THE HYDRIDE-TRANSFER REACTION

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I. INTRODUCTION

A common phenomenon in organic chemistry is the transfer of a hydrogen atom with its pair of electrons from one carbon to another. This reaction, the hydride-transfer reaction, has the characteristics that the hydrogen transferred does not exchange with the labile protons in the medium nor does it react with these labile protons to form molecular hydrogen.

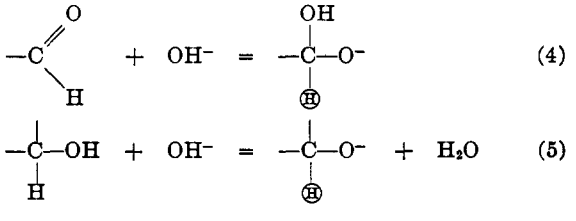
The carbon accepting the hydride ion must have an actual or potential open sextet of electrons; thus the reaction may fall into the realm of carbonium-ion chemistry. However, carbonium ions are not necessarily required because any unsaturated carbon atom (as in C=C, C=O, etc.) can potentially shift electrons to give an open sextet. This potentiality can develop by addition of a proton to the unsaturated system as in equations 1 to 3, and in fact the hydride-transfer reactions are frequently acid-catalyzed.

$$>C{=}O + H^+ = >\overset{+}{C}{-}OH \quad (1)$$

$$>C{=}C< + H^+ = >\overset{+}{C}{-}CH< \quad (2)$$

$$-C{\equiv}N + H^+ = -\overset{+}{C}{=}NH \quad (3)$$

The carbon donating the hydride ion is also subject to catalytic acceleration. A negative charge generated adjacent to a carbon atom holding hydrogen will increase its tendency to release the hydrogen as a hydride ion. This negative charge can be generated either by addition of a negative ion, as exemplified in equation 4, or by proton removal, as in equation 5. The hydride to be donated is circled in both equations.



(4)

(5)

Since hydride-transfer reactions involve either ions or polar transition states, owing to the heteropolar nature of the bond changes, the reactions customarily occur in polar solvents or at least in polar micelles in a nonpolar solvent. Also, since the two participating carbon atoms are separated only by the migrating hydride ion, the reaction can be hindered by severe steric crowding.

The transfer of a hydride ion results in oxidation-reduction. Possible hydride donors and their concomitant products are as follows:

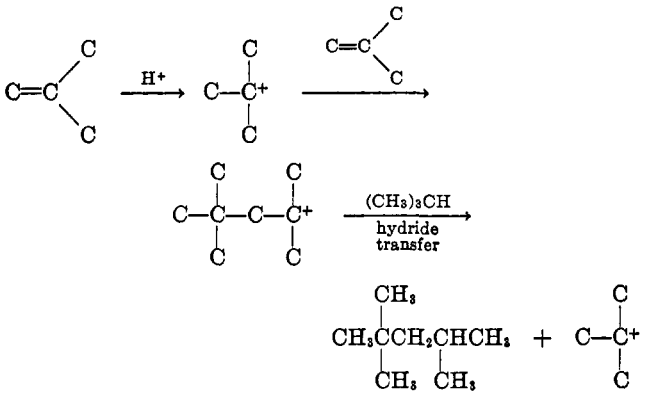
Hydride Donors	Product (Hydride Acceptors)
Hydrocarbons	Alcohols or derivatives (olefins, ethers, etc.)
Alcohols	Aldehydes or ketones
Aldehydes	Acids
Formic acid	$CO_2 + H^+$

The products in the above table are naturally the hydride acceptors. The above four half-reactions can combine to give a number of possible reaction types, most of which have been observed.

II. HYDROCARBONS AS HYDRIDE DONORS

The reaction of hydrocarbons as hydride donors with olefins, in their protonated forms, as hydride acceptors is of great importance in the industrial production of high-octane gasoline. A typical example is shown in the following familiar sequence. A large number of reactions of this type are known and have been summarized (11).

The nature of these reactions has been elucidated (50) by showing that the reaction of isobutane with deuterium sulfate leads to the formation of isobutane with a maximum of nine hydrogen atoms exchanged. The tenth hydrogen atom completely failed to equilibrate.



Under the same conditions this tenth hydrogen atom, and only this hydrogen atom, rapidly exchanged with

$$(CH_3)_3CH \xrightarrow{D_2SO_4} (CD_3)_3CH$$

one hydrogen, the tertiary hydrogen atom, in isopentane (50). Thus in 97 per cent sulfuric acid hydride transfer is occurring only between the tertiary carbon atoms in isobutane and isopentane, and the reaction can be formulated as a hydride transfer between the hydrocarbons and the protonated olefins (*tert*-alkyl cations) present in small amounts in these systems, as shown below (50).

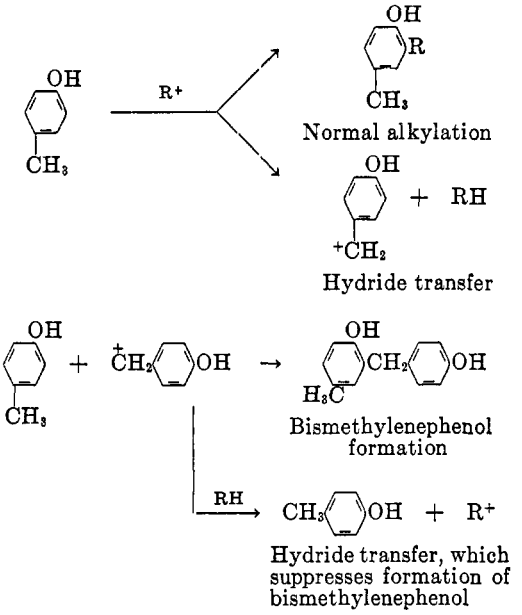
$$(CH_3)_3CH + CH_3CH_2CD(CH_3)_2 \xrightleftharpoons{H_2SO_4} (CH_3)_3CD + CH_3CH_2CH(CH_3)_2$$

The hydride-transfer reactions between aliphatic tertiary carbon atoms can occur with amazing rapidity. Bartlett, Condon, and Schneider (6) showed that in the reaction represented by equation 6 the *tert*-amyl bromide was formed in less than 10^{-3} sec. at 25°C., using aluminum bromide as the catalyst. A similar result was obtained when isopropyl chloride was used in place of *tert*-butyl chloride (6).

$$(CH_3)_3CCl + (CH_3)_2CHCH_2CH_3 \xrightarrow{AlBr_3} (CH_3)_3CH + (CH_3)_2CBrCH_2CH_3 \quad (6)$$

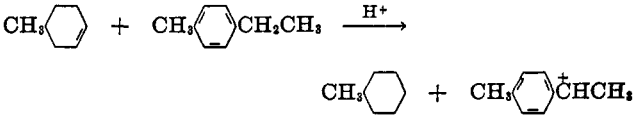
Although hydride transfers involving secondary alkyl cations take place in aluminum halide systems (6, 11), they have not been reported in sulfuric acid despite the fact that rearrangements involving *sec*-alkyl cations do occur (11, 23). The alkyl cations in sulfuric acid may well be a somewhat different species from those in aluminum halide media. In sulfuric acid the cations could be bonded to the sulfuric acid similarly to the "oxygen bonding" which has been postulated to interpret the activity coefficient behavior of arylmethyl cations (19).

The donation of hydride to arylmethyl cations by aliphatic hydrocarbons has not been directly observed, presumably owing to the greater stability of the arylmethyl cations relative to the aliphatic alkyl cations which would necessarily be produced. However, such a step was postulated to explain the action of isopentane when it suppressed the formation of bismethylenephenols in the alkylation of *p*-cresol. Alkylation of *p*-cresol with tertiary alkylating agents proceeds in good yield with 1–25 mole per cent boron trifluoride, but with 50 mole per cent boron trifluoride the reaction becomes more complex. Bismethylenephenols appear, presumably owing to the generation of benzyl cations by hydride abstraction from the methyl group in *p*-cresol by the *tert*-alkyl cation. The benzyl-type cation alkylates other *p*-cresol molecules, yielding bismethylenephenols (45). This side reaction is suppressed by the addition of isopentane, which acts by donating hydride to the intermediate benzyl-type cations, thus destroying them and preventing the formation of bismethylenephenols as outlined in the diagram below (45), in which R = $CH_3CH_2\overset{|}{C}(CH_3)_2$.

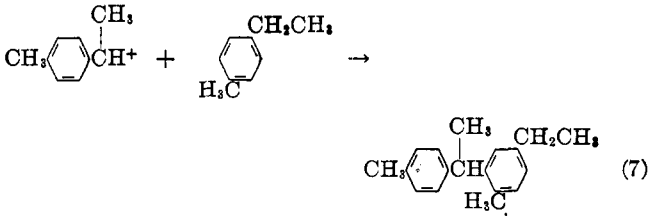


The reverse process, the reaction of arylalkanes with aliphatic alkyl cations, has been proposed to explain the formation of bismethylenephenols in the scheme above, as well as the formation of diarylmethanes in the alkylation of alkylbenzenes with aliphatic olefins. The olefin as its cation abstracts hydride ion from the alkylbenzene to yield an arylalkyl cation. This subsequently reacts with the alkylbenzene to yield diarylmethane derivatives. This reaction becomes dominant when 4-methyl-, 2,4-dimethyl-, and 2,4,6-trimethylethylbenzenes are alkylated with 4-methylcyclohexene (52) as exemplified in the equations below.

Hydride transfer:



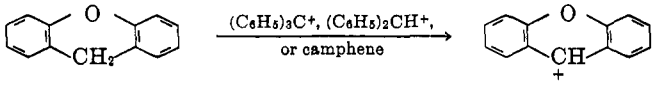
Alkylation:



(7)

It is also the dominant reaction when a number of 4-methylalkylbenzenes are alkylated with 4-methylcyclohexene (37, 52, 53, 54). Alkylation of *p*-xylene or 4-chlorotoluene with 1,1-dichloroalkanes and *tert*-butyl chloride also yields diarylmethanes among other products, and these diarylmethanes again arise through hydride-transfer reactions (63).

The transfer of hydride ion from arylmethanes to arylmethyl cations or aliphatic alkyl cations has been directly observed. Xanthene (I) is converted to the xanthyl cation (II) in over 80 per cent yield by phosphoric acid solutions of triphenylmethyl cation, diphenylmethyl cation, or camphene. The xanthyl cation was identified by its absorption spectrum (22).



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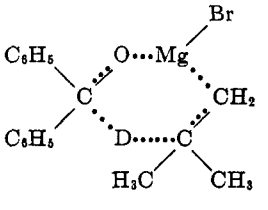
Cycloheptatriene reacts with the triphenylmethyl cation to form the cycloheptatrienyl cation and triphenylmethane (15). The triphenylmethyl cation can similarly abstract hydride from $(C_7H_8)Mo(CO)_3$ to yield $(C_7H_7^+)Mo(CO)_3$ (16).

The reaction of benzyl alcohol with benzene, toluene, or diphenylmethane, in the presence of aluminum chloride as catalyst, yields anthracene derivatives (71). Dihydroanthracenes would be the direct product of this alkylation and the anthracenes ultimately produced must arise by some oxidative process such as abstraction of hydride from the dihydroanthracenes by benzyl cations.

Two groups of reactions exemplify the donation of hydride by hydrocarbons to carbonyl compounds. First is the reduction of carbonyl compounds to alcohols by certain Grignard reagents (43, 48, 51). The nature of these reactions was elucidated by showing that in the reduction of benzophenone to benzhydrol by isobutylmagnesium bromide (equation 8), only deuterium from

$$(C_6H_5)_2C{=}O + (CH_3)_2CDCH_2MgBr \rightarrow (C_6H_5)_2CDOH + (CH_3)_2C{=}CH_2 \quad (8)$$



the β-position, and not from the α- or γ-position, was transferred to the benzophenone (26). The transition state was formulated in the usual cyclic manner, as shown in the formula below equation 8.

The aromatization of partially hydrogenated aromatics by quinones has been formulated as a hydride-transfer reaction (10). A number of examples have been reported (10).

A single example has been reported whereby an acid derivative was reduced to an aldehyde by a hydrocarbon (4). Acetyl chloride acetylates decalin in the presence of aluminum chloride. The acetylation presumably first requires the removal of hydride from decalin to produce an olefinic bond capable of undergoing acetylation. Some form of CH_3CO^+ would presumably be responsible for this hydride removal; this interpretation was supported by the isolation of acetaldehyde as a reaction product (4).

The great variety of olefin isomerizations are generally interpreted as internal transfer of hydride, since this interpretation best explains the acid catalysis. Since these reactions have been reviewed (11), they will be omitted from this review.

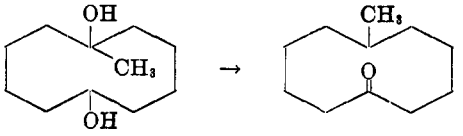
III. ALCOHOLS AS HYDRIDE DONORS

Primary and secondary alcohols are excellent hydride donors, as shown by the disproportionation of diarylmethanols to diarylmethanes and diarylketones. 4,4′-Dimethoxydiphenylmethanol is converted to 4,4′-dimethoxybenzophenone and 4,4′-dimethoxydiphenylmethane by acids. When the reaction was run in CCl_3COOD, no deuterium was incorporated into the diarylmethane, confirming the nature of this reaction as hydride transfer (7). Other examples are the conversion of benzhydrol to diphenylmethane and benzophenone (12, 29), of 9-xanthenol to xanthene and xanthone (7, 66), and of 2,3,4,5,6-pentamethylbenzyl alcohol to hexamethylbenzene and presumably pentamethylbenzaldehyde, which was unstable under the reaction conditions (21). In all of these disproportionations it is entirely possible that the hydride transfer takes place intramolecularly in an intermediate ether (7).

The conversion of benzhydryl ether in deuterium perchlorate to benzophenone and diphenylmethane, containing no deuterium, was interpreted to indicate internal hydride transfer within the ether (3). However, if the ether had been hydrolyzed and hydride transfer had taken place between an alcohol molecule and its corresponding cation, the diphenylmethane would still have been deuterium-free.

With aliphatic alcohols, internal hydride transfers are known in certain cases of the pinacol rearrangement. The conversion of 1-methyl-1,6-cyclodecanediol to 6-methylcyclodecanone (29) (equation 9) approaches an intermolecular transfer, and suggests that inter-

molecular hydride transfers in aliphatic alcohols may be anticipated.



(9)

Bartlett and McCollum (7) have reported a number of examples of triphenylmethanol (as its cation) abstracting hydride from aliphatic alcohols. The triphenylmethyl cation was quantitatively converted to triphenylmethane and the aliphatic alcohols were converted to their corresponding carbonyl compounds. The following alcohols reacted: ethanol, 1-propanol, 2-methyl-1-propanol, 2-propanol, 2-butanol, 3-methyl-2-butanol, and 3,3-dimethyl-2-butanol. Diethyl and diisopropyl ethers also reacted. The reaction with diethyl ether had been known for some time (49). Methanol and dioxane failed to react (7). For one example, the reaction was demonstrated to be hydride transfer by the sequence shown in equation 10.

$$(C_6H_5)_3C^+ + CH_3C(OH)DCH_3 \rightarrow (C_6H_5)_3CD + CH_3COCH_3 \quad (10)$$

The work of Bartlett and McCollum (7) shows why these hydride-transfer reactions have been previously unnoticed and undeveloped. The reactions take place at appreciable rates over a narrow range of sulfuric acid concentrations. If the acid concentration is too high, the alcohol is converted to the unreactive protonated alcohol; if the acid concentration is too low, the triphenylmethyl cation is not generated in sufficient concentration.

Although the ester of an alcohol may donate hydride less readily than the free alcohol, it is much less basic, so that the unprotonated ester predominates in regions where the alcohol would be protonated. This latter effect apparently overshadows the first, since 2-propyl benzoate decolorizes the triphenylmethyl cation in 55 per cent sulfuric acid faster than does 2-propanol (22).

Another technique that has improved the rates of the above reactions is the use of polyphosphoric acid (22). The low water activity favors the formation of the arylmethyl cations without concomitantly increasing the protonation of the free alcohols, esters, and ethers. It is evident that such an effect will increase the rate of hydride transfer. For example, in polyphosphoric acid the diphenylmethyl cation abstracts hydride from 2-propyl benzoate. The reaction fails in sulfuric acid solutions (22).

The 4,4′,4″-trimethoxytriphenylmethyl cation also abstracts hydride from 2-propanol. This cation is more stable than the triphenylmethyl cation, so that it is not surprising that it abstracts hydride from 2-propanol at 1/1000 the rate (7, 29). The relative rates for a series of triarylmethyl cations should be predictable from the σ-ρ equations, providing sigma (+) parameters (20) are employed.

Bis(4-methoxyphenyl)chloromethane reacts with ethanol to produce acetaldehyde and the diarylmethane (5). Several triphenylmethyl ethers form triphenylmethane on pyrolysis (36); these may be hydride abstractions by some form of the triphenylmethyl cation, although a free-radical path is also possible.

Alcohols can serve as hydride donors to carbonyl compounds. 4,4′-Dimethoxybenzhydrol plus acetone in 50 per cent sulfuric acid yields 4,4′-dimethoxybenzophenone and 2-propanol (7). In 45 per cent sulfuric acid 4,4′-dimethoxybenzhydrol as its cation abstracts hydride from 2-propanol to form acetone and the diarylmethane (7). Thus the 2-propanol–acetone system can either oxidize or reduce the dimethoxybenzhydrol depending on the acid concentration and on the relative concentrations of 2-propanol and acetone (7).

Benzaldehyde is reduced by several aliphatic secondary alcohols to benzyl alcohol in 9 *M* sulfuric acid and to benzyl chloride in concentrated hydrochloric acid (25).

The Meerwein–Ponndorf reduction and the Oppenauer oxidation are both hydride-transfer reactions (24), as shown by the fact that the hydrogen transferred does not exchange with labile protons in solution (60, 77). The literature on this reaction is extensive and will not be reviewed here, other than to note a modification whereby acetone is reduced to 2-propanol by refluxing with triethanolamine (46). The triethanolamine presumably is functioning both as catalyst and as hydride donor.

The particular efficacy of aluminum alkoxides in promoting these reactions can be interpreted as a result of their activation of both the hydride donor and the hydride acceptor. The aluminum alkoxides with their open sextet of electrons coördinate to the carbonyl oxygen which develops the open sextet on the carbonyl carbon. Concomitantly the aluminum alkoxides possess more of a negative charge on the alcohol oxygen than in the free alcohol, and this facilitates the departure of hydride.

The base-catalyzed racemization of α-methylbenzyl alcohol and 3-methyl-1-butanol, as well as the conversion of α-fenchol to β-fenchol, probably proceed via hydride-transfer reactions which interconvert alcohol and carbonyl compound, since ketones were necessary catalysts (24).

Closely related to the above racemizations are the base-catalyzed alkylations of active methylenes by alcohols. A scheme involving hydride transfer (equations 11 to 14) is plausible but not completely established. The underlined formulas are the ultimate reactants and products. Note that RCHO occurring in equation 11 is regenerated in equation 13 and thus functions only as a catalyst.

$$RCHO + \underline{CH_2<} \rightarrow RCH{=}C< + \underline{H_2O} \quad (11)$$

$$\underline{RCH_2OH} + OH^- \rightarrow RCH_2O^- + H_2O \quad (12)$$

$$RCH{=}C< + RCH_2O^- \xrightarrow{\text{hydride transfer}} RCH_2\bar{C}< + RCHO \quad (13)$$

$$RCH_2\bar{C}< + H_2O \rightarrow \underline{RCH_2CH<} + OH^- \quad (14)$$

This scheme would be applicable to the formation of 9-benzylfluorenes from benzyl alcohol and substituted fluorenes (68) and of 9-alkylfluorenes from aliphatic alcohols and fluorene (65). The self-alkylation of aliphatic alcohols—as, for example, the conversion of 1-butanol to 2-ethyl-1-hexanol (57)—falls into this category.

The alkylation of malonic acid by 9-xanthenol to produce xanthylacetic acid (79) could be similarly formulated. However, the formation of β,β,β-triphenylpropionic acid from malonic acid and triphenylmethanol (34) shows that these reactions need not proceed via condensation of carbonyl with active methylene. This last reaction is probably alkylation of the enol form of malonic acid by the triphenylmethyl cation followed by decarboxylation, and a similar path is plausible for the formation of xanthylacetic acid via xanthylmalonic acid.

The alkylation of amines by benzyl alcohol to produce benzylamines (67) can be formulated to proceed by a series of reactions analogous to those shown in equations 11 to 14.

The transfer of hydride between aliphatic alcohols and ketones should be catalyzed by mineral acids as well as the usual aluminum alkoxides, because in principle the protonated ketone can abstract hydride from the free alcohol. A search for this reaction under the most favorable conditions—namely, the acidity which maximized the product of the concentrations of free alcohol and protonated ketone—revealed that it does occur. Refluxing 2-propanol in 60 per cent sulfuric acid gave acetone upon the addition of 2-butanone or cyclohexanone. The yield of acetone distilled out and isolated as the dinitrophenylhydrazone was 5 per cent and 28 per cent, respectively. Under these conditions, no acetone is produced unless another ketone is added (22). The rate of this reaction rapidly diminishes at acid concentrations higher or lower than 60 per cent, as expected, and this partially explains why this reaction has been overlooked.

The Sommelet reaction has been recognized as a hydride-transfer reaction and the subject reviewed (2).

The reduction of diazonium ions by alcohols or H_3PO_2 occurs by hydride transfer, as shown by reductions using ethanol and H_3PO_2 in deuterium oxide. The aromatic hydrocarbon produced contained no deuterium (59, 74). This conclusion is further supported by the fact that ethers can be used in place of the alcohols (28). These reductions may take another path (free-radical ?), because the catalysis by ferrous ion, permanganate ion, and dichromate ion (28) and by cupric ion (55) is not readily explicable in terms of the hydride-transfer process. Further, reduction of diazonium compounds by formaldehyde in deuterium oxide does lead to partial introduction of deuterium, and this reduction appears to involve a third reaction path (47, 59).

IV. ALDEHYDES AS HYDRIDE DONORS

This reaction has not yet been observed in acid solution, although its base-catalyzed counterpart, the Cannizzaro reaction, has been known for many years. The Cannizzaro reaction involves hydride transfer, as shown by equation 15 (30, 32). Whether the hydride is transferred intermolecularly or intramolecularly has been the subject of considerable discussion.

$$2C_6H_5CDO \rightarrow C_6H_5CD_2OH + C_6H_5COOH \quad (15)$$

Closely related is the Tishchenko reaction (equation 16), which has been often studied for synthetic purposes (14, 33, 44, 72).

$$2RCHO \rightarrow RCOOCH_2R \quad (16)$$

V FORMIC ACID AS HYDRIDE DONOR

Formic acid and some of its derivatives are excellent donors of hydride in hydride-transfer reactions. The triphenylmethyl cation (9) and other triarylmethyl cations (78) are quantitatively reduced to triarylmethanes. The result of an experiment with deuterium, shown in equation 17, was interpreted in terms of the hydride-

$$(C_6H_5)_3C^+ + DCOOH \rightarrow (C_6H_5)_3CD + CO + H^+ \quad (17)$$

transfer reaction (69). The possibility exists that these hydride transfers take place intramolecularly within the formate ester. The pyrolysis of formate esters of aliphatic 1,2-diols yields olefins (35); hence this reaction can be formulated as hydride transfer. Somewhat surprisingly, the reduction of simple aliphatic alkyl cations by formic acid has never been reported.

The reductive alkylation of amines by aldehydes and ketones in the presence of formic acid has been recognized as involving hydride transfers (56, 70). The condensation product of the amine and carbonyl compound (III) can lose hydroxide ion in the acid solution to form the carbonium ion IV, which abstracts hydride from the formic acid.

$$\underset{\text{III}}{R_2NCOH} \xrightarrow{H^+} \underbrace{R_2NC^+ \longleftrightarrow R_2\overset{+}{N}{=}C<}_{\text{IV}} \xrightarrow{HCOOH} R_2NCH<$$

The above alkylation of amines can take several forms. With the simplest carbonyl compound, formaldehyde, the amines are methylated. In this type, examples are known where the reaction proceeds without the addition of formic acid (1). Although the formaldehyde

initially serves as the hydride donor, the formic acid produced also donates hydride because the end product is carbon dioxide. Although other aldehydes (but not ketones) could in principle also donate hydride, specific examples have not been found among the alkylation of amines. Although the above methylation of amines is an old reaction (73), only two references (8, 61) to it were found over the past ten years.

Another particular case is the use of ammonia, the simplest of all amines. This reaction, known as the Leuckart reaction, has often been used for the conversion of ketones to amines (18, 39, 56, 70, 73). Nickel has been reported to catalyze the reaction (42), but these are not the usual conditions employed.

Benzaldehyde has been converted to benzyl alcohol and toluene by formic acid (17), but the reaction conditions, 200°C. and a copper catalyst, leave the nature of the reaction uncertain.

VI. BIOLOGICAL SYSTEMS

The most extensive work on hydride-transfer reactions in biological systems has been on oxidation-reductions involving diphosphopyridine nucleotide (DPN) (27, 75). In the oxidation of CH_3CD_2OH by diphosphopyridine nucleotide in the presence of yeast, one deuterium atom was added to the diphosphopyridine nucleotide. On reversing this reaction, this deuterium-labelled diphosphopyridine nucleotide gave its deuterium back to the acetaldehyde without equilibrating it with solvent protons. This work has been extended (58, 62) to show that the deuterium goes to the 4-position of the pyridine ring in diphosphopyridine nucleotide.

The interconversion of α-oxo acids and α-amino acids could occur if the imine derivative of the carbonyl group of the oxo acid abstracted hydride ion from the α-carbon atom of the amino acid. However, the enzymatically catalyzed reaction between α-D-alanine and α-oxoglutaric acid gave glutamic acid with no excess deuterium (41). Either the α-amino acids were undergoing a separate hydrogen–deuterium exchange with solvent on the α-carbon atom or the hydride-transfer mechanism was not operative.

The epimerization of sugars could also conceivably occur via hydride transfer. Removal of hydride from a secondary alcohol group would form the keto group. Stereospecific addition of hydride back to the carbonyl group would re-form the alcohol with possible epimerization. The experimental results do not as yet demonstrate such a path. In the enzymatic conversion of glucose to fructose, no carbon–deuterium bonds were formed when the reaction was run in deuterium oxide, indicating that an internal hydride transfer took place (31). In contrast, the conversion of tetramethylglucose to tetramethylmannose and the conversion of fructose 6-phosphate to glucose 6-phosphate occurred with formation of carbon–deuterium bonds (31).

VII. RELATED REACTIONS

In view of the possibility of hydrogen formation, it is one of the remarkable features of the hydride-transfer reaction that carbon atoms with open sextets can remove certain hydrogen atoms with amazing rapidity, while these same hydrogen atoms are unattacked by protons in the highly acid solutions. Compounds containing hydrogen attached to elements other than carbon also exhibit this phenomenon but to a lesser degree. Although these reactions are technically outside the scope of this review, brief mention will serve to orient the field of hydride transfers.

Silanes should donate hydride more readily than alkanes because of the increased electropositive nature of silicon relative to carbon. Thus silanes generally evolve hydrogen in strong acids. The reaction of several alkyl chlorides with triethylsilane in the presence of aluminum chloride to form the alkane demonstrates that hydride transfer from silicon to carbon (76) can take precedence over formation of hydrogen. Periodic chart relations suggest that similar reactions may be found for hydrogen attached to boron as well as phosphorus in its lower oxidation states. The latter case is exemplified by the reductions with H_3PO_2 (59).

With metal hydrides such as lithium aluminum hydride, sodium hydride, or calcium hydride, the hydride ion is so readily donated that the metal hydride reacts with labile protons to form hydrogen gas, so that transfer of the hydride ion to carbon is generally restricted to aprotic solvents.

The donation of hydride ion to carbon by molecular hydrogen is indicated by the conversion of propene to propane by hydrogen gas in the presence of aluminum chloride (40). Molecular hydrogen also inhibits the cleavage of alkanes in the presence of aluminum halides (11, 13, 38, 40, 64). This effect has been usually interpreted in terms of donation of hydride by molecular hydrogen to the intermediate alkyl cations. This limits their concentration and lifetime and thus inhibits cleavage and other alkyl cation reactions.

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