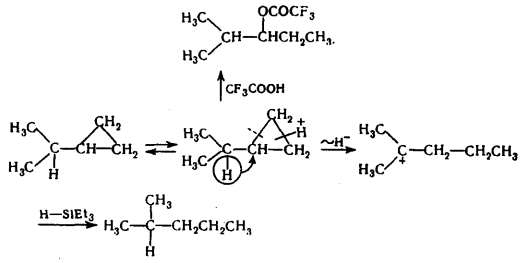


Table 3. Comparative results for the ionic hydrogenation of unsymmetrical trimethylcyclopropane and of 2,3-dimethylbut-2-ene.

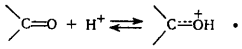
Hydrocarbon	Tim, h			
	1	3	6	12
1,1,2-Trimethylcyclopropane	27	32	49	65
2,3-Dimethylbut-2-ene	20	38	45	67

The rates of hydrogenation of 1,1,2-trimethylcyclopropane and of 2-methylpent-1-ene are approximately the same[29].

It is interesting to compare these data with results obtained by Peterson[34], who has found that butylcyclopropane reacts 300 times as rapidly as hex-2-ene with trifluoroacetic acid. From this he concludes that cyclopropane hydrocarbons react more rapidly than the corresponding alkenes with this acid. If this conclusion is regarded as generally applicable, our results indicate that protonation is not the rate-determining stage in the ionic hydrogenation of cyclopropanes.

III. IONIC HYDROGENATION OF THE CARBONYL GROUP

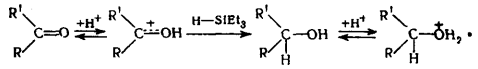
In acid media the carbonyl group in ketones and aldehydes is capable of protonation, the following equilibrium being established in the solutions:



Hydride transfer with formation of the alcohol might be expected to occur on addition of a hydride-ion donor to the reaction mixture. Ionic hydrogenation of the carbonyl group in ketones and aldehydes on treatment with trifluoroacetic acid and a silane is in fact observed. However, the composition of the reaction products depends on the structure of the initial ketones and aldehydes.

1. Ketones

Under conditions of ionic hydrogenation aliphatic ketones[35] (acetone, butan-2-one, cyclohexanone, phenylpropan-2-one) give a mixture of the alcohol and its trifluoroacetate. Aromatic and aliphatic–aromatic ketones (acetophenone, benzophenone, pentamethylacetophenone, Michler's ketone), however, undergo further reduction, the reaction product being a hydrocarbon. This difference in behaviour between aliphatic and aromatic ketones is easily explained by means of the general reaction scheme:



If R′ = Ar, further change is possible:

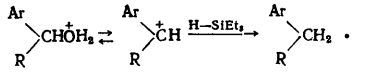


Table 4. Ionic hydrogenation of ketones.

Ketone	Ketone : silane : acid	Time, h	Yield, %	
			alcohol + trifluoroacetate	hydrocarbon
Butan-2-one	1:1.5:3	10	80	—
Cyclohexanone	1:1:2	10	55	—
Cyclohexanone	1:2.5:2	20	75	—
Acetophenone	1:2.5:2	10	—	70
Benzophenone	1:2.5:2	15	—	94

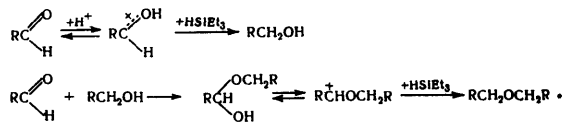
Protonation of the resulting alcohol followed by elimination of water may lead to the formation of secondary carbonium ions. In the case of aromatic and aliphatic–aromatic ketones, however, the carbonium ion is stabilised by the adjacent benzene ring(s). Such a carbonium ion is shown by the ionic hydrogenation of styrene[17] to react with a

silane to form a hydrocarbon. Similarly, the hydrogenation of cyclopropyl methyl ketone results in the formation of ethylcyclopropane and *trans*-pentene, the latter of which has been shown earlier to appear in attempts at the ionic hydrogenation of ethylcyclopropane.

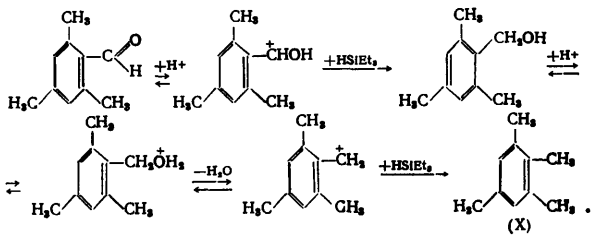
The introduction of electron-acceptor substituents into the benzene ring of an aromatic ketone should diminish the reaction velocity. In fact, Michler's ketone forms bis-*p*-dimethylaminophenylmethane in 75% yield after being heated with a large excess of acid at 80°C for 40 h, whereas benzophenone is converted into diphenylmethane at 55°C almost completely after 15–20 h.

2. Aldehydes

Aldehydes react extraordinarily rapidly with triethylsilane in trifluoroacetic acid to form a mixture of an ether and an alcohol (and the trifluoroacetate of the latter)[36], the amounts of ether and alcohol being approximately the same in the case of aliphatic aldehydes, whereas aromatic aldehydes are almost entirely converted into ethers (e.g. benzaldehyde gives 80% of dibenzyl ether immediately the reactants are mixed). Such a result cannot be explained by condensation of alcohol formed in the first stage, since in trifluoroacetic acid alcohols form little or no ether at all. Moreover, conducting the ionic hydrogenation of an aldehyde in the presence of an alcohol having a different hydrocarbon radical yields an unsymmetrical ether. These facts suggest that production of the ether involves the intermediate formation of a hemiacetal:



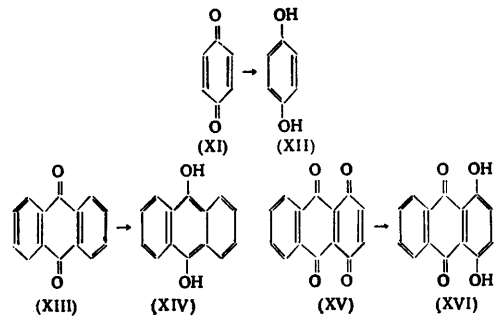
The benzyl cation might be expected to be stable, so that its lifetime would be sufficient for reaction with the silane, and consequently the ionic hydrogenation of benzaldehyde would yield toluene. However, it has been shown[36] that toluene is not formed under these conditions. Hanazaki and Nagakura[37] showed that the stability of the 2,4,6-trimethylbenzyl cation is comparable with that of the α-methylbenzyl cation, which is formed by the protonation of acetophenone. From this it could be expected that 1,2,3,5-tetramethylbenzene would be formed by the ionic hydrogenation of 2,4,6-trimethylbenzaldehyde. In fact, this hydrocarbon (X) is formed under these conditions in 70% yield:



(X)

3. Quinones and αβ-Unsaturated Ketones

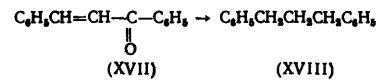
It was of interest to ascertain the mutual influence of carbon–carbon and carbon–oxygen multiple bonds conjugated with one another. The first compounds chosen for investigation were quinones[38]. Study of the ionic hydrogenation of quinones has shown that benzoquinone (XI) is converted into quinol (XII), anthraquinone (XIII) into anthraquinol (XIV), and anthra-1,4:9,10-diquinone (XV) into quinizarin (XVI):



(XI) (XII) (XIII) (XIV) (XV) (XVI)

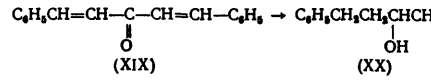
It is interesting that the resulting quinizarin does not undergo further ionic hydrogenation either on prolonged heating of the mixture or on the addition of trifluoroacetic acid.

The ionic hydrogenation of 1,3-diphenylpropenone (XVII) leads to the formation of 1,3-diphenylpropane (XVIII) in 80% yield:



(XVII) (XVIII)

The hydrogenation of 1,5-diphenylpenta-1,4-dien-3-one (XIX) gives 1,5-diphenylpentan-3-ol (XX) as the main product[39]:



(XIX) (XX)

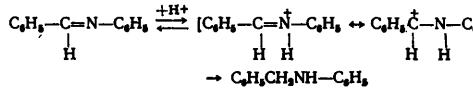
4. Carboxylic Acids

The carbonyl group in carboxylic acids and esters does not undergo ionic hydrogenation.

IV. IONIC HYDROGENATION OF A C=N BOND

The electronic structures of the C=N and C=O bonds have much in common, this being responsible for the similarity in their chemical properties, apparent especially in addition reactions. From this it could be supposed that azomethines would undergo ionic hydrogenation to form amines.

It has in fact been found[40] that benzylideneaniline and *o*- and *p*-benzylidenetoluidines react with triethylsilane and trifluoroacetic acid. With molar proportions of anil, silane, and acid of 1:1:3 at 60–70°C the amines are formed in yields respectively of 78%, 86%, and 95% after 60 min.



In contrast to the above anils, cyclohexylidene-*o*-toluidine does not form an amine under these conditions. The reason for such behaviour requires further study.

V. IONIC HYDROGENOLYSIS

The fact that cyclopropane hydrocarbons containing no multiple bonds undergo ionic hydrogenation enables us to hope that certain single bonds may be hydrogenated under these conditions. Compounds containing an atom having a lone pair of electrons were chosen to test this hypothesis. Addition of a proton produces a cation. If then a bond is ruptured with formation of a new cation, it is in principle possible for this to interact with a hydride-ion donor. The concentration of this cation must be sufficient for such interaction to occur. The first class of such compounds to be studied was the disulphides.

Table 5. Ionic hydrogenolysis of disulphides.

Disulphide	Yield of thiol, %
$(t\text{-}C_4H_9)_2S_2$	67
$(C_6H_5)_2S_2$	45
$(4\text{-}CH_3OC_6H_4)_2S_2$	73.5
$(2\text{-}NO_2C_6H_4)_2S_2$	0
$[2.4\text{-}(NO_2)_2C_6H_3]_2S_2$	0

1. The S–S Bond

Disulphides have been found [41] to interact with trifluoroacetic acid and triethylsilane, the S–S bond being cleaved and hydrogenated to form the corresponding thiols as the sole products of the reaction. Unchanged disulphide was isolated.

Table 6. Interaction of sulphenyl chlorides with triethylsilane.

Sulphenyl chloride	Solvent	Reaction product (yield, %)	Sulphenyl chloride	Solvent	Reaction product (yield, %)
C_6H_5SCl	none	disulphide (95)	$2\text{-}NO_2\text{-}4\text{-}ClC_6H_3SCl$	CF_3COOH	disulphide (65), thiol (30)
C_6H_5SCl	hexane	disulphide (slow reaction)	$4\text{-}NO_2C_6H_4SCl$	hexane	disulphide (slow reaction)
S_2Cl_2	none	no reaction			
S_2Cl_2	CF_3COOH	S, $CF_3COOSiEt_3$			
$2\text{-}NO_2C_6H_4SCl$	CCl_4	no reaction	$4\text{-}NO_2C_6H_4SCl$	CF_3COOH	disulphide (98)
$2\text{-}NO_2C_6H_4SCl$	HCOOH	disulphide (quantitative)	$2.4\text{-}(NO_2)_2C_6H_3SCl$	CF_3COOH	no reaction
$2\text{-}NO_2C_6H_4SCl$	CF_3COOH	disulphide (76), thiol (18)			

Separate experiments had shown that trifluoroacetic acid does not visibly react with a disulphide in the absence of a silane, and in the absence of the acid the silane does not react with the disulphide.

The scheme

$$RSSR + CF_3COOH \rightleftarrows RSH + [RS]^+CF_3COO^-$$
$$[RS]^+CF_3COO^- + H{-}SiEt_3 \rightarrow RSH + (SiEt_3)OCOCF_3$$
$$RSSR + H{-}SiEt_3 + CF_3COOH \rightarrow 2RSH + CF_3COOSiEt_3$$

was proposed for the reaction. It is supported by the fact that sulphenyl chlorides, which are potential sources of the sulphenium ion [42], react with triethylsilane under mild conditions, to give a theoretical yield of reduction products [43] (see Table 6). The general scheme of the reaction is

$$RSCl \overset{+H^+}{\rightleftarrows} [RS]^+ + HCl;\ [RS]^+ + H{-}SiEt_3 + CF_3COOH \rightarrow$$
$$\rightarrow RSH + CF_3COOSiEt_3;\quad RSH + RSCl \rightarrow RSSR + HCl\ .$$

Formation of the thiol precedes that of the disulphide, since nitro-disulphides do not react with the silane in trifluoroacetic acid (Table 5). The fact that a thiol results from the reaction means that its rate of formation exceeds the rate of interaction with the initial sulphenyl chloride.

Table 5 shows that electron-donor substituents increase the yield of thiols, whereas electron-acceptor substituents prevent the reaction. Increase in acidity raises the yield of thiol. This is consistent with the view that the first act in the reaction is protonation, leading to rupture of the S–S bond. It is noteworthy that the interaction of sulphenyl chlorides with trifluoroacetic acid and a silane involves hydrogenation of the S–Cl single bond with the formation of HCl and HSR.

2. The C–O Bond

It has already been noted that aromatic and aliphatic–aromatic alcohols undergo ionic hydrogenation of the C–O bond to form a hydrocarbon and water. Results obtained for the ionic hydrogenation of ketones and aldehydes show that ethers do not undergo this reaction under mild conditions. With a large (tenfold) excess of trifluoroacetic acid, however, certain ethers are able to react with a silane to form a hydrocarbon [44].

Table 7. Ionic hydrogenolysis of ethers.

Ether	Hydrocarbon	Yield, %
$t\text{-}C_4H_9OC_2H_5$	$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3$	60
$(C_6H_5)_2CHOCH(C_6H_5)_2$	$C_6H_5CH_2C_6H_5$	60
$C_6H_5CH_2OC_2H_5$	$C_6H_5CH_3$	7
$C_6H_5CH_2OCH_2C_6H_5$	$C_6H_5CH_3$	3

Table 7 indicates that ionic hydrogenation occurs with those ethers which, on protonation followed by rupture of the C–O bond, are capable of forming a relatively stable carbonium ion. The hydrogenolysis of an ether can be represented by the following scheme

$$ROR' \overset{+H^+}{\rightleftarrows} \underset{\displaystyle H}{\overset{+}{\underset{|}{R}}}OR' \rightarrow ROH + R'^+$$
$$R'^+ + H{-}SiEt_3 \rightarrow R'H\ .$$

VI. MECHANISM OF IONIC HYDROGENATION

The ionic hydrogenation of a multiple bond comprises two acts—addition of a proton to form a cation and transfer to the latter of a hydride ion to form the hydrogenation product—the relative rates of which depend on the structure of the reactants. The sequence of the acts may even be reversed as a consequence of this structure. Such a

reaction was reported by Knunyants, Cheburkov, and Aronov [45], who hydrogenated perfluoro-2,4-dimethylpenta-2,3-diene by the action of hydrogen sulphide and sodium hydrogen sulphide in sulpholan. These workers considered it probable that the first act in the reaction was the removal by the allene of a hydride ion from the hydrosulphide, followed by addition of a proton from the hydrogen sulphide:

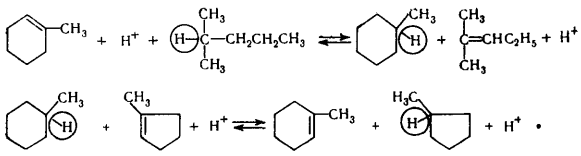
$$(CF_3)_2C{=}C{=}C(CF_3)_2 \xrightarrow[\text{sulpholan}]{H_2S+NaHS} (CF_3)_2CHCH{=}C(CF_3)_2 + S \ .$$

It is quite obvious that triethylsilane is not the only possible hydride-ion donor in ionic hydrogenation, just as trifluoroacetic acid is not the sole possible donor of protons.

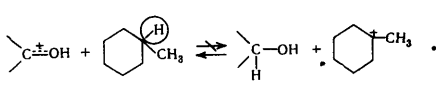
1. Donors of Hydride Ions

In the consideration of possible hydride-donors it must be borne in mind that the less stable a carbonium ion the more active it is as a hydride-ion acceptor but the shorter its lifetime (or the less probable its formation in a kinetically free state). And conversely, the more stable carbonium ions live longer, but are less active. Compounds which can act as hydride-ion donors in other reactions are of interest for use as possible donors of hydride ions in ionic hydrogenation. Examples of such compounds are saturated hydrocarbons containing a tertiary carbon atom. Their ability to act as hydride-ion donors has been demonstrated by Ipatieff and Pines [5-7], Haaf and Koch [8], Kramer [46], and Setkina et al. [47].

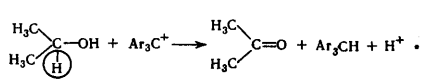
A mixture of four hydrocarbons—methylcyclohexene, methylcyclohexane, 2-methylpentane, and 2-methylpent-2-ene—was isolated from the reaction between methylcyclohexene and 2-methylpentane in trifluoroacetic acid. Similarly, the interaction between methylcyclopentene and methylcyclohexane in trifluoroacetic acid yielded a mixture of methylcyclopentene, methylcyclopentane, methylcyclohexane, and methylcyclohexene:



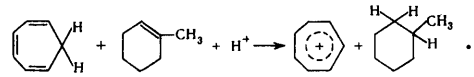
However, it has proved impossible to use a hydrocarbon containing a tertiary carbon atom as a hydride-ion donor to hydrogenate the carbonyl group. The apparent explanation is that the carboxonium ion is too stable to detach a hydride ion from the hydrocarbon, while the tertiary carbonium ion which should result is less stable. Since no reaction takes place between a hydrocarbon containing a tertiary carbon atom and a protonated ketone, it might be expected that the reverse reaction between an alcohol and a tertiary carbonium ion would occur:



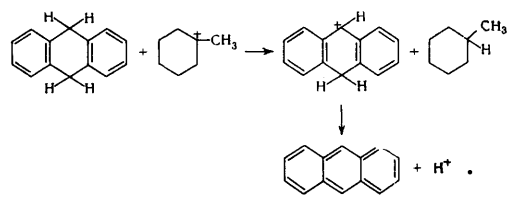
Actually, the reaction discovered by Bartlett [48] between an aliphatic alcohol and a triarylmethanol in sulphuric acid is in effect a reaction between an alcohol and a carbonium ion:



We have studied cycloheptatriene as another hydride-ion donor in ionic hydrogenation. The ability of cycloheptatriene to donate a hydride ion is due to the fact that the stable aromatic ion tropylium is thereby formed. Cycloheptatriene has been used as a hydride-ion donor in various reactions by Kursanov and Vol'pin [49], Dauben [50], Volz [51], and other workers [52]. It has been found [16,17] to react with methylcyclohexene in trifluoroacetic acid to form methylcyclohexane. Owing to competition by the polymerisation of cycloheptatriene in acid medium, however, the yield of the saturated hydrocarbon is low (~5%):



9,10-Dihydroanthracene proved to be a good hydride-ion donor in ionic hydrogenation. Its ability to donate a hydride ion was demonstrated by Braude and Linstead [53], Bonthron and Reid [54], and Nenitzescu and Balaban [55]. Kursanov, Parnes, and Bolestova [24] have found that 9,10-dihydroanthracene is able to give up a hydride ion to methylcyclohexene protonated with trifluoroacetic acid. This results in the formation of anthracene and methylcyclohexane (yield 70%):



The use of dihydroanthracene as a hydride-ion donor has enabled a stronger acid than trifluoroacetic to be used, which is impossible with triethylsilane, since the latter reacts with strong acids with the evolution of hydrogen.

An attempt to use acenaphthene as hydride-ion donor has shown merely the theoretical possibility of such a reaction, since the yield of saturated hydrocarbon is very small.

It follows from the above results that various hydride-ion donors can be employed in the ionic hydrogenation of alkenes, but so far the best results have been achieved with trialkylsilanes and 9,10-dihydroanthracene.

Methyldiethylsilane and mono-, di-, and tri-phenylsilanes have also been used as hydride-ion donors. In the series of phenylated silanes the ability to transfer a hydride ion diminishes in the sequence $(C_6H_5)_2SiH_2 > C_6H_5SiH_3 > (C_6H_5)_3SiH$ [17]. A similar relationship had been established earlier by Kursanov, Setkina, and Novikov [15].

2. Donors of Protons

Trifluoroacetic acid has been used as proton donor in ionic hydrogenation because, while being a strong acid ($H_0 = -3.2$), it possesses great ionising and solvating power [10]. Study of the effect of the quantity of acid on the yield of alkane has shown that the reaction takes place only in the presence of excess of acid, and is strongly accelerated by increase in this excess.

With a hundredfold excess of acid, isomerisation also becomes appreciable, this being absent when smaller quantities of trifluoroacetic acid are used. The work of Kursanov and Setkina [18-21] on the isotopic exchange of hydrogen in trifluoroacetates has shown the influence of acidity on the formation of carbonium ions from trifluoroacetates. These workers have established that the rate of

formation of carbonium ions is equal to the rate of formation of alkenes. It has also been found that, with $H_0 = -3.2$, trifluoroacetates of tertiary alcohols form carbonium ions. Those of secondary alcohols do not undergo heterolysis at this acidity, and carbonium ions are not formed. With increase in acidity, however, secondary carbonium ions are, nevertheless, formed.

Table 8. Effect of quantity of trifluoroacetic acid on yield of methylcyclohexane.

Molar ratio of acid to methylcyclohexene	Yield of methylcyclohexane, %	Duration of expt., h
1	4	120
2	73	120
10	78	1
100	80	0.3

3. Mechanism of the Hydride Migration

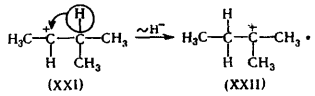
Hypotheses on the intramolecular and intermolecular transfer of a hydride ion were put forward long ago, but their proof encountered considerable difficulties because the hydride-ion acceptor was most often an unstable carbonium ion, the appearance of which during the reaction was very difficult to establish.

The hypothesis of hydride migration would appear to be inconsistent with the absence of molecular hydrogen evolution when the reaction is conducted in acid medium. Actually, in this case it would be necessary to expect that gaseous hydrogen would be produced by the process

$$H^- + H^+ \rightarrow H_2 .$$

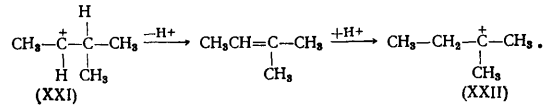
However, this discrepancy can be explained on the assumption that hydride migration takes place without the formation of a kinetically independent hydride ion, the transfer of a hydride ion taking place directly from molecule to molecule (or ion). In fact, a sufficiently active acceptor should be present to detach a hydride ion from a molecule. The solvated proton of an acid may not possess the required activity, so that it will not react with the hydride-ion donor and molecular hydrogen will not be formed. However, it is then impossible to check the act of hydride-ion transfer, which may involve the proton and the two electrons migrating in either one or more steps.

The question of the mechanism of the act of hydride-ion transfer is part of the general problem of establishing the mechanism of nucleophilic substitution. Just as the latter can be regarded as occurring in two steps (an electron, followed by an atom), hydride transfer can be divided into two steps (electron and hydrogen atom). However, whether hydride migration actually takes place in two steps, and if so in what cases, will be shown by future research. It must be stressed that the question of whether hydride transfer takes place in one or two stages is a matter of the relative rates of these steps. If the rate of the second step—transfer of a hydrogen atom to an already formed radical—considerably exceeds the rate of the first step, this is identical for chemical reactions to a one-step hydride transfer:



(XXI) (XXII)

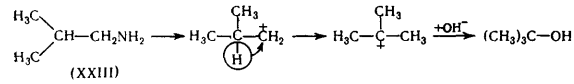
However, the same result will be achieved if the carbonium ion (XXI), having lost a proton, is converted into an alkene, which adds a proton from the medium to form a tertiary carbonium ion (XXII):



(XXI) (XXII)

Cannell and Taft showed[56] that under certain conditions the isomerisation of a carbonium ion cannot be explained by the intermediate formation of an alkene. They studied the deamination of isobutylamine (XXIII) by the action of nitrous acid in a medium containing deuterium oxide. The main reaction product was t-butyl alcohol: i.e. the initially formed isobutyl cation had rearranged to a t-butyl cation. If isomerisation occurred as a result of intramolecular hydride transfer (Scheme 3), the t-butyl alcohol formed should not contain deuterium bound to carbon. If, on the other hand, isomerisation were a consequence of the reversible formation of an alkene (Scheme 4), the t-butyl alcohol should contain deuterium bound to carbon (XXIV).

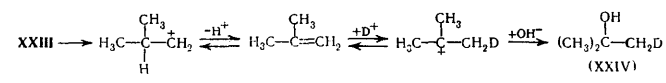
Scheme 3



(XXIII)

It was found that, if the reaction is conducted at pH > 3 and 38°C, the t-butyl alcohol will not contain deuterium bound to carbon. Since alkenes (but-1-ene, but-2-ene, isobutene) are formed as well as the alcohol in the reaction, it is obvious that no protonation of the alkenes takes place under the experimental conditions, isomerisation of the carbonium ion being a consequence of hydride transfer (Scheme 3). In a more acid medium, in which protonation of alkenes takes place, isomerisation of the carbonium ion will occur both as a consequence of intramolecular hydride migration and as a consequence of reversible formation of alkenes (Scheme 4).

Scheme 4



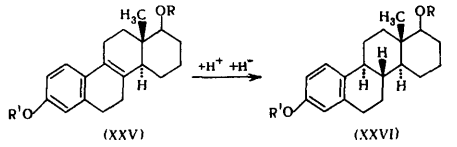
(XXIV)

From the above work it may be concluded that in any case, under certain conditions, isomerisation of the carbonium ion will occur as a result of intramolecular hydride transfer.

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The stereochemical study of ionic hydrogenation is of great interest. Carey and Tremper have shown[57] that the ionic reduction of 1-phenyl-4-t-butylcyclohexene yields a mixture of *trans*- and *cis*-1-phenyl-4-t-butylcyclohexanes. If a disubstituted silane is used as hydride-ion donor, the *trans* : *cis* ratio is ~ 4 independently of the nature of the substituents (alkyl, aryl). If three substituents are attached to the silicon atom, this ratio is ~ 2. This fact is explained by these workers on the basis that the transition state in the *trans*-form is sterically more difficult for trisubstituted silanes. The *trans*-form is the predominant product in all cases because it is thermodynamically more favourable.

It has been shown quite recently[58] that the ionic hydrogenation of $\Delta^{8(9)}$-dehydro-D-homo-oestrogens (XXV) occurs stereospecifically to give D-homosteroids of *trans-anti-trans*-configuration (XXVI):



(XXV) (XXVI)

Thus the reaction of ionic hydrogenation is of great interest for theoretical organic chemistry, and is also a convenient method for the selective reduction of various classes of organic compounds.

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Institute of Organoelementary Compounds,
USSR Academy of Sciences, Moscow