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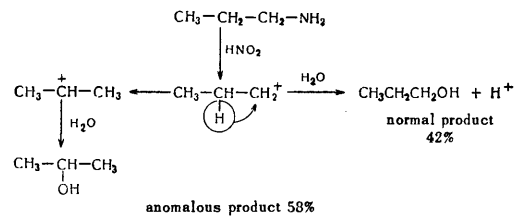
Kapsukas Vilna State University

NEW DATA ON HYDRIDE-TRANSFER REACTIONS

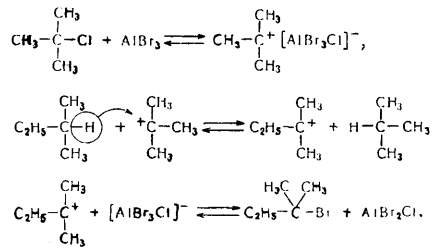
D. N. Kursanov and Z. N. Parnes

There are many organic reactions involving intermolecular transfer of hydrogen in the form of a proton. Such processes, which are fairly well understood, do not however constitute the only possible pathway for hydrogen transfer: in particular, a hydrogen nucleus associated with a pair of electrons may be transferred from one molecule to another. Processes of this sort are known as hydride-transfer reactions[1,2]. The present review is not concerned with the problem of the form and extent of association between a hydrogen nucleus and an electron pair in these reactions. However, the fairly high affinity of a hydrogen atom for an electron, 17.5 kcal mole^{-1}, suggests that such association may exist in hydride transfers[3].

As far as we know, the concept of intramolecular hydride transfer was first introduced in 1932 by Whitmore[4] to explain the anomalous course of reactions which may involve the formation of carbonium ions as intermediates. According to Whitmore, the latter isomerise through intramolecular hydride transfers. For example, Whitmore gives the following explanation of the formation of isopropanol, in addition to n-propanol, when nitrous acid reacts with n-propylamine:



The concept of intermolecular hydride transfer was introduced by Bartlett *et al.*[5] in 1944. They studied the reaction of isopentane with t-butyl chloride in the presence of aluminium bromide. Using an ingenious technique and apparatus, they shortened the time of contact of the components to 0.001 sec and obtained isopropyl bromide and isobutane. The reaction appears to involve intermolecular hydride transfer:



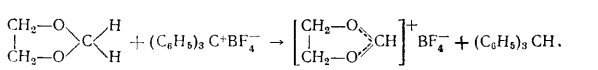
In recent years the concept of intermolecular and intramolecular hydride transfer has been widely employed to interpret the mechanism of complex reactions, and also to some extent in the search for new synthetic methods. Hydride transfers have been included in many mechanisms proposed for a large number of important organic reactions: the mechanism of the Meerwein–Ponndorf–Verley reaction proposed by Woodward *et al.*[6]; the mechanism of the Cannizzaro reaction proposed by Hammett[7]; the mechanism of the Tishchenko reaction proposed by Pfeil[8]; the mechanism of the Leuckart reaction proposed by Pollard and Young[9], and by Titov[10]; the mechanisms of aluminium chloride catalysed reactions of saturated hydrocarbons, proposed by Nenitzescu[2]; the mechanism of the isotopic hydrogen exchange in saturated hydrocarbons under the action of sulphuric acid, proposed by Otvos *et al.*[11], and a similar mechanism propsed by Kursanov and Setkina[12]; and many others.

In general, hydride transfer involves the transfer of a hydrogen nucleus with an electron pair, H: (subsequently to be called a hydride ion), from a donor to an acceptor. The acceptors are very often carbonium ions; the donors can belong to many different classes. When the migrating hydrogen atom is initially bound to a carbon atom, hydride transfer results in the formation of a new carbonium ion. Obviously the activity of a given substance as a hydride donor increases with increase in the stability of the corresponding carbonium ion.

A characteristic feature of the mechanisms quoted above and of many of the mechanisms discussed in a recent review by Deno *et al.*[13] is the fact that hydride transfer is effected through as powerful a hydride acceptor as the carbonium ion. This in fact frequently results in a certain arbitrariness of the proposed mechanisms,

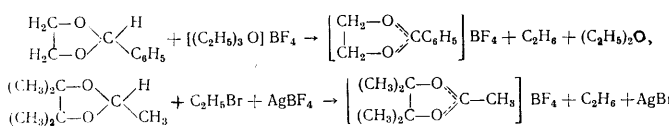
since in many cases the existence of the intermediate carbonium ions is difficult to demonstrate, particularly of those which are the most active and consequently the least stable. The most self evident and convincing hydride--transfer reactions are those in which the carbonium ion formed as a result of the transfer is stable.

In this connection much interest attaches to the recently published paper by Meerwein *et al.*[14], who employed triphenylmethyl fluoroborate as the hydride acceptor, which is converted in the reaction to triphenylmethane. The hydride donor used was 1,3-dioxolane which, as a result of the transfer, is converted into a carboxonium (dioxolenium) ion:

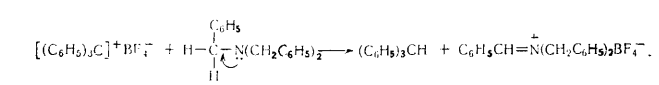


Dioxolenium salts are stable[15]. 2-Methyl-1,3-dioxolane, 2-phenyl-1,3-dioxolane, and 2,4,4,5,5-pentamethyl-1,3-dioxolane react similarly. The yields of triphenylmethane in all these reactions vary from 58 to 84% and those of the dioxolenium salts from 64 to 100%.

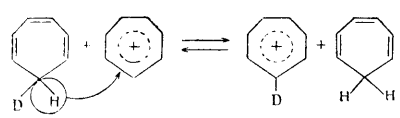
Since ethylfluoroborate is unstable, in order to demonstrate the ability of an ethyl cation to remove a hydride ion, the authors allowed 1,3-dioxolanes to react with a mixture of ethyl bromide and dry silver fluoroborate or triethyloxonium fluoroborate. In all cases, 1,3-dioxolenium fluoroborates and ethane were formed:



Aliphatic-aromatic tertiary amines may also be employed as hydride donors. Thus in the reaction between triphenylmethyl fluoroborate and tribenzylamine (in acetonitrile solution) triphenylmethane is formed in 89% yield and benzylidenedibenzylammonium fluoroborate in 94% yield:



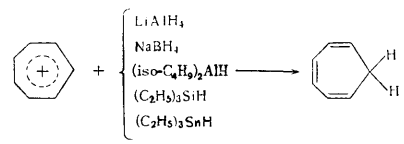
Parnes *et al.*[16,17] employed cycloheptatriene as a hydride donor and a stable carbonium ion — tropylium — as an acceptor. The formation of tropylium in reactions with cycloheptatriene and of cycloheptatriene in reactions with tropylium is clear and unambiguous evidence of the existence of hydride transfers. The first such reaction studied was that between tropylium bromide and cycloheptatriene. In order to be able to follow this reaction, the cycloheptatriene was monodeuterated:



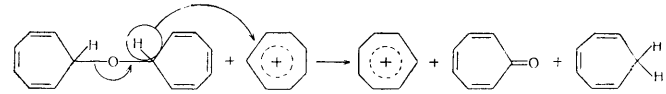
After a few hours at room temperature the deuterium is uniformly distributed among all the hydrogen atoms of the cycloheptatriene and the tropylium, *i.e.* equilibrium has been attained. The reaction takes place in various solvents: acetic acid, methanol, ethanol, nitromethane, etc. Second-order rate constants [$K_{10} = 1.04 \times 10^{-3}$, $K_{15} = 1.41 \times 10^{-3}$, $K_{20} = 2.16 \times 10^{-3}$, and $K_{30} = 4.3 \times 10^{-3}$] and the activation energy, $E = 12$ kcal, have been determined for this reaction in acetic acid solution[18].

It had been shown earlier that the tropylium ion does not enter into hydrogen exchange even with such powerful proton (deuteron) donors as sulphuric acid and hydrogen bromide in the presence of aluminium bromide[19]. It is evident that the exchange between cycloheptatriene and tropylium is a reversible hydrogen transfer. The fact that the reaction will occur in acid media, *i.e.* in the presence of protons, shows that free hydride ions are not formed and that the hydride transfer is effected in an activated complex. It is very probable that the energy of the activated complex in the hydride-transfer reaction is reduced because of the low energy of the system of two electrons in the field of three nuclei. The absence of free hydride ions in organic hydride--transfer reactions has also been noted by other authors (see, for example, the work of Nenitzescu[2]). Since cycloheptatriene on releasing a hydride ion is converted into the stable tropylium ion, it follows that the former must be an active hydride donor. Conversely, it is to be expected that the tropylium ion will prove to be a relatively weak hydride acceptor. In order that the stable tropylium ion should remove a hydride ion from the molecule of another substance, it is necessary that the latter should be a powerful hydride donor, *i.e.* that following hydride transfer it should yield a species no less stable than the tropylium ion.

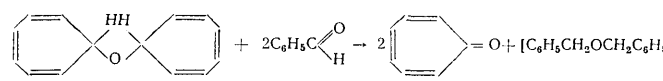
It has been shown that tropylium is vigorously reduced, in quantitative yield, to cycloheptatriene under the action of such powerful hydride donors as sodium borohydride, lithium aluminium hydride, and diisobutylaluminium hydride. Tropylium can remove a hydride ion from triethylsilane and triethylstanane with the formation of cycloheptatriene in ~70% yield:



Tropylium can remove a hydride ion from cycloheptatrienyl ether[20-22] which results in a chain reaction: tropylium is converted into cycloheptatriene on reaction with the hydride ion and one half of the ether molecule is converted to tropone and the remainder to tropylium, which can again remove a hydride ion from another cycloheptatrienyl ether molecule. Thus each molecule of the ether finally yields one molecule of tropone and one molecule of cycloheptatriene:

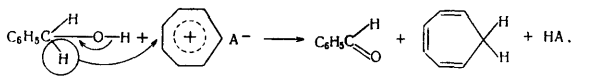


Both cycloheptatrienyl residues can be converted to tropone when benzaldehyde is used as the hydride acceptor:

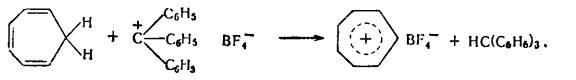


The tropylium ion can react with benzyl alcohol to yield benzaldehyde and cycloheptatriene. In acetic acid solution this reaction is practically quantitative. It has been shown that reaction between tropylium bromide and D-benzyl alcohol (C_6H_5CHDOH) results in the formation of deuterated

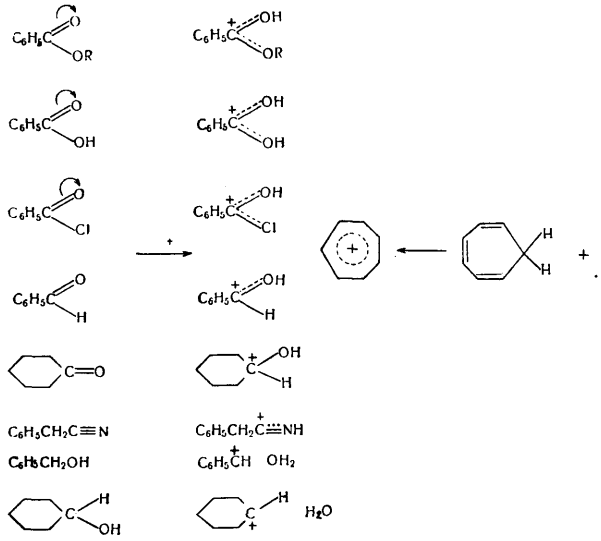
cycloheptatriene. The kinetic isotopic effect, as in other cases of hydride transfer, proved to be small and equal to 2.1:



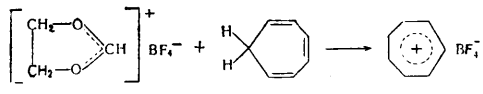
It follows from the above data that the tropylium ion can remove a hydride ion from a wide variety of substances. However, tropylium cannot be reduced to cycloheptatriene either by benzaldehyde, or by acetic acid, or even by formic acid, *i.e.* it is a relatively weak hydride acceptor. Conversely, cycloheptatriene must be a strong hydride donor. The available methods for the preparation of tropylium are based on the fact that cycloheptatriene readily gives up a hydride ion when acted upon by Lewis acids, PCl_5, concentrated H_2SO_4,[23] and the triphenylmethyl carbonium ion[24]:



In phosphoric acid, cycloheptatriene is converted to the tropylium ion under the action of benzoic acid esters, benzoyl chloride, benzaldehyde, cyclohexanone, benzyl cyanide, benzyl alcohol, and cyclohexanol. It is interesting that the reaction does not occur in acetic acid. Probably in phosphoric acid all the above compounds form carbonium (carboxonium, carbammonium) ions which can remove a hydride ion from cycloheptatriene:



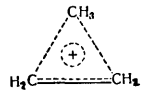
Meerwein's 1,3-dioxolenium ion[15] can also remove a hydride ion from cycloheptatriene with the formation of tropylium:



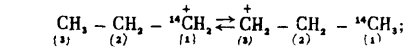
The formation of the tropylium ion in reactions is very easy to detect since it forms an insoluble chloroplatinate $(C_7H_7)_2PtCl_6$, and with acetylacetone it yields a cycloheptatrienyl derivative, $CH_3COCH(C_7H_7)COCH_3$ (m.p. 123°–124° after recrystallisation from petroleum ether)[25].

In view of the ready transfer of hydride from cycloheptatriene to carbonium (carboxonium, carbammonium) ions and the ease with which this reaction can be controlled, application of cycloheptatriene may help in elucidating the mechanism of many reactions involving hydride transfer.

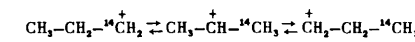
Recently, apart from studies on hydride transfers involving stable carbonium ions, further advances have been made in the investigation of hydride-transfer reactions with the participation of unstable carbonium ions. Tracer-atom techniques have revealed reactions based on the isomerisation of the propyl cation. For example, Roberts and Halmann[26] found that when nitrous acid acts on [$^{14}C_{(1)}$]propylamine, $CH_3\overset{(3)}{C}H_2\overset{(2)}{C}H_2\overset{(1)}{N}H_2$, a rearrangement takes place as a result of which some of the ^{14}C is displaced from position 1. The authors thought that the rearrangement was of the pinacol type and that ^{14}C moves to position 2. To explain this, Roberts and Halmann suggested that the reaction involves the formation of a non-classical carbonium ion as an intermediate:



Recently Reutov and Shatkina[27] re-examined the reaction of [$^{14}C_{(1)}$]propylamine with nitrous acid. They isolated both n-propanol and isopropanol from the reaction mixture. To establish the location of ^{14}C in propanol, they determined the ^{14}C content of the molecule as a whole and then oxidised the alcohol to acetic acid. They then determined the ^{14}C content in the acid and subjected it to the Schmidt degradation, which results in the formation of methylamine. The ^{14}C content in the methylamine proved to be the same as in the acetic acid. Thus in n-propanol ^{14}C is present in either position 1 or 3 but not in 2. The authors explain the isomerisation of the propyl cation by the migration of a hydride ion, either in one stage from $C_{(3)}$ to $C_{(1)}$:



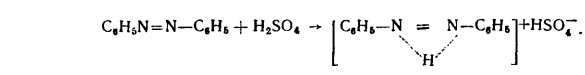
or in two stages:



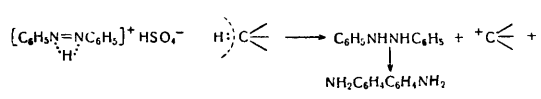
The second of the above mechanisms is analogous to that proposed by Whitmore[4] for the isomerisation of carbonium ions, and to the mechanism of the isomerisation of the carbonium ions prepared from hydrocarbons by the action of sulphuric acid[11] or aluminium chloride[28].

In all the above examples the hydride acceptor was a carbonium ion or at least a molecule containing a carbon atom with a partial positive charge.

Nesmeyanov and Golovnya[29] recently found that protonated azobenzene, formed by the action of strong acids on azobenzene[30], is a good hydride acceptor:

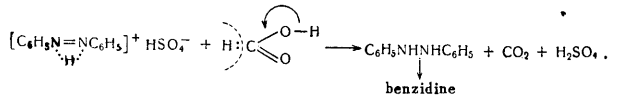


On combination with a hydride ion, it is converted to hydrazobenzene, which in the presence of acid undergoes the usual rearrangement to benzidine:

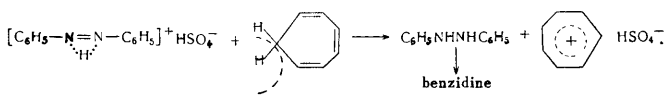


The authors found that protonated azobenzene can remove a hydride ion from a wide variety of organic compounds, itself undergoing conversion to benzidine. In many cases the hydride-transfer reaction was established only from the formation of benzidine. In the majority of cases the other reaction products are unstable carbonium ions, which later undergo many more or less complicated reactions resulting in the formation of stable compounds. In particular, carbonium ions can be frequently stabilised by the removal of a proton and the formation of unsaturated compounds. The latter polymerise in the presence of sulphuric acid forming resinous products of unknown constitution. Hydride transfers have been established in this way in reactions with acetone, cyclohexanone, acetic acid, succinic acid, benzaldehyde, butyl ether, benzene, thiophen, nitrobenzene, cyclohexane, and n-hexane.

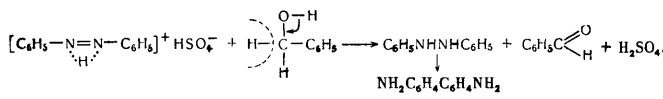
In many cases Nesmeyanov and Golovnya were able to identify both reaction products. Thus in the reaction between protonated azobenzene and formic acid carbon dioxide was found in addition to benzidine:



In the reaction with cycloheptatriene a good yield of a tropylium salt was obtained in addition to benzidine:



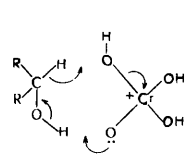
Reaction with benzyl alcohol results in the formation of benzaldehyde as the second product:



These products are fully consistent with the suggested mechanism and serve as its confirmation.

It is noteworthy that protonated azobenzene as a hydride acceptor is comparable in effectiveness with carbonium ions, and possibly even superior to them. It removes a hydride ion not only from all the compounds which undergo hydride transfer with carbonium ions, but also from benzene, nitrobenzene, and thiophen, which do not react with carbonium ions. Dehydroaromatic compounds are probably formed initially and then undergo further changes.

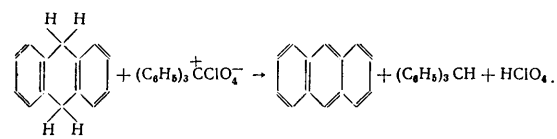
Reactions are known in which the hydride ion is transferred to atoms other than carbon or nitrogen. Much work has been done on the chromic acid oxidation of hydrocarbons containing a tertiary carbon atom[31], alcohols[32-36], and aldehydes[37]. Roček[34,37] showed that hydride transfer is the rate-determining stage in the oxidation of alcohols and aldehydes. To explain the mechanism of the alcohol oxidation, Roček and Krupička proposed the following cyclic scheme:



in which hydride transfer to the chromic acid oxygen is the slowest stage. To demonstrate the correctness of his scheme, Roček[34] studied the kinetics of the oxidation of a large number of primary alkyl and aralkyl alcohols containing various substituents and having the general formula RCH_2OH. The inductive effect of the substituents was examined. Following the application of the Hammett–Taft equation, Roček found that for the majority of substituents† the relation between $\log K$ and σ^* is linear. Thus the oxidation of primary alcohols by chromic acid obeys the Taft equation: $\log (K/K_0) = \rho^*\sigma^*$. This equation describes the same relationship for the aliphatic series as had been found by Hammett for aromatic compounds. K_0 is the rate constant for the unsubstituted compound, K the rate constant for the substituted compound, σ^* a function of the substituent, and ρ^* a function of the reaction.

The following substituents were employed: Cl_3C, Cl_2CH, $(CH_3)_3\overset{+}{N}$, $CNCH_2$, $ClCH_2C_6H_4$, $HOCH_2$, CH_3OCH_2, H, $C_6H_5CH_2$, $C_6H_5CH_2CH_2$, CH_3, C_2H_5, n-C_3H_7, cyclohexyl, iso-C_3H_7, neopentyl, and n-C_5H_{11}. Since the oxidation of of neopentyl, and trochloroethyl alcohols also obeys the Taft equation, steric effects do not have much influence on the reaction. $\rho^* = -1.06 \pm 0.06$. The negative value indicates that a decrease in the electronegativity of the substituent leads to an increase in the reaction rate. This is consistent with the postulate that hydride transfer is the rate-determining stage. If Westheimer's mechanism[38] were correct, *i.e.* if the rate-determining stage were proton transfer in the initially formed ester, ρ^* would have to be positive since increase in electronegativity of the substituent enhances proton mobility. Roček's scheme for the oxidation of aldehydes is analogous to that for the alcohols, the rate-determining stage being hydride transfer from the aldehyde to the chromic acid oxygen.

It might be useful to interpret the mechanism of the action of many oxidising agents in terms of hydride transfers, since removal and addition of hydride ions constitute some of the simplest oxidation and reduction reactions respectively. Braude and Linstead[39] dehydrogenated dihydroaromatic compounds under the action of quinones, and explained the reaction in terms of hydride transfer. Bonthrone and Reid[40] found that when dihydroanthracene, tetrahydropyrone, and other similar compounds are allowed to react with triphenylcarbonium perchlorate, aromatic compounds are obtained. For example:



There is reason to believe that in future considerable progress will be made in the elucidation of the role of hydride transfer in oxidation–reduction processes.

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† Except methyl alcohol (R = H), benzyl alcohol (R = C_6H_5), and choline perchlorate [R = $(CH_3)_3\overset{+}{N}CH_2$].

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PRINCIPAL FACTORS IN THE FREE-RADICAL CHLORINATION OF ALKANES

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I. INTRODUCTION

The utilisation of natural and petroleum gases for the heavy organic chemical industry is an important task for the national economy. The huge reserves of gas and petroleum provide the chief raw material for the chemical industry. Saturated hydrocarbons, or alkanes, constitute the bulk of the natural and accompanying gases and a considerable proportion of petroleum, so that the employment of alkanes for organic synthesis is of particular interest. Among the varied processes for their chemical treatment (chlorination, chlorosulphonation, dehydrogenation, oxidation, sulphonation, nitration, etc.) one of the most important is chlorination. This reaction can take place by three different mechanisms depending on the way in which the bond between the atoms in the chlorine molecule is broken.

In the symmetrical, homolytic rupture of the Cl–Cl bond, chlorination subsequently proceeds by a free-radical chain mechanism independently of the method by which the free chlorine atoms were produced (photochemically, thermally, chemically, by means of radiation, etc.)[1-6].

$$\begin{aligned} Cl_2 &\rightarrow Cl\cdot + Cl\cdot \\ Cl\cdot + RH &\rightarrow R\cdot + HCl \\ R\cdot + Cl_2 &\rightarrow RCl + Cl\cdot \text{ etc.} \end{aligned} \qquad (I)$$

Chlorination can take place by an ionic mechanism, the chlorine molecule undergoing heterolytic fission, in the presence of chlorides of metals which are able to form complex ions[7], *e.g.* the chlorides of Fe, Cu, Sb, Sn, Bi, Ti, Al, As, etc.

$$\begin{aligned} FeCl_3 + Cl-Cl &\rightarrow Cl^+[FeCl_4]^- \\ Cl^+[FeCl_4]^- + RH &\rightarrow [RHCl]^+[FeCl_4]^- \\ [RHCl]^+[FeCl_4]^- &\rightarrow RCl + HCl + FeCl_3 \text{ etc.} \end{aligned} \qquad (II)$$

Chlorides of S, I, P, and some other non-metals act in a similar way.