MECHANISM OF HYDROGEN EXCHANGE AND OF SOME PROTOLYTIC REACTIONS IN SOLUTIONS

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In a previous paper [1] general considerations were put forward about the modes of isotopic exchange of hydrogen in solutions. They can now be corroborated and developed in more detail as a result of investigations which were subsequently undertaken. The problem of the mechanism of hydrogen exchange is of general interest since it is associated with the important problem of the mechanism of many hydrogen transfer reactions and in particular with protolytic reactions in solutions.

I. Rapid and Slow Exchange

Depending upon their ability to undergo hydrogen exchange in solutions, numerous investigated compounds [2, 3] form two sharply differentiated groups. In the first of these the exchange proceeds substantially instantaneously at any given temperature without need for a catalyst. This is true of the N–H, O–H, S–H, Cl–H bonds and many others, although not of all compounds with acid-base donors of deuterium, for example, with D_2O, C_2H_5OD. We propose to call this the rapid type of exchange. In the second group of compounds, exchange either does not take place at all or it only proceeds more or less slowly. The possibility of its occurrence and its velocity are determined by the structure of the molecules and by the nature of the substituents present, by the reaction of the medium and by the properties of the deuterium donor. Exchange of this type (which we call slow) exhibits a strong dependence upon the temperature and upon the presence of catalysts for protolytic reactions. The slow type of exchange is characteristic of the C–H bonds in organic compounds. From the table we see that the type of exchange is not governed either by the properties of the individual bonds in which the exchange proceeds or by the nature of the atom with which the exchanging atom of hydrogen is directly linked. In particular, contrary to the prevalent conception, it is not characterized by the energy, by the polarization, or by the "ionic quota" of the bond.

TABLE

Bond	Bond energy	Length of bond	Dipole moment	Atomic refraction	Constant of bond strength $f \cdot 10^{-3}$	Difference of electronegative activity
N–H	83.7	1.01	1.31	3.42	7.1	0.98
C–H	87.3	1.09	0.4	3.52	5.1	0.52
S–H	87.5	1.35	1.03	8.79	4.0	0.41
Cl–H	102.7	1.28	0.68	7.07	5.1	0.98
H–H	103.4	0.74	0	2.20	5.1	0
O–H	110.2	0.97	1.51	2.63	7.5	1.33

Rapid or slow exchange in the bond of X–H is determined by the presence or absence of free (unsaturated) electronic pairs round the atom X. If these are present, then a deuteron (or proton) may add on to one of them with simultaneous detachment of a proton from the electron pair linked with the other. This process, whose mechanism is considered in detail below, can be represented by the following scheme for, for example, exchange between H_2S and D_2O:

$$D^+ + :\underset{\displaystyle H}{\overset{\displaystyle \cdot\cdot}{\underset{\cdot\cdot}{S}}}:H = D:\underset{\displaystyle H}{\overset{\displaystyle \cdot\cdot}{\underset{\cdot\cdot}{S}}}: + H^+ \qquad (1)$$

It takes place in a single elementary act and evidently does not require an appreciable activation energy. Hence the exchange takes place very quickly even at low temperature. In the absence of a free

electron pair, as for example in the C−H bonds of organic compounds, the deuteron can only add on at the same electron pair to which the proton is bound, after elimination of the latter. This process demands a considerable activation energy and exchange proceeds either slowly or not at all, depending upon the factors determining the strength of the C−H bond and its ability to release a proton. Various mechanisms possible for this process are considered below.

With the objective of confirming these ideas, several fresh examples of hydrogen exchange were studied in our laboratory. In the Si−H bonds of organosilicon compounds, there are no free electron pairs round the silicon atom and no hydrogen Exchange is manifested in them. In a paper by Khaskin and the author [4] the absence was shown of exchange in triethyl-, triphenyl- and triethoxysilanes $(C_2H_5)_3SiH$, $(C_6H_5)_3SiH$ and $(C_2H_5O)_3SiH$ with D_2O, C_2H_5OD and $(CH_3)_2ND$ even on prolonged heating above 100 deg. This result could not have been predicted on the basis of analogy with exchange in the corresponding tertiary carbon compounds since the Si−H and C−H bonds differ very markedly not only in strength but also in the sign of polarization [5]. In ammonia, various amines and amides [6], possessing a free electron pair round the nitrogen atom, indications of slow exchange were not detected in a single instance, whereas in the ammonium ion the exchange has a measurable kinetics and takes place in the process of hydrolysis with participation of ammonia. This is confirmed by the dependence, found by Sulima and the author [7], of the exchange velocity in ammonium salts on the presence of concentrated strong acids which suppress hydrolysis. This mechanism occurs in slow exchange in the Co: NH_3, Pt: NH_3 and Pd : NH_3 bond of the series of hexammino- and tetrammino- salts whose kinetics depend largely on the pH of the solution [3] *. Hypophosphorous and phosphorous acids have the well-authenticated structure of $O=PH_2(OH)$ and $O=PH(OH)_2$ corresponding to the absence of a free electron pair round the phosphorus atom. In harmony with this, Sulima and the author [9] found that exchange with D_2O does not occur in the P−H bond of phosphorous acid and its anion and only proceeds very slowly in hypophosphites at 100 deg. In hypophosphorous acid, however, it proceeds in the P−H bond even at 25° with a half-period of 16 minutes. It is impossible on the basis of only the reciprocal influence of atoms to explain these large differences in the exchange susceptibility in such similarly constituted substances. Exchange in hyposphosphorous acid is associated with its tautomeric transformation into the $HP(OH)_2$ form, as is confirmed by a comparison of its exchange and oxidation kinetics. **

According to some literature date [3] gaseous H_2 does not exchange hydrogen for the deuterium of heavy water in the absence of catalysts promoting cleavage of the H:H molecule. Exchange also does not occur in the B−H bonds of borohydrides not possessing a free electron pair round the boron atom; nor is there exchange between BH_4^- and D_2O [13] and between $B_2H_6 \cdot ND_3$ and liquid ND_3 [3].

The now known cases of slow hydrogen exchange are limited to the examples considered and to numerous examples of exchange in the C−H bonds of diverse organic compounds. They are all characterized by the absence of free electron pairs round the atom with which the exchanging hydrogen atom is linked. On the other hand, not a single case is known*** where exchange would proceed very quickly if such pairs were present. We can therefore claim that the considerations here discussed are sufficiently well founded.

II Mechanism of Rapid Exchange

Rapid exchange of hydrogen between a substance XH (see * on next page) and heavy water (or other deuterium donor with acid-base functions) is usually explained by electrolytic dissociation:

$$XH + D_2O = X^- + HD_2O^+ = XD + HDO, \qquad (2)$$

if XH is an acid, or

$$XH + D_2O = DXH^+ + OD^- = XD + HDO, \qquad (3)$$

if XH is a base relative to water (or the dissolved catalyst). However, an unmeasurably high velocity of exchange is observed even with extremely weak acids and bases and it is not appreciably slowed down by addition of a large excess of strong acids or bases when the equilibrium concentrations of the products of dissociation of XH fall to 10^{-10} and lower. Such low concentrations of ions cannot lead to rapid exchange.

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* Here and later references are made to [2] and [3] as sources of original literature.

** In a study of the reduction of diazonium salts in D_2O Miklukhin and Rekasheva [11] also found slow exchange in the P−H bonds of hypophosphorous acid. In a recent investigation Jenkins and Yost [10] obtained results in agreement with ours for exchange of H_3PO_2 with T_2O. In their paper exchange was also explained by tautomerism, although only on the basis of the above-mentioned comparison of the exchange and oxidation kinetics.

*** Apart from indication [12] of slow exchange between gaseous : PH_3 and liquid D_2O, the kinetics of which is possibly determined by the diffusion of the poorly soluble phosphine in the bulk of the solution.

It is necessary to assume that rapid exchange proceeds independently of the electrolytic dissociation of (2) or (3) (which is not the cause of the rapid type of exchange) and of the simultaneously proceeding parallel reaction (also capable of leading to exchange), and that therefore the velocity of rapid exchange is not directly associated with the strength of the acids and bases taking part in the exchange. According to the considerations here advanced, rapid exchange between substance XH and a deuterium donor YD is effected in a single elementary act through the intermediate state (a) by simultaneous transfer of a proton to the free electron pair of atom Y and of a deuteron to the same pair of atom X:

$$\ddot{X}H + \ddot{Y}D = \underset{\uparrow \quad \downarrow}{\overset{\ddot{}}{X}\!\!-\!\!H} = :XD + :YH \qquad (4)$$

$$D\!-\!Y$$

(a)

This symmetrical process does not require a high activation energy apart from that expended on a favorable orientation of the exchanging molecules and on equalizing the interatomic distances of X—H and Y→D. The activation energy of anomalous electronegativity, according to Grotthus, possessing a similar mechanism, is only 2-3 kcal/mole as calculated from its temperature coefficient. On the other hand, the symmetrical structure of the intermediate state and the encirclement by molecules of solvent exclude abnormally low values of the exponent. Reactions with these characteristics proceed unmeasurably fast even at low temperature. Exchange according to scheme (1), which differs from (4) by the participation of three molecules in one elementary act, may proceed in a strongly acidic medium with a large excess of hydroxyl ions.

Electrolytic dissociation (2) may be represented, taking account of solvation of ions, by the following exemplary scheme:

$$YD + XH + YD = YD....\overset{-}{X}....\overset{+}{H}....YD = YDX^- + HYD^+. \qquad (5)$$

Unlike (4) this process requires considerable energy for scission of the X—H bond, which is compensated to a greater or lesser degree by the energy of solvation of the ions. Its activation energy depends both on the properties of the scissionable bond and on the energy of interaction of the solvent of YD with the solvatable ions. These account for the diverse values of the strength of acids and bases in dependence upon their structure and the solvent; they also account for the diverse rates of dissociation which proceeds more slowly, for instance, in C—H bonds. The very low acidity of hydrocarbons is apparently due to the absence of free electron pairs, so that the energy of cleavage of a proton from the C—H bond is not compensated by the simultaneous covalent addition of a molecule of the solvent to the formed carbanion according to scheme (5).

In hydroxyl compounds rapid exchange is likewise not associated with the formation of free hydroxyl ion, while in presence of free electron pairs it proceeds by the same mechanism (4):

$$\begin{array}{l} R\!-\!\ddot{O}\!-\!H \\ \quad\uparrow\quad\downarrow \\ ROH + \ddot{Y}D = D\!-\!Y = ROD + YH \end{array} \qquad (6)$$

For example, in ethyl alcohol an exchange equilibrium is rapidly established with D_2O [14].

Attention has already been drawn by Miklukhin [16] to the role in hydrogen exchange of intermediate complexes formed by hydrogen bonds.

Exchange of water with liquid ND_3, DBr, D_2S, etc. does not introduce any fundamental changes into these schemes. The acidic or basic properties of these solvents, of decisive importance for the slow type of exchange, should not play an important role in the rapid type of exchange.

III Mechanism of Slow Exchange

In the absence of free electron pairs round atom X, exchange may likewise take place by a mechanism formally identical with (4), but with the important difference that a deuteron may only join on covalently to that electron pair which previously bound the proton and only after the removal of the latter has freed the pair.

* Here and later, for the sake of simplicity, the symbols XH and YH used to denote both the exchanging bonds and the exchanging molecules themselves.

This process has a considerably higher activation energy than is the case in the rapid type of exchange. In the intermediate quaternary complex formed by hydrogen bonds, such a proton transition does not occur at all or is greatly slowed down in dependence on the height of its potential barrier. The latter is determined by the structure and arrangement of the electronic densities in the exchanging molecules; it is also influenced by the properties of the medium, whereas these factors have little importance for rapid exchange.

The ratio of the velocities of electrolytic dissociation of (2) or (3) and of the type (4) process determines the mechanism of slow exchange. If electrolytic dissociation is the faster process, then exchange takes place through the stage of formation of free ions according to the scheme:

$$XH + YD = X^- + HYD^+ = XD + YH \qquad (7)$$

in an alkaline medium, or

$$XH + YD = DXH^+ + Y^- = XD + YH \qquad (8)$$

in an acid medium, and other intermediate stages are possibly involved. This is usually referred to as the ionization mechanism. But if a type (4) process proceeds more quickly than electrolytic dissociation, then exchange is accomplished in a single act via the intermediate complex formed with hydrogen bonds and not with covalent bonds:

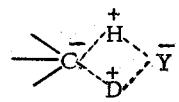
$$XH + YD = \begin{matrix} X\text{----}H \\ \vdots \quad\quad \vdots \\ D\text{----}Y \end{matrix} = XD + YH. \qquad (9)$$

This is usually known as the association mechanism. Both mechanisms are very common in the C—H bonds of organic compounds, and the rest of this paper will be devoted to their consideration.

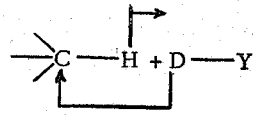
IV. The Association Mechanism

Due to the great electrophilicity of the proton, the association mechanism of hydrogen exchange resolves itself into a mechanism of electrophilic substitution. Systematic study of the exchange with deuteroacids in aromatic compounds has shown that it is facilitated by the same factors which facilitate electrophilic substitution (sulfonation, nitration, halogenation, etc.), namely, high acidity of the deuterium donor and of the substituent which increases the electron density at the carbon atom in the C—H bond in which the exchange is proceeding. For example, Shatenshtein [17] showed that exchange of hydrocarbons with liquid deuterium bromide is accelerated by introducing electropositive substituents, $-CH_3$ and $-OCH_3$, and is slowed down by introducing electronegative substituents, $-CN$ and $-NO_2$.

In typical cases the electrophilic substitution of hydrogen proceeds apparently via the intermediate quaternary complex



but we must also reckon with the possibility of other mechanisms of electrophilic substitution entering into consideration in organic chemistry, for example:



with participation of a third molecule.

Comparison of the rate of exchange of benzene with pure and dilute D_2SO_4 [15] and other date confirm that free hydroxyl ions are not involved in the association mechanism. This markedly differentiates it from the ionization mechanism (8) in an acidic medium. Other differences between both mechanisms will be indicated below.

V. The Ionization Mechanism

The ionization mechanism must be considered typical of slow exchange with basic donors. It is favored by factors which facilitate the first ionization step - basicity of the medium or the presence of basic catalysts and substituents reducing the electronic density at the carbon atom in the exchanging C−H bond. The influence of substituents, as we know, is manifested in a complex manner and cannot by any means always be precisely predicted. We can cite a number of examples, however, in which it is simply correlated with the exchange susceptibility [2, 3]. Methane, ethane and benzene do not exchange hydrogen with water, but in nitromethane, nitroethene, nitroethane and 1,3,5-trinitrobenzene, exchange takes place and is catalyzed by alkalies. The former are capable of rearranging into aci-forms with detachment of a proton from the C−H bond. In presence of alkali, exchange also proceeds in acetamide and acetonitrile. In these examples electrons are attracted by the negative NO_2 CN and CO groups. The enhanced ability of the C−H bond to undergo ionization round the ternary C≡C bond is manifested in the facility of exchange of acetylene with water in presence of alkali. In exchange by the ionization mechanism an extremely important part is played by $\sigma - \pi$ conjugation, whose importance for various organic chemical reaction has been demonstrated by Nesmeyanov [19]. The dependence of exchange of α-hydrogen on the conjugation in the H−C−C=O chain was confirmed by Nesmeyanov, Kursanov and co-workers [20] in cyclic ketones, acetylacetonates and dibenzoylmethane, and later by Shatenshtein [23] in hydrocarbons. Exchange in the methylene group of acetylacetone and ethyl acetate proceeds considerably faster than in acetone due to the participation of two C=O groups linked to the α-carbon in the conjugation. For the same reason exchange proceeds relatively easily in the methylene group of malonic esters and ethyl cyanoacetate, which may be correlated with their known facility of condensation with carbonyl compounds. In acetates the conjugation in two chains − the H−C−C=O chain and the M−O− C=O chain − comes simultaneously into play and, as Mikhulin [22] showed, exchange in their methyl group proceeds with greater facility the lower the polarity of the M − O bond. Conjugation of the C − H bond with the nucleus in the methyl group of toluene is insufficient for exchange in the latter with water, but in our laboratory we found [31] that exchange proceeds in nitrotoluenes and is catalyzed by alkalies, as was to be expected.

Up to recently the study of hydrogen exchange in the liquid phase had been almost entirely restricted to aqueous solutions where the acidic properties of the C−H bond are manifested only to a very minor extent and their differences are largely equalized. Recent papers by Shatenshtein and co-workers [23] deal with the slow hydrogen exchange of many hydrocarbons in liquid ND_3 which is a much stronger base than water. In it, especially in presence of the even stronger base, potassium amide, exchange takes place with greater facility than in water, and its velocity quantitatively characterizes the acidity of the hydrocarbons [24]. The difference between mechanisms (7) and (9) is particularly clearly manifested by the inhibiting effect of substituents on the exchange of hydrocarbons with ND_3 and DBr. All these, as well as a series of other data, confirm the modes of slow hydrogen exchange in solution here discussed.

VI. Steps of the Ionization Mechanism

The ionization mechanism of exchange (8) in an acid medium is typical of carbonyl and certain other compounds capable of adding on a proton to the C=O, C=N, etc. bonds. It differs fundamentally from the associative electrophilic mechanism (9) in that the addition of a proton (or deuteron) and exchange take place at different carbon atoms with migration of the reaction center [19] and in separate steps.* In the first, usually rapid, step a proton is transferred from the acidic solvent or catalyst to the dissolved molecule. In the resultant onium cation the neighboring C−H bond is weakened and this leads to exchange or to other protolytic reactions involving one or more slower steps. This general scheme is confirmed by a series of kinetic studies [3].

There are insufficient well-founded experimental data about the individual intermediate steps of exchange according to the ionization mechanism (7) and in particular (8). Various schemes have been advanced for these and other protolytic reactions; we shall consider only the most typical of these [3, 16, 18, 26]. Their comparison may give a criterion of their reliability.

There is such a great similarity between hydrogen exchange, enolization, racemization and halogenation of ketones in presence of bases that an identical mechanism must be assumed for the first slow step: transition of proton from the C−H bond to the base B:

$$R-\underset{\underset{CH_3}{|}}{C}=O + B = \left[R-\underset{\underset{CH_2}{|}}{C}-O\right]^- + BH^+ \qquad (10)$$

* The difference between mechanisms (8) and (9) roughly corresponds to the difference between a "bimolecular" (S_E2) mechanism and a "monomolecular (S_E1) mechanism (to use the terminology of the English school [18]). This terminology cannot be considered a happy one since a solvent or catalyst usually participates in the reaction and this renders very indeterminate the difference in the molecularity and kinetic order of the slow step.

The reverse reaction (10) with BD^+ leads to exchange; while addition of a proton to the oxygen leads to enolization. The duality of the reaction of the intermediate ion is explained, according to Nesmeyanov [19], by transfer of a reaction center on the conjugated chain from the α-carbon to the carbonyl oxygen under the influence of the reagent, and does not require to be explained by any fundamentally inaccurate or sterile resonance or mesomerism concepts.

This mechanism is confirmed by many experimental facts, but it is unsuitable for oxygen exchange of ketones with H_2O^{18} in presence of alkalies because it evidently does not lead to such an exchange. For the latter it is suggested that the slow step is the addition of hydroxyl to the carbonyl carbon:

$$R-\underset{R}{C}=O + O^{18}H^- = R-\underset{R}{C}\begin{matrix}O^- \\ O^{18}H\end{matrix} \qquad (11)$$

followed by migration of a proton from one oxygen atom to the other and later by addition of a proton (from the alkaline solvent) with formation of a symmetrical orthostructure $R_2C(OH)_2$. In order to get round these difficulties, some authors prefer a mechanism of primary addition of water at the double carbonyl bond:

$$R-\underset{R}{C}=O + H_2O^{18} = R-\underset{R}{C}\begin{matrix}OH \\ O^{18}H\end{matrix} \qquad (12)$$

Such primary steps as (11) or (12) with diverse variants of the succeeding steps are assumed for reactions of hydrolysis of carboxylic esters, oxygen exchange in aldehydes, carboxylic acids and their esters, etc. in presence of bases or in a neutral nedium. In D_2O^{18} however, acetone exchanges both hydrogen and oxygen with commensurate velocities [25]. On the basis of the mechanisms considered, it is necessary to assume that we have simultaneously, and with similar velocities, the reaction (10) of detachment of a proton and reaction (11) or (12) of addition of hydroxyl ion or water. The unsatisfactory character of such a hypothesis indicates the dubiousness of these mechanisms.

Even greater difficulties stand in the way of a detailed knowledge of mechanism (8) of isotopic exchange and other protolytic reactions of carbonyl compounds in presence of acidic catalysts. For the above-mentioned reactions of ketones, the first (rapid) step is considered to be the transfer of a proton from the acid BH to carbonyl oxygen:

$$R-\underset{R}{C}=O + BH = R-\underset{R}{C}-OH^+ + B^- \qquad (13)$$

Addition of a proton to carbonyl weakens the neighboring C—H bond and the proton can transfer from it to water with formation of an enol. Transfer of a proton from the C—H bond to the base remains the slow step if we ignore the cases of a very weak acid BH and molecules with a very strongly polarized C—H bond. This mechanism accounts for enolization but not for exchange, for which it is necessary to assume subsequent steps with participation of the enol. Consequently, in an alkaline medium, hydrogen exchange is regarded as a reaction proceeding in parallel with enolization and independently of it; in acid medium it is considered to proceed via the enolization step. Such a dualism is likewise doubtful.

For the hydrolysis of carboxylic esters in presence of acids after a step analogous to (13), further steps with participation of water are necessary. Various suggestions have been made apropos of the latter and they can be reduced to three fundamental variants [26]: 1) cleavage of alcohol with formation of a $[R-C=O]^+$ ion, ion, followed by addition of water to it; 2) exchange of a proton for an alcohol radical between $\left[R-C\begin{matrix}OH \\ OR\end{matrix}\right]^+$ and water; 3) addition of water to the same ion with formation of the orthoester of the monocarboxylic acid, which then splits off alcohol. Esterification reactions proceed trhough the same steps in the reverse order. Similar schemes explain the oxygen exchange in ketones and carboxylic acids; in this connection, for consistency with kinetic data and the presence of general acid catalysis, we must assume the slow step of transfer of a proton from acid to carbonyl or from the latter to the base conjugated with the acid BH [25]. Both are equally unlikely.

The unsatisfactory nature of all these schemes induced some authors [18, 27] to revert to the old trimolecular mechanism of Lowry, according to whom a proton (or deuteron) is transferred in one elementary act from acid to substrate and from the latter to the base, for example:

$$YD + XH + B = Y + DX + HB. \qquad (14)$$

This mechanism in turn was rejected because the kinetic equations did not contain a term corresponding to it involving the product of three concentrations, but such a conclusion cannot be considered convincing. In particular the trimolecular mechanism of exchange of hydrogen between alkenes and ND_3 was confirmed by

Shatenshtein [23] who found that exchange is accompanied by isomerization with rearrangement of the double bond.

If the deuterium donor YD and the acceptor B are different reaction centers in the same molecule, then mechanism (14) is similar to mechanism (9) for slow exchange.

VII. Exchange in radicals

Reactions in solutions with participation of free radicals are very common, and we may suggest that a radical mechanism is also encountered in reactions of hydrogen exchange of dissolved substances. This problem is intimately associated with the study of the hydrogen bond in free radicals about which very little is yet known.

Kursanov and co-workers [28] found that saturated aliphatic hydrocarbons exchange all the hydrogen atoms with concentrated D_2SO_4, if they contain tertiary carbon, and that exchange does not take place if the latter is absent. They explain this by a chain process with participation of $R_3C^{\cdot}$ radicals or of R_3C^+ ions, resulting in rearrangement of the chain and rapid exchange of hydrogen with the acid during the period of their brief existence. Such an exchange demands mechanism other than those considered above. If exchange proceeds in the carbonium ion, then the weakening of the C—H bond by the positive charge of the ion is probably insufficient to account for the rapid exchange. But if it proceeds in the radical, then we can explain the mechanism on the basis of the observation, by Fomenko and Sadovinkova [29], of absence of exchange in triphenylmethyl with D_2O or $(CD_3)_2CO$ even after prolonged heating at 100°. Unambiguous data were likewise not obtained for exchange of radicals with D_2O in a study of Kolbe's electrochemical synthesis with the help of deuterium [16].

Until new experimental data are obtained, another question which remains open is that of the role of transfer of radicals or atoms of differing isotopic composition in hydrogen exchange in solutions. Also requiring study is the possibility of participation of hydride anions in the exchange.

SUMMARY

1. A classification of reactions of isotopic exchange in solutions is advanced which is confirmed by experimental data. Such reactions are of the slow or fast type depending upon the presence or absence of free electron pairs round the atom with which the exchanging hydrogen atom is linked.

2. Exchange of the rapid type proceeds independently of the electrolytic dissociation — a process taking place in parallel.

3. The fundamental mechanisms of the slow type of exchange are discussed.

4. The unsatisfactory features of previously advanced mechanisms of protolytic reactions of carbonyl compounds are demonstrated.

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