Translated from *Uspekhi Khimii* **59** 106–131 (1990) U.D.C. 541.128;541.183.3

The mechanism of the dehydration of alcohols and the hydration of alkenes in acid solution

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ABSTRACT. Kinetic data for the hydration of unsaturated compounds, the dehydration of alcohols, and the isotope exchange of the oxygen atom in alcohols and aqueous solutions of strong acids are analysed to establish the detailed mechanisms of these reactions. The catalytic action of the acid is caused not only by its ability to protonate the reactant but also by the possibility of the formation of reactive complexes of the reactant with the acid hydrates or the molecules of the undissociated acids. Equations are presented whereby the influence of the ionising capacity of the medium on the effective rate constants for the reactions indicated can be taken into account quantitatively. The question of the involvement of carbonium ions as reactive intermediates in reactions involving the dehydration of alcohols, the hydration of unsaturated compounds, and the isotope exchange of the oxygen atom in alcohols is examined. Complexes of the reactant with a solvated proton, the acid molecules, and the acid hydrates are the intermediates in these reactions. The relative contributions of the complexes to the effective rate constant depend on the acid concentration in the aqueous solution.

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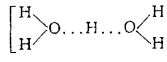
I. Introduction

The study of the detailed mechanisms of the strong acid-catalysed reactions involving the hydration of unsaturated compounds (UC) and the dehydration of alcohols (ROH) in aqueous solutions is of interest for the development of a theory of acid catalysis and for the quantitative estimation of the influence of the structure of organic substances on their reactivity. Systematic studies on the kinetics and the detailed mechanisms of these reactions were initiated at the beginning of the 1940s. Certain data on this question are contained in a monograph (Ref. 1, p. 210) and a review.[2]

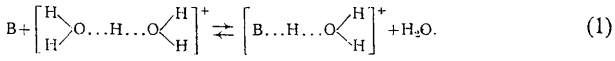
Judging from the kinetics, the dehydration of ROH and the hydration of UC in aqueous solutions are complex reactions. As a rule, the kinetic data were analysed previously from the concept that in aqueous solutions of strong acids a proton adds to the reactant base and that the protonated form is the intermediate reactive complex which can be formed either in the equilibrium stage or in the rate-limiting stage. This idea constitutes a gross simplification of the real picture of the complex interaction in solutions.

Many facts have now accumulated which make it possible to expand our knowledge about the nature of the ionising and catalytic action of acids.

Protonation is only one of the forms of ionisation in aqueous solutions of strong acids. Ionisation can entail the formation also of complexes of the base with the molecules of the undissociated acid and with the acid hydrates,[3] some of which may be reactive in the reactions investigated. It has been established that in aqueous solution, protons are present not as H_3O^+ ions but as $H_5O_2^+$ ions, which exist as a result of the formation of the strong hydrogen bond


(Ref.4)

Naturally, these ions are solvated by the solvent. Protonation in aqueous solution is a reaction involving the substitution of a water molecule in the $H_5O_2^+$ ion by the base B:


(1)

The protonated form BH_3O^+ is a complex of the base with the H_3O^+ ion, which also exists by virtue of the presence of a strong hydrogen bond.[5] The reaction products can be formed simultaneously via several pathways.

It is of interest to analyse the available literature kinetic data on the hydration of UC and the dehydration of ROH taking into account the ideas described above concerning the ionising capacity and catalytic activity of strong acids in aqueous solutions. This paper is in fact devoted to this problem. Valuable information about the detailed mechanisms of these reactions can be obtained from experimental data for the isotope exchange of the oxygen atom of the OH group in alcohols and the racemisation of optically active alcohols in acid media and also by measuring the isotope effects on replacement of a hydrogen atom by deuterium. These questions are examined in this review for this reason.

II. Kinetics of the hydration of alkenes and the dehydration of alcohols on the basis of the carbonium ion concept

Kinetic measurements are usually made using low concentrations of the UC and the ROH which do not affect the catalytic properties of the solution. In this case the UC hydration and the ROH dehydration reactions at constant acid concentration are first order relative to the concentration of the organic reactant. As a rule, these reactions are reversible:

$$R'-CH=CH_2+H_2O \underset{k_{dehydr}}{\overset{k_{hydr}}{\rightleftharpoons}} R'-\underset{OH}{CH}-CH_3$$

and

$$-dc_{UC}/dt = dc_{ROH}/dt = k_{hydr}\,c_{UC} - k_{dehydr}\,c_{ROH}, \quad (2)$$

where k_{hydr} includes also a function characterising the concentration of water in solution.

Interpretation of the results of kinetic measurements carried out in a medium with a constant acid concentration yields the rate constant $k_{sum} = k_{hydr} + k_{dehydr}$. The equilibrium concentrations of the UC and of the alcohol obtained (c^{∞}_{UC} and c^{∞}_{ROH}) are measured for the separate determination of k_{hydr} and k_{dehydr}. According to Eqn. (2),

$$c^{\infty}_{ROH}/c^{\infty}_{UC} = k_{hydr}/k_{dehydr}.$$

It is noteworthy that most of the kinetic studies on the UC hydration and the ROH dehydration reactions have been carried using aqueous solutions of strong acids—sulphuric, perchloric, and nitric. The acidity functions H_0 and also the thermodynamic activities of the acid and water at 25 °C are known for such solutions. For sulphuric acid solutions, these quantities have been measured also at other temperatures.

An increase in the concentration of the strong acid in moderately concentrated and concentrated aqueous solutions leads to a sharp increase in k_{hydr} and k_{dehydr}. As a rule, a linear relation is observed between lg k_{hydr} and H_0:

$$\lg k_{hydr} + \alpha' H_0 = \text{const}. \quad (3)$$

The quantity α' is sometimes close to unity but in the vast majority of cases $\alpha' > 1$ and is in the range 1.1–1.4. The linear relation between lg k_{hydr} and H_0 can be explained by the formation of the protonated form of the alkene, which is regarded as the intermediate complex in the hydration of the UC. According to Whitmore,[6] this ion includes a positively charged carbon atom with six electrons:

$$R-CH=CH_2+H^+ \rightleftarrows R-\overset{+}{C}H-CH_3.$$

The Whitmore carbonium ion is a σ-complex.

The earlier studies on the kinetics and mechanism of the hydration of UC and the dehydration of ROH were devoted to the detection of the existence in acid solutions of Whitmore carbonium ions as intermediate reactive species. According to Whitmore, one of the ways of obtaining such carbonium ions involves the addition of a proton to the double bond of the UC. It is suggested that this reaction is reversible. It is also assumed that the reactions involving the elimination of an alkene from alkyl halides and alcohols are unimolecular and proceed via the same mechanism (Ref. 7, p. 540). In the case of alkyl halides, the reactant dissociates in the slow step into the carbonium ion and the anion X^-:

$$R_2CH-CR_2X \rightarrow R_2CH-\overset{+}{C}R_2 + X^-.$$

The step in which the carbonium ion decomposes into an alkene and a proton is rapid:[7]

$$R_2CH-\overset{+}{C}R_2 \rightleftarrows R_2C=CR_2 + H^+.$$

According to Whitmore,[6] as a result of the protonation of the ROH in the formation of an alkene from an alcohol in an acid a stable oxo-compound (the protonated form of the alcohol) is formed initially and then decomposes in the slow step into a carbonium ion and water:

$$CH_3CH_2OH + H^+ \overset{\text{fast}}{\rightleftharpoons} CH_3-CH_2\overset{+}{O}H_2,$$

$$CH_3-CH_2OH_2^+ \overset{\text{slow}}{\rightleftharpoons} CH_3-\overset{+}{C}H_2 + H_2O,$$

$$CH_3-CH_2^+ \overset{\text{fast}}{\rightleftharpoons} CH_2=CH_2 + H^+.$$

As in the majority of the available publications, H^+ for simplicity is a solvated proton with solvation shell of indefinite composition and ROH_2^+ denotes the protonated form of the alcohol.

If the mechanisms of the formation of carbonium ions presented above do indeed occur and the ions have the properties attributed to them, then the following features due to the high reactivity of carbonium ions and their rapid equilibration with the UC in an acid medium should be manifested.

1. The hydration should be accompanied by the still more rapid isomerisation of one UC to another, provided that the same carbonium ion is formed on protonation.

2. In the presence of deuterium or tritium oxides in the medium, isotope exchange of the hydrogen atoms attached to the carbon atoms of the double bond of the UC should be observed. This exchange should precede the rate-limiting step of the hydration of the UC.

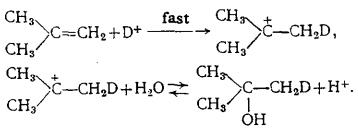
In order to observe the postulated effects, mainly aliphatic alcohols and the UC obtained from them have been used. As early as 1940, a study was published[8] from which it followed that, even if the Whitmore ions are formed, they are incapable of exchanging a hydrogen atom at the carbon atoms of the double bond: the dimer obtained on dimerisation of anethole in a solution of DCl in methanol contained no more deuterium than the initial monomer. Unfortunately, at the time this result did not receive due attention.

The study of the hydration in 0.973 M HNO_3 solution in water at 25 °C of the two isomeric alkenes 2-methylbut-2-ene and 2-methylbut-1-ene, from which the same carbonium ion should be formed on protonation, i.e.

$$\left.\begin{array}{l} H_3C-\underset{CH_3}{C}=CH-CH_3 + H^+ \\ H_2C=\underset{CH_3}{C}-CH_2-CH_3 + H^+ \end{array}\right\} \rightarrow CH_3-\overset{CH_3}{\overset{|}{\overset{+}{C}}}-CH_2-CH_3,$$

showed[9] that at 50% conversion of the UC into an alcohol there is no appreciable isomerisation of the initial alkene. The hydration of these alkenes results in the formation of only one product—t-pentyl alcohol. Consequently, on dissolution of the alkene in an acid, there is no rapid and reversible addition of the proton to the alkene with the subsequent interaction of the ion formed with a water molecule in the rate-limiting step. The exchange for deuterium of the hydrogen atoms attached to the carbon atoms of the double bond was not observed[10–12] in solutions of alkenes and alcohols in acids. Thus the alkene isolated from the reaction mixture after the fiftieth conversion of 2-methylbut-2-ene into an alcohol in 1 M HNO_3 solution in deuteriated water (50% deuterium) did not contain measurable amounts of deuterium.[10] In the alcohol obtained on hydration of isobutene to D_2SO_4, there is only one C–D bond.[11]

This result was subsequently confirmed experimentally[12] in the hydration of isobutene in deuterium-containing perchloric acid. Indeed, if the "classical" carbonium ion is formed and is not in equilibrium with the alkene, then the t-butyl alcohol obtained on hydration of isobutene in the deuteriated acid will contain only one C–D bond:

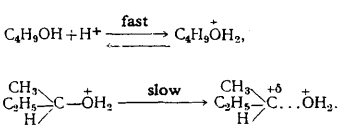


The measurements were performed under conditions where the contribution of the alcohol dehydration reaction to the overall rate of reaction can be neglected. As a rule, the equilibrium hydration of the UC is displaced towards the alcohol and $k_{dehydr} \ll k_{hydr}$. It has also been shown[11] that, on formation of an alkyl sulphate from ethylene, the hydrogen atom does not undergo isotope exchange.

The exchange of a hydrogen atom for deuterium, expected in the presence of Whitmore carbonium ions (σ-complexes), was also not observed in the experiments with arylalkenes. Thus the interaction of 2-phenylpropene has been investigated[13] in ethanol in the presence of a 17% D_2SO_4 solution. After the attainment of 24% and 54% conversions, the deuterium content in the unreacted UC in the five positions of the hydrogen atoms not incorporated in the aromatic ring was only 0 ± 2% in the former case and 10 ± 5% in the latter case. In the same study, it was shown by NMR that, in the formation of the ethyl ether derived from *cis*-2-phenylbut-2-ene (11% D_2SO_4 in C_2H_5OD), the unreacted 2-phenylbut-2-ene contains no hydrogen atoms.

For 15% conversion of styrene-ββ-d_2 to the carbinol in 43.4% $HClO_4$ solution, the unreacted styrene-ββ-d_2 contained no additional D atoms.[13] This fact shows that the exchange of hydrogen atoms cannot precede the rate-limiting step of the hydration reaction and even if a Whitmore carbonium ion is formed it is not in equilibrium with the UC. It is noteworthy that the formation of such carbonium ions is believed to be a thermochemically unfavourable reaction.[14] The results described led investigators to revise the principle postulates of the carbonium ion concept.

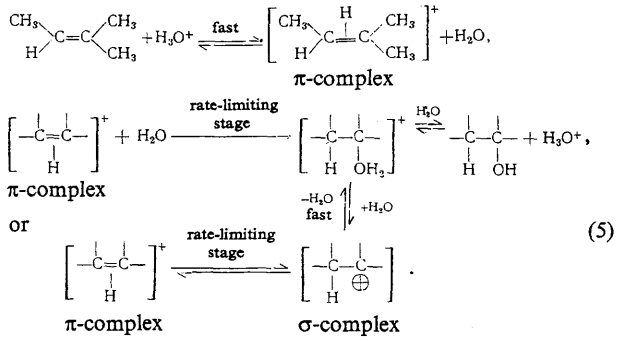
It is believed[15,16] that the intermediate reactive species in the exchange reaction of the oxygen atom in s-butyl alcohol is not a Whitmore carbonium ion but a carbonium ion linked to a water molecule; it is formed from the protonated alcohol in the slow stage and is converted into the product in the rapid stage:



(4)

Such an ion does not exchange the hydrogen atom of the C–H bond for either deuterium or tritium.

It has been suggested[17] that the carbonium ion has the structure of the π-complex proposed by Dewar in which the bond between the proton and the UC is formed via the π-orbitals of the double bond.[18] This proton is not equivalent to the protons attached to the carbon atoms of the double bond. It has been postulated that the π-complex is in equilibrium with the UC and that the concentration of such complexes determines the rate of the limiting step of the hydration of the UC. The proposed equilibrium and rate-limiting steps of the hydration of 2-methylbut-2-ene are described by the equations



(5)

The conclusion that there is an equilibrium between the UC and the π-complex was reached from results of experiments on the hydration of 2-methylbut-2-ene in 0.973 M HNO_3 at 30 °C in a mixture of D_2O and H_2O with different ratios $n = c_{D_2O}/(c_{D_2O} + c_{H_2O})$.[17] An increase in n altered the effective hydration rate constant in the mixed solvent k^n_{hydr}. The observed effect was described quantitatively on the following assumptions: the protonated form of the UC, produced in the equilibrium step, is the reactive form in its hydration; the observed reaction rate is the sum of the rate of hydration via pathways involving the participation of the solvated proton and deuteron; the specific rate constants for these pathways can be measured by employing solutions with $n = 0$ and $n = 1$ respectively; the activity of the protons and deuterons for different n can be calculated from literature data.[19]

It was shown subsequently[12,20] that, in order to describe the dependence of the observed hydration rate constant on n, it is necessary to take into account not only the ratio of the concentrations of protons and deuterons but also the differences between the isotope enrichments of the solvent and the C–H bonds of the alcohol formed on hydration of the UC. According to Scheme (5), the π-complex is obtained from the UC in the rapid and equilibrium stages, while the rate-limiting step of the hydration reaction can be both bimolecular and unimolecular. In the former case, the π-complex reacts with H_2O to produce the protonated form of ROH. In the unimolecular rate-limiting step, the π-complex is converted into a σ-complex, which is subsequently rapidly converted into the protonated alcohol. In the reverse alcohol dehydration reaction, the π-complex should be converted in the rapid and equilibrium step into the σ-complex which is formed according to the mechanisms presented above, on protonation of ROH and then splits off water.

We believe that Scheme (5) can operate only in rare cases, because, in conformity with this Scheme, it has been assumed that the ionisation of ROH and UC reduces solely to the protonation reaction and because the hypothesis of the formation of a π-complex from the UC in the rapid and equilibrium stages is controversial.

As experimental data on the UC hydration and ROH dehydration reactions accumulated, the view according to which the transfer of a proton to the UC in the hydration reaction takes place in the rate-limiting step became increasingly firmly established. Such transfer is indicated by the catalytic acceleration of the hydration reaction by weak acids. For example, the hydration of *p*-methoxy-α-methylstyrene,[21,22] cyanoketen dimethylacetal,[23] and 2-dichloromethylene-1,3-dioxolan[24] is catalysed by carboxylic acids and buffer mixtures. A similar phenomenon has also been observed for other UC.[25,26] It has been suggested that, in catalysis by undissociated molecules of weak acids, the proton is transferred in the rate-limiting step.

The reaction rate constant k and the acid dissociation constant K_{dis} are related by the Brønsted equation

$$k/p = (qK_{dis}/p)^{\alpha},$$

where p and q are statistical corrections and α is a coefficient to which the significance of a measure of the degree of proton transfer in the transition state has been attributed (Ref. 27, p. 345). If $\alpha = 1$, it is assumed that the proton transfer takes place in the equilibrium step. The Brønsted equation has also been used to obtain information about the degree of proton transfer in the rate-limiting step of the hydration of the UC in catalysis by strong acids. For this purpose, measurements were made of the dependence of the rate constant k_{hydr} on n, i.e. on the mole fraction of D_2O in a mixed solvent consisting of D_2O and H_2O or the mole fraction of T_2O and H_2O.[12,23,24] It was found that the dependence of lg k_{hydr} on n for reactions with proton transfer in the equilibrium and rate-limiting steps is described by identical formulae. It is logical to postulate that in the catalysis of the hydration of UC by strong acids in aqueous solutions proton transfer to the UC can also be achieved in the rate-limiting step.

Attempts have also been made on the basis of such ideas to calculate the lifetime of the carbonium ions (carbocations). For example, it has been shown[28] that the lifetime of the carbocations formed from 2,3-dimethylbut-2-ene in dilute aqueous acid solutions ($HClO_4$, H_3PO_4, HSO_4^-) at 25 °C is $\sim 10^{-10}$ s.

The proton transferring agents can be ion pairs, solvated protons, and the molecules of the undissociated acid. This does not naturally rule out the possibility of proton transfer to the UC in the rapid and equilibrium steps.

As already mentioned above, in catalysis by strong acids lg k_{hydr} frequently varies more markedly than H_0. This fact and also the correlation between lg k_{hydr} and the σ^+ constants of the substituents have been explained by proton transfer to the reactant in the rate-limiting step.[13]

In order to test the concept of "classical" carbonium ions, the kinetics of the exchange of ^{16}O for ^{18}O in alcohols have been studied. The results of measurements under identical conditions of the rate constants for such exchange (k_{exch}) and the dehydration of ROH cannot be explained on the assumption that the "classical" carbonium ion is the intermediate reactive species in these reactions. As already mentioned above, it has been suggested[15,16] that the carbonium ion incorporates a water molecule. In the view of the above workers, the exchange of the oxygen atom in the alcohol takes place in the rapid step and the unimolecular step involving the formation of this ion is rate-limiting, as shown in Scheme (4). In the study of the kinetics and mechanism of the exchange of the oxygen atom in alcohols, measurements have been made as a rule also of the rate constant for the dehydration of ROH in order to be certain that the exchange does not occur as a consequence of the reversibility of the ROH dehydration and UC hydration reactions. As a result, a bimolecular mechanism has been proposed for the exchange of the oxygen atom in alcohols.

It has been found[15] that under identical conditions k_{dehydr} for s-butyl alcohol is much smaller than k_{exch}. Subsequent studies demonstrated that this rule holds also in the majority of other cases, but there are exceptions. However, in elucidating the causes of these deviations, additional confirmation of the validity of the bimolecular exchange mechanism was obtained.

Comparison of the rate constants for the exchange involving t-butyl alcohol in ^{18}O-enriched sulphuric acid with the rate of dehydration of the alcohol in the unlabelled acid showed that at 55 °C in 0.045 and 0.45 M H_2SO_4 solutions, the constant k_{exch} is greater than k_{dehydr} by factors of 30 and 27 respectively.[29] At 75 °C in 0.045 M H_2SO_4 solution, $k_{exch}/k_{dehydr} = 20.7$. The alcohol concentration in the experiments was 1.04 M. The constant k_{exch} was greater than k_{dehydr} also in the case of t-pentyl alcohol:[30] at 25 °C, $k_{exch} = 7.72 \times 10^{-4}$ min^{-1} in 0.96 M H_2SO_4 solution, while $k_{dehydr} = 1.59 \times 10^{-4}$ min^{-1} in 1.5 M H_2SO_4 solution. The ROH concentration was 0.5 M in these experiments.

Comparison of the constants k_{exch} and k_{dehydr} for n-butyl and neopentyl alcohols proved to be more complex because the alkenes formed from them at 125 °C in 0.5 M sulphuric acid solution undergo further reactions.[31] The products of the reaction of n-butyl alcohol are s-butyl alcohol, di-n-butyl ether and a mixture of butenes. t-Pentyl alcohol and a mixture of pentenes are formed from neopentyl alcohol. The rate of the decomposition reaction was determined from the decrease in the concentration of the initial alcohol. Table 1 presents the measured[31] k_{exch} and the decomposition rate constants k_{decomp} for n-butyl and neopentyl alcohols.

Table 1. The constants k_{exch} and k_{decomp} for n-butyl (0.729 M) and neopentyl (0.242 M) alcohols at 125 °C (according to the data of Dostrovsky and Klein[31]).

Alcohol	$[H_2SO_4]$, M	$10^2 k_{exch}$, min^{-1}	$10^2 k_{decomp}$, min^{-1}
n-Butyl	0.46	33.6	9.84
Neopentyl	0.48	0.84	30.6

There are good grounds for the assumption that the primary products of the decomposition of n-butyl and t-pentyl alcohols are alkenes whose hydration entails the formation of s- and t-butyl alcohols. One can therefore assume that $k_{decomp} = k_{dehydr}$. According to the data in Table 1, $k_{exch} > k_{dehydr}$ for n-butyl alcohol. On the other hand, $k_{exch} < k_{dehydr}$ for neopentyl alcohol. Thus n-butyl alcohol is more reactive in the exchange reaction than neopentyl alcohol. The experimental data for the exchange of the oxygen atom in ROH[15,29,30] show that the exchange and dehydration proceed via different mechanisms. The same conclusion follows from the results of a study[31] where it was shown that but-1-ene and but-2-ene are formed from n-butyl alcohol in an acid medium, but the product of the hydration of both alkenes is s-butyl alcohol. The formation of the latter from but-1-ene has been demonstrated by experiments on the hydration of [^{14}C]-but-1-ene under conditions similar to those used in the study of the exchange of the ^{16}O atom. s-Butyl and n-butyl alcohols have been obtained from [^{14}C]-but-1-ene, but the content of n-butyl alcohol in the hydration products was only 0.001. Consequently the exchange of ^{16}O in n-butyl alcohol is not a consequence of the dehydration of the latter with subsequent hydration of but-1-ene. It was therefore concluded[31] that the exchange of the oxygen atom in n-butyl alcohol proceeds exclusively via a bimolecular mechanism:

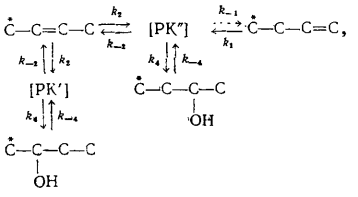
$$H_2{}^{18}O + CH_3(CH_2)_2CH_2OH \rightleftarrows H_2O + CH_3(CH_2)_2{}^{18}OH.$$

It follows from Table 1 that under identical conditions k_{exch} is greater for n-butyl alcohol than for neopentyl alcohol. This can be explained by steric hindrance in the bimolecular exchange mechanism involving neopentyl alcohol.

Fundamental conclusions concerning the mechanisms of the dehydration of ROH, the hydration of UC, and the exchange of the oxygen atom in alcohols have been reached by Manassen and Klein.[32] They investigated the reactions of but-1-ene and s-butyl alcohol in 0.555 M $HClO_4$ solutions at 101.4 °C.

1) $CH_3CH_2CH=CH_2 + H_2O \rightleftarrows CH_3CH_2CH(OH)CH_3$,
2) $CH_3CH_2CH=CH_2 \rightleftarrows CH_3CH=CHCH_3$,
3) $CH_3CH_2CH(OH)CH_3 \rightleftarrows CH_3CH=CHCH_3 + H_2O$,
4) $CH_3CH_2CH(^{18}OH)CH_3 + H_2{}^{16}O \rightleftarrows CH_3CH_2CH(^{16}OH)CH_3 + H_2{}^{18}O$.

Overall, the reactions investigated can be represented by the following Scheme:



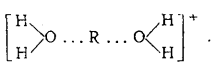
where [PK′] and [PK″] are reactive complexes.

Analysis showed that

$$k_{isom} = k_{-1}k_2/(k_2 + k_4),$$

where k_{isom} is the isomerisation rate constant.

Using 2-butanol labelled with ^{18}O and ^{14}C, it was possible to investigate under the same conditions the exchange of the oxygen atom of the alcohol with water and the isomerisation of the alcohol. It was found that $k_{isom} = (3.102 \pm 0.072) \times 10^{-4}$ min^{-1} and $k_{exch} = (4.490 \pm 0.093) \times 10^{-4}$ min^{-1}. The authors[32] believe that the data for all four reactions investigated can be best described by assuming that the intermediate is a planar carbonium ion linked to a water molecule on either side of the plane; the central carbon atom is thus "pentavalent". The intermediate in the reaction involving the exchange of the oxygen atom in ROH has in their view the composition



This composition of the intermediate was also adopted in subsequent studies (see, for example, McClellend[33]).

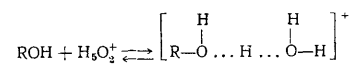
The ideas about the equilibrium and rate-limiting steps in the dehydration of ROH, the hydration of UC, and the exchange of the oxygen atom in alcohols described above do not permit a quantitative description of the effect of the ionising capacity of the aqueous acid solution on the experimental (effective) rate constants for these reactions. This situation can be accounted for by the fact that, in the analysis of kinetic data obtained in solutions at a variable concentration of the acid catalyst, no account is taken of the fact that (1) the protonated form of the reactant B is the complex BH_3O^+ [see Eqn. (1)], (2) the intermediates are not only such ions but also complexes of the reactant-base with acid molecules, acid hydrates, etc., and (3) when the concentration of the acid in solution is varied within wide limits the hydration and dehydration reactions can proceed via several pathways, i.e. all the ions and molecules capable of forming a reactive complex with the reactants can exhibit a reactivity. The relative contribution of each pathway to the effective rate constant depends on the acid concentration.

An attempt is made below to explain certain literature data taking into acocunt the mechanism proposed for the ionisation of acids.

III. A method for the determination of the mechanism of the dehydration of alcohols and the hydration of unsaturated compounds from kinetic data

The modern physical methods do not permit the determination of the concentration and composition of the intermediate reactive complexes RC in the course of a kinetic experiment on the hydration of UC and the dehydration of ROH. Conclusions concerning the composition of RC and the influence of the medium on their concentration have been made on the basis of the dependence of k_{hydr} and k_{dehydr} on the ionising properties of the medium. The mechanism of the ionisation of alcohols in acid media has not so far been studied in detail and there are no reliable data for the basicity constants of aliphatic alcohols. However, there is no doubt that the ionisation of alcohols can lead to the formation of protonated forms, ion pairs, and complexes with components of the solution (for example, with the acid molecules HA).

According to Vinnik et al.,[5] the formation reaction of the protonated form of the alcohol ($ROH.H_3O^+$) can be described by the equation



The hypothesis of the formation of the ion pair $ROH.H_3O^+.A^-$ and the complexes ROH.HA has been justified by experimental data for the ionisation of tertiary amines, azulene and its derivatives,[3] and also indole derivatives[34] in moderately concentrated and concentrated aqueous solutions of strong acids. It follows from the literature data described above that hitherto there have been no clear-cut ideas about the structure and properties of the ionised form of the alkene in aqueous acid solutions. The function which would make it possible to take into account the influence of the acidity of the medium on the degree of conversion of the UC into the ionised form is also unknown. The ionised form can be produced either in the equilibrium or in the rate-limiting states. Unfortunately, most investigators assume that in aqueous solutions of strong acids the ionisation of bases reduces solely to their protonation and in cases where it is not possible to describe the experimental data they assume that the ratio of the activity coefficients of the unionised and protonated forms of the test base and of the Hammett indicators depends on the acid concentration in different ways.

There have also been attempts to select correlation equations for the description of such reactions. It has been suggested that the ionisation of each base is described by its own acidity function.[35–37] For example, we may designate such a function for the UC by H_s. The function H_0 measured by means of indicators and the function H_s are linked by the equation

$$H_s + \lg c_{H^+} = (1 - \Phi_c)[H_0 + \lg c_{H^+}], \quad (6)$$

which has been obtained on the assumption that

$$\lg f_{H^+} - \lg \frac{f_{SH^+}}{f_S} = (1 - \Phi_c)\left[\lg f_{H^+} - \lg \frac{f_{BH^+}}{f_B}\right],$$

where f are the concentration activity coefficients of the corresponding species, c_{H^+} is the concentration of solvated protons, and Φ_c is a coefficient independent of the H_0 for the medium according to its significance.

If the reactive species is a protonated form of the UC produced in the equilibrium stage and converted into the reaction products in the

rate-limiting stages, then, provided that the degree of protonation of the UC is low, we obtain according to Lucchini et al.[35]

$$\lg k_{hydr} + H_0 = \lg k_0 + (\Phi_{RC} - \Phi_c)[H_0 + \lg c_{H^+}],$$

where k_0 is a constant and Φ_{RC} is a coefficient corresponding to Φ_c when the base is RC.

On the other hand, if the proton adds to the UC in the slow stage, i.e.

$$UC + H_5O_2^+ \xrightarrow{slow} RC \rightarrow \text{products},$$

then

$$\lg k_{hydr} + H_0 = \lg k_0 + \Phi_{RC}[H_0 + \lg c_{H^+}].$$

When this method of analysis of kinetic data is used, one cannot naturally obtain information about the specific reaction mechanism, the composition of the RC, and about the equilibrium and rate-limiting stages.

If the rate-limiting stage is the formation of the protonated form, then it is believed[38,39] that the rate of protonation of bases can be characterised by means of the kinetic activity function H_c^*. An attempt has been made to apply this function in the analysis of data for the kinetics of the hydration of styrene and its derivatives.[40]

It is important to note that the attempts to explain the kinetics of the UC hydration and ROH dehydration reactions solely on the basis of the concept of carbonium ions as intermediate reactive species simplified the real mechanism of these reactions because no account was then taken of the catalytic action of other ions, neutral species, and ion pairs in the aqueous solution of strong acids.

As can be seen from Eqn. (2), k_{hydr} and k_{dehydr} are effective overall constants. In order to elucidate their physical significance, it is essential to establish how they depend on the ionising capacity of the acid solutions a_δ. The ionisation reaction of UC and alcohols can be described with the aid of the equations

$$UC + \delta \overset{K_i^{UC}}{\rightleftarrows} UC.\delta,$$

$$ROH + \delta \overset{K_i^{ROH}}{\rightleftarrows} ROH \cdot \delta,$$

where K_i^{UC} and K_i^{ROH} are the ionisation equilibrium constants. Ions or molecules whose addition converts the reactant into the ionised form are designated by

$$K_i^{UC} = \frac{a_{UC} a_S}{a_{UC.\delta}} = \frac{c_{UC}}{c_{UC.\delta}} a_\delta \frac{f_{UC}}{f_{UC.\delta}},$$

$$K_i^{ROH} = \frac{a_{ROH} a_\delta}{a_{ROH \cdot \delta}} = \frac{c_{ROH}}{c_{ROH \cdot \delta}} a_\delta \frac{f_{RCH}}{f_{ROH \cdot \delta}}.$$

In many reactions in acid solutions, the intermediate RC is either the ionised form of the reactant or its complex with the molecules and ions from the solution. Equations designed to take into account the influence of the medium on the rates w and the hydration and dehydration rate constants, derived on the assumption that the catalytic action of the acid is due to the conversion of the reactant into the ionised form, which is either itself the RC or is capable of forming such RC rapidly and reversibly on interaction with species from the solution, are presented below. If the RC in the dehydration reaction has the composition ROH.δ, then

$$w_{dehydr} = k \frac{a^*}{f^*} = k \frac{a_{RC}}{f^*} = \frac{k_{true}}{K_i^{ROH}} \frac{a_{ROH} a_\delta}{f^*} = \frac{k_{true}}{K_i^{ROH}} c_{ROH} a_\delta \frac{f_{ROH}}{f^*},$$

$$\frac{w_{dehydr}}{c_{ROH}} = \frac{k_{true}}{K_i^{ROH}} a_\delta \frac{f_{ROH}}{f^*} = k_{dehydr}, \qquad (7)$$

where k_{true} is the true rate constant independent of the acid concentration in the aqueous solution, a^* and f^* are respectively the activity and the activity coefficient of the activated complex, and a_{RC} is the activity of the RC expressed in terms of the activity of the unionised alcohol ROH and the species δ.

Since the UC hydration and ROH dehydration reactions proceed via the same RC, in its formation from the UC a water molecule should add to the ionised form UC.δ:

$$UC.\delta + H_2O \overset{K_{RC}^{UC}}{\rightleftarrows} RC,$$

$$K_{RC}^{UC} = a_{UC.\delta} a_{H_2O} / a_{RC}. \qquad (8)$$

Then

$$w_{hydr} = k \frac{a^*}{f^*} = k \frac{a_{RC}}{f^*} = \frac{k_{true}}{K_{RC}^{UC}} \frac{a_{UC.\delta} a_{H_2O}}{f^*} =$$

$$= \frac{k_{true}}{K_{RC}^{UC}} \frac{a_{UC} a_\delta a_{H_2O}}{K_i^{UC} f^*} = \frac{k_{true} c_{UC} a_{H_2O} f_{UC} a_\delta}{K_{RC}^{UC} K_i^{UC} f^*}, \qquad (9)$$

$$\frac{w_{hydr}}{c_{UC}} = \frac{k_{true}}{K_{RC}^{UC} K_i^{UC}} a_{H_2O} a_\delta \frac{f_{UC}}{f^*} = k_{hydr}.$$

In Eqns. (7) and (9), w_{dehydr} and w_{hydr} are the rates of dehydration of ROH and hydration of UC in an aqueous solution with a specified acid concentration. These equations were obtained subject to the condition that the degree of conversion of ROH and UC into the ionised form is low. In Eqns. (7) and (9), δ denotes the following species:

(1) the H_3O^+ ions participating in the protonation of the base, whereupon $a_\delta = h_0$,

(2) the $H_5O_2^+$ ions participating in the formation of the RC in accordance with the equation

$$ROH + H_5O_2^+ \rightleftarrows ROH \cdot H_5O_2^+; \qquad (10)$$

whereupon $a_\delta = a_{H_5O_2^+} = h_0 a_{H_2O}$, since one can assume that $h_0 = a_{H_3O^+}$,[5]

(3) the ion pairs $H_3O^+.A^-$ participating in the formation of the complex in accordance with the equation

$$ROH + H_3C^+ \cdot A^- \rightleftarrows ROH \cdot H_3O^+ \cdot A^-; \qquad (11)$$

whereupon $a_\delta = a_{HA} \cdot a_{H_2O}$, i.e. the activity of the ion pair of the strong acid $H_3O^+.A^-$ is expressed in terms of the product of the thermodynamic activities of the acid (a_{HA}) and water (a_{H_2O}), and

(4) the acid molecules HA participating in the formation of the complex of the base with one or two molecules of the undissociated acid:

$$ROH + HA \rightleftarrows ROH \cdot HA, \qquad (12)$$

$$ROH + 2HA \rightleftarrows ROH \cdot 2HA; \qquad (13)$$

in the first case $a_\delta = a_{HA}$ and in the second $a_\delta = a_{HA}^2$.

Naturally, these examples do not exhaust the possibilities for the complex formation (ionisation) of bases in aqueous solutions of strong acids.

Eqns. (7) and (9) can be used to find the composition of the RC from kinetic data. For this purpose, it is essential to establish the dependence of k_{dehydr} on known functions characterising the ionising capacity of the acid solution. The problem reduces to the selection of a function a_δ for the description of the influence of the medium on the effective rate constant subject to the conditions that the multipliers f_{ROH}/f^* and f_{UC}/f^+ in Eqns. (7) and (9) respectively are independent of the acid concentration in solution.[41]

Unfortunately, it has not so far been established unambiguously how the ratios $f_{ROH}/f_{ROH.\delta}$ and $f_{UC}/f_{UC.\delta}$ really change when the acid concentration in solution is varied. In many cases, the reactive form of alcohols is the protonated form, its complexes with water molecules, and ion pairs, and the influence of the medium on the effective rate constant can frequently be described by assuming that $f_{ROH}/f_{ROH.\delta}$ is independent of the acid concentration in solution. This can be explained by the fact that, as in the ionisation of nitroanilines, in the ionisation of alcohols the rearrangement of the electronic structure of the molecule has little effect on its solvating capacity.

The formation of the arenium carbonium ion is accompanied by a significant rearrangement of the electronic structure of the UC.[42,43] Although the structures of the ionised form of aliphatic UC have not so far been established, there are grounds for the assumption that in the given instance the electronic structure of the UC rearranges. Hence it follows that, depending on the medium, there is a possibility that in the ionisation of the UC the ratios of the activity coefficient of the unionised and ionised forms of the UC may change.

It is known that, when the acid concentration in aqueous solution is varied, the activity coefficients of the unionised forms of the UC (f_{UC}) and of the alcohol obtained from it (f_{ROH}) do not vary in the same way. Consequently, depending on the composition of the medium, the quantities $f_{ROH}/f_{ROH.\delta}$ and f_{UC}/f^* should also vary in different ways.

The reactive complex ROH.δ is one of the ionised forms of the alcohol; Eqns. (10)–(13) reflect the stoichiometry of their formation. Taking into account the arguments described above stating that the composition of the medium does not influence the ratio $f_{ROH}/f_{ROH.\delta}$, one may postulate that in the ROH dehydration reaction it is also independent of the acid concentration. The reactions analysed in this review are slow and we therefore assume that the reactive complex and the activated complex obtained from it are in equilibrium with the reactants. This enables us to assume that the ratios f_{ROH}/f^* and f_{ROH}/f_{RC}^{ROH} vary in the same way as the acidity of the medium is varied (the activity coefficient of RC in the ROH dehydration and UC hydration reactions is designed by f_{RC}^{ROH}).

We replaced f^* in Eqn. (2) by f_{ROH}/f_{RC}^{ROH}, whereupon

$$k_{dehydr} = \frac{k_{true}}{K_i^{ROH}} a_\delta \frac{f_{ROH}}{f_{RC}^{ROH}}. \quad (14)$$

By adjusting f_{ROH} and f_{RC}^{ROH} to water as the standard and by setting them equal to unity, we obtain

$$k_{dehydr} = \frac{k_{true}}{K_i^{ROH}} a_\delta. \quad (15)$$

Eqn. (14) can be used to establish the composition of the RC from kinetic data.

In order to determine the composition of the activated complex in the ROH dehydration reaction, it is necessary to select a species δ such that Eqn. (7) for k_{dehydr} includes the multiplier f_{ROH}/f^*, which is independent of the acid concentration in solution. The function a_δ found in this way does in fact characterise the composition of the RC. For this purpose, it is essential to know the rate constant for the hydration of the UC and for the dehydration of the ROH obtained from it under identical conditions.

Unfortunately, despite the comparatively large number of studies on the hydration of UC and the dehydration of ROH, the equilibrium concentrations of the UC and the ROH and hence the constants k_{dehydr} and k_{hydr} found under identical conditions are quoted in only an insignificant proportion of the relevant communications.

The available data (which are admittedly very few in number) confirm the above postulate: the multiplier f_{ROH}/f_{RC}^{ROH} in Eqn. (14), reflecting the influence of the medium on k_{dehydr}, does not change within the limits of the error of the measurement as the acid concentration in aqueous solution is varied. This is illustrated by the data in Tables 2–4, which present the constants k_{hydr} and k_{dehydr}, the function a_δ, and the ratios k_{dehydr}/a_δ and $k_{hydr}/a_\delta a_{H_2O}$ for the hydration and dehydration reactions.

Judging from the data in Table 2, a virtually constant ratio $k_{dehydr}/h_0 a_{H_2O}$ is retained during the dehydration of 2-cyclohexenol in the H_2SO_4 concentration range 4.9–42.0%. The function a_δ is in this case equal to $h_0 a_{H_2O}$ and the RC and the activated complex are therefore formed via the addition of the $H_5O_2^+$ ion to the ROH molecule and in the case of UC via the addition of the $H_5O_2^+$ ion and the H_2O molecule. The ratio $c_{ROH}^\infty/c_{UC}^\infty = f_{UC}/f_{ROH}$ depends significantly on the acid concentration in solution. Consequently the function $a_\delta a_{H_2O} = h_0 a_{H_2O}^2$ does not describe the influence of the medium on the ionisation of cyclohexa-1,3-diene.

Table 2. Kinetics of the hydration of cyclohexa-1,3-diene and the dehydration of 2-cyclohexenol (according to the data of Jensen et al.[44]).

$[H_2SO_4]$, wt.%	$10^2 k_{dehydr}$, min^{-1}	$10^2 k_{hydr}$, min^{-1}	$\lg(k_{dehydr}/h_0 a_{H_2O})$	$\lg(k_{hydr}/h_0 a_{H_2O})$	$c_{ROH}^\infty/c_{UC}^\infty$
Temperature 70 °C					
4.9	1.7	3.3	—1.60	—1.30	1.92
9.7	4.1	10.9	—1.64	—1.19	2.65
21.7	17.3	76.9	—1.73	—1.01	4.45
32.2	61.7	345.0	—1.74	—0.88	8.72
Temperature 60 °C					
4.9	0.5	0.9	—2.13	—1.95	1.90*
9.7	1.5	3.7	—2.07	—1.67	2.46
21.7	6.8	29.0	—2.16	—1.47	4.24
32.2	22.4	125.0	—2.25	—1.37	5.59
Temperature 40 °C					
21.7	0.95	4.0	—3.09	—2.40	4.23
32.2	4.15	28.2	—3.09	—2.16	6.31
42.0	15.6	199.8	—3.07	—1.67	12.8

*The equilibrium UC and ROH concentrations are not quoted by Jensen et al.[44] They were calculated using the values of $c_{ROH}^\infty/c_{UC}^\infty$ at 70 and 80 ° C.

Similar conclusions follow from the results obtained in the study of the hydration of 2-phenylpropene and the dehydration of 2-phenyl-2-propanol in H_2SO_4 solutions[13] (Table 3) and of the dehydration of t-pentyl alcohol in HNO_3 solutions[30] (Table 4).

The virtual constancy of the quantity $k_{dehydr}/h_0 a_{H_2O}$ when the composition of the medium is varied implies that the activity of the RC in these reactions should be expressed in terms of the product of the activities of ROH and the $H_5O_2^+$ ion for the dehydration of ROH and in terms of the activities of the $H_5O_2^+$ ion and the water molecule in the hydration reaction.

There are instances where k_{hydr} and k_{dehydr} vary in the same way as the acid concentration is varied. Evidently, in the determination of the reaction mechanism from the influence of the composition of

the medium on k_{hydr} in such cases one must take into account the fact that, in the formation of the RC, one H_2O molecule more adds to the UC than to the ROH.

Table 3. Kinetics of the hydration of 2-phenylpropene and the dehydration of 2-phenyl-2-propanol at 25 °C (according to the data of Deno et al.;[13] k_{hydr} and k_{dehydr} are expressed in min^{-1}).

$[H_2SO_4]$, wt.%	$\lg k_{hydr}$	$\lg k_{dehydr}$	$\lg \frac{k_{hydr}}{h_0 a_{H_2O}}$	$\lg \frac{k_{dehydr}}{h_0}$	$\lg \frac{k_{hydr}}{h_0 a_{H_2O}}$	$\lg \frac{k_{dehydr}}{h_0 a_{H_2O}}$
4.8	−1.99	−3.14	−1.87	−3.03	−1.86	−3.02
9.8	−1.59	−2.62	−1.90	−2.95	−1.88	−2.93
19.6	−0.82	−2.02	−1.80	−3.05	−1.75	−3.00
29.6	−0.12	−1.27	−1.70	−2.97	−1.58	−2.85
40.5	+0.72	−1.05	−1.50	−3.52	−1.25	−3.27

Table 4. Kinetics of the dehydration of t-pentyl alcohol in nitric acid at 30 °C [the values of k_{dehydr} (in min^{-1}) were taken from Boyd et al.[30]].

$[HNO_3]$, M	$-\lg k_{dehydr}$	$-H_0$	$-\lg a_{H_2O}$	$-\lg(k_{dehydr}/h_0 a_{H_2O})$
0.973	3.86	0.29	0.02	4.13
1.50	3.51	0.58	0.03	4.06
2.01	3.29	0.79	0.03	4.05
3.00	2.91	1.12	0.05	3.98
4.00	2.70	1.45	0.07	4.07
4.94	2.51	1.68	0.10	4.09

Table 5. Kinetics of the hydration of 2-(4-methoxyphenyl)propene and the dehydration of 2-(4-methoxyphenyl)-2-propanol in sulphuric acid at 25 °C [the values of k_{hydr} (min^{-1}) and k_{dehydr} (min^{-1}) were taken from Deno et al.[13]].

$[H_2SO_4]$, wt.%	$\lg k_{hydr}$	$\lg k_{dehydr}$	$\lg(k_{hydr}/h_0)$	$\lg(k_{dehydr}/h_0)$	$\lg(k_{dehydr}/a_{H_2SO_4})$	$\lg(k_{dehydr}/a_{H_2SO_4}a_{H_2O})$	$c^{\infty}_{ROH}/c^{\infty}_{UC}$
4.8	−0.37	−1.44	−0.28	−1.33	2.32	1.25	11.7
7.1	−0.18	−0.99	−0.30	−1.11	2.12	1.31	6.8
9.8	−0.13	−0.66	−0.20	−0.99	2.08	1.29	6.7
14.1	+0.46	−0.14	−0.20	−0.80	1.93	1.33	3.7

Table 5 presents data for the hydration of 2-(4-methoxyphenyl)-propene and the dehydration of the corresponding alcohol in aqueous H_2SO_4 solutions, from which it follows that, when the acid concentration is varied from 4.8 to 14.1 wt.%, $c^{\infty}_{ROH}/c^{\infty}_{UC}$ and hence f_{ROH}/f_{UC} vary by a factor of 3.17. The ratios $k_{dehydr}/a_{H_2SO_4}a_{H_2O}$ and k_{hydr}/h_0 hardly vary with composition.

From the above, one must assume that in the given instance the constancy of the quantity $k_{dehydr}/a_{H_2SO_4}a_{H_2O}$ indicates the formation of an RC from the ROH, an H_2SO_4 molecule, and an H_2O molecule. The constancy of k_{hydr}/h_0 does not characterise the mechanism of the rate-limiting step.

From the results presented, we assume that, when the strong acid concentration in aqueous solution is varied, the ratio f_{ROH}/f^{ROH}_{RC} hardly changes.

Thus, in order to establish the mechanism of the rate-limiting step of the hydration of the UC and of the dehydration of the ROH, it is necessary to find by Eqn. (15) the function a_δ in order to determine the influence of the acid concentration in solution on k_{dehydr}. The function a_δ is the activity of the species or complex which adds to the reactant and converts it into the RC. The latter is in equilibrium with the activated complex and with the molecules and ions from which it is formed. There is also a possibility of reactions where the RC is not formed. In such cases, a_δ is a function describing the influence of the medium on the activity of the activated complex and the term ka_{RC}/f^* should be eliminated from Eqns. (7) and (9).

Thus the determination of the mechanism of the UC hydration and ROH dehydration reactions reduces to finding the function a_δ from data for the dependence of k_{dehydr} on the ionising properties of the medium. We suggest that such information about the dependence of k_{hydr} on the ionising properties of the medium cannot be obtained without taking into account the contribution by the multiplier f_{UC}/f^* [see Eqn. (16)] to k_{hydr}. For this purpose, it is essential to measure the equilibrium concentrations c^{∞}_{ROH} and c^{∞}_{UC} in experiments on the hydration of the UC.

Since the ratio f_{ROH}/f^* does not change as the acid concentration in solution is varied, f^* in Eqn. (9) can be replaced by f_{ROH}, whereupon

$$k_{hydr} = \frac{k_{true}}{K^{UC}_{RC} K^{UC}_{i}} a_{H_2O} a_\delta \frac{f_{UC}}{f_{ROH}}. \quad (16)$$

The ratio f_{UC}/f_{ROH} can be found knowing the equilibrium constant K_{eq} for the UC hydration reaction:

$$K_{eq} = \frac{c^{\infty}_{ROH}}{c^{\infty}_{UC} a_{H_2O}} \frac{f_{ROH}}{f_{UC}}. \quad (17)$$

Simultaneous solution of Eqns. (16) and (17) yields the formula for the determination of a_δ using k_{hydr}:

$$k_{hydr} = \frac{k_{true}}{K^{UC}_{RC} K^{UC}_{i} K_{eq}} a_\delta \frac{c^{\infty}_{ROH}}{c^{\infty}_{UC}}. \quad (18)$$

There are cases where the ratio $c^{\infty}_{ROH}/c^{\infty}_{UC}$ is independent of the acid concentration in the aqueous solution and k_{dehydr} and k_{hydr} vary in the same way as the ionising properties of the medium are varied.[22,45,46] The function a_δ found with the aid of Eqns. (16) and (18) yields in this case information about the species which reacts with ROH rapidly and reversibly to form the RC. For the formation of such a complex from the UC, the particiption of a water molecule is also necessary. Examples illustrating the wide variety of the mechanisms of the dehydration of ROH and the hydration of the UC are presented below. It follows from the data in Table 2 that the RC in the 2-cyclohexenol dehydration reaction and cyclohexa-1,3-diene hydration reaction is formed from an ROH molecule and the $H_5O_2^+$ ion in conformity with Eqn. (10). In the rate-limiting stage, this complex decomposes to the reaction products

(UC, H_2O, ROH) and the catalyst $H_5O_2^+$ is regenerated simultaneously:

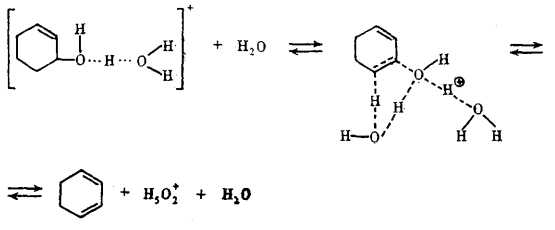
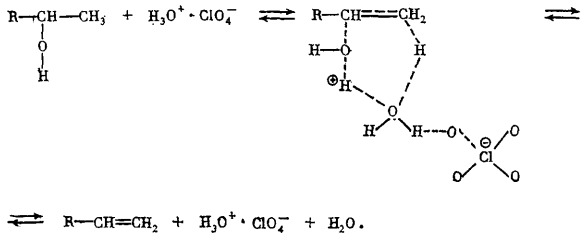


Table 6. Kinetics of the dehydration of 1-phenylethanol and the hydration of styrene in perchloric acid at 25 °C [the values of k_{hydr} (min^{-1}) and k_{dehydr} (min^{-1}) were taken from Schubert and Keefe[22]].

$[HClO_4]$, wt.%	$\lg k_{hydr}$	$\lg k_{dehydr}$	$\lg(k_{dehydr}/a_{HClO_4}a_{H_2O})$
36.40	−2.48	−4.11	−6.67
39.50	−2.13	−3.76	−6.69
43.40	−1.62	−3.23	−6.68
47.10	−1.04	−2.65	−6.67
49.25	−0.69	−2.30	−6.65
51.90	−0.30	−1.87	−6.67

In the hydration reaction of styrene and its derivatives and in the dehydration reactions of the corresponding alcohol in perchloric acid, the $H_3O^+.ClO_4^-$ ion pairs are catalytically active (Table 6).[22] In this reaction, the RC are formed from ROH and an ion pair of the type $H_3O^+.A^-$, where A^- is the ClO_4^- anion [see Eqn. (11)]:



The sums $k_{dehydr} + k_{hydr}$ and the ratios $c^{\infty}_{ROH}/c^{\infty}_{UC}$ have been obtained in experiments at 25 °C in perchloric acid not only with styrene (36.4−51.9% $HClO_4$) but also with *p*-ethylstyrene (29.5−41.9% $HClO_4$), *p*-chlorostyrene (36.45−51.9% $HClO_4$), *p*-methoxy-α-methylstyrene (1.03−29.5% $HClO_4$), and *p*-nitrostyrene (59.0−68.5% $HClO_4$).[22] The reactions of the reactants enumerated, except the last two, proceed only via the mechanism with $a_\delta = a_{HClO_4}a_{H_2O}$. In this case, the quantities

$$\lg(k_{dehydr}/a_{HClO_4}a_{H_2O}) = \lg(k_{true}/K_i^{ROH})_{HA.H_2O}$$

are −7.11 ± 0.003, −6.67 ± 0.04, and −5.49 ± 0.08 for *p*-chlorostyrene, styrene, and *p*-methylstyrene respectively. The same mechanism operates in the reaction of *p*-methoxy-α-methylstyrene in solutions at $HClO_4$ concentrations of 20.65% and above, where $\lg(k_{true}/K_i^{ROH}) = -3.82 \pm 0.03$. In more dilute $HClO_4$ solutions, the reaction also proceeds via the mechanism with $a_\delta = h_0 a_{H_2O}$. Schubert and Keefe[22] quote $c^{\infty}_{ROH}/c^{\infty}_{Cu}$ for *p*-nitrostyrene only in the experiment with 63% $HClO_4$ solution. We assumed that, as for the other reactants listed above, this quantity is independent of the $HClO_4$ concentration. The ratio $k_{dehydr}/a_{HClO_4}a_{H_2O}$ for *p*-nitrostyrene is not constant. We explain this by the fact that the dehydration of 1-(*p*-nitrophenyl)-ethanol and the hydration of *p*-nitrostyrene proceeds via two pathways and that their contributions to k_{dehydr} and k_{hydr} are comparable in the test solutions. For one pathway, $a_\delta = a_{HClO_4}a_{H_2O}$ at 25 °C and $\lg(k_{true}/K_i^{ROH})_{HA} = -9.96$ while for the other pathway $a_\delta = a_{HA}$ and $\lg(k_{true}/K_i^{ROH})_{HA} = -10.89$ (in the given case HA is $HClO_4$).

This mechanism of the catalytic action of aqueous acid solutions operates, as will be shown below, also in reactions with other reactants. The constancy of the ratio $k_{dehydr}/a_{HClO_4}a_{H_2O}$ is evidence that the catalytic action is manifested in this reaction by ion pairs with participation of the acid. The effect of the anion reduces in our view to the facilitating the abstraction of the H atom from a C−H bond in the ROH and in transferring it to a carbon atom in the UC. It follows from the data in Table 5 that, in the dehydration of 2-(4-methoxyphenyl)-2-propanol in sulphuric acid, the ratio $k_{dehydr}/a_{H_2SO_4}$ also remains constant. Unfortunately experiments were performed in dilute sulphuric acid solutions where the activity of water changes little. Therefore in the present instance there is no certainty that the function a_δ is equal to the activity of sulphuric acid $a_{H_2SO_4}$ and not to the activity of the $H_3O^+.HSO_4^-$ ion pairs.

The catalytic action of sulphuric acid molecules can be illustrated by data for the dehydration of β-hydroxy-β-phenylpropionic acid (Table 7).[47] The quantity $k_{dehydr}a_{H_2SO_4}$ in 38.32% H_2SO_4 solution is greater than its average value for the range 39.68−69.0% H_2SO_4. This can be explained by the contribution of yet another dehydration pathway which is manifested in more dilute solutions. The numerical values of $\lg(k_{true}/K_i^{ROH})_{HA}$ are −5.78 ± 0.01 at 45 °C and −6.50 ± 0.11 at 25 °C.

The values of k_{dehydr} for β-(*p*-chlorophenyl)-β-hydroxypropionic acid in 53.46−64.13% sulphuric acid solutions at 45 °C have been published.[48] In these solutions, $a_\delta = a_{H_2SO_4}$ and $\lg(k_{true}/K_i^{ROH})_{HA} = -5.25 \pm 0.1$. It follows from Eqn. (12) that the reaction complex with $a_\delta = a_{HA}$ is formed from ROH and an acid molecule (in our case H_2SO_4):

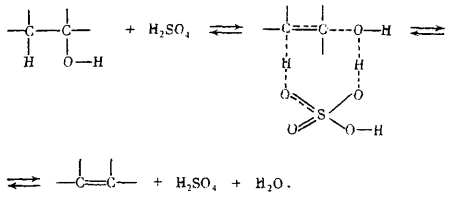


Table 7. Kinetics of the dehydration of β-hydroxy-β-phenylpropionic acid in sulphuric acid at 44.7 °C [the values of k_{dehydr} (min^{-1}) were taken from Noyce and Lane[47]].

$[H_2SO_4]$, wt.%	$\lg k_{dehydr}$	$\lg a_{H_2SO_4}$	$\lg(k_{dehydr}/a_{H_2SO_4})$
38.32	−3.69	−0.89	−4.58
39.68	−3.62	+1.06	−4.68
51.87	−2.19	+2.53	−4.72
58.05	−1.36	+3.40	−4.76
65.45	−0.36	+4.51	−4.87
65.45	−0.32	+4.51	−4.83
69.00	+0.25	+5.03	−4.78
69.00	+0.26	+5.03	−4.77

ROH dehydration and UC hydration reactions are also known in which the catalytic action of the acid is caused by the formation of a complex from the ROH and two acid molecules, i.e. $a_\delta = a_{HA}^2$—for example, the dehydration reactions of the alcohols $XC_6H_4CH.(CF_3)CH_2OH$ and the hydration reactions of the alkenes $XC_6H_4C.(CF_3)=CH_2$ (X = *p*-Me, H, or *p*-Cl) in concentrated sulphuric acid at 25 °C. Calculation based on literature data[49] shows that the quantities $\lg(k_{dehydr}/a^2_{H_2SO_4}) = \lg(k_{true}/K_i^{ROH})_{HA^2}$ are respectively −18.51 ± 0.11 (X = H), −18.86 ± 0.05 (X = *p*-Me, in the range 76.3−83.6% H_2SO_4), and −18.95 ± 0.08 (X = *p*-Cl, in the range 83.6−87.1% H_2SO_4). Judging from the above data,[49] for X = *p*-MeO the reaction at H_2SO_4 concentrations in the range 70.1−76.1% proceeds mainly via the formation of an RC with $a_\delta = a_{H_2SO_4}$; under these conditions, $\lg(k_{dehydr}/a_{H_2SO_4}) = \lg(k_{true}/K_i^{ROH})_{HA} = -10.3$.

Thus it follows from the data in Tables 2−8 that the catalysis of the ROH dehydration and UC hydration reactions in aqueous solutions of acids is determined by the formation of complexes of the reactants with $H_5O_2^+$ ions, $H_3O^+.A^-$ ion pairs, and HA acid molecules. These examples illustrate the catalytic activity of species of predominantly one type among those listed above. However, when the range of acid concentrations is extended and also when the temperature is varied, other reaction pathways also operate. This is seen, in particular, from the data in Table 7.[47] At relatively low sulphuric acid concentrations, the quantity $k_{dehydr}/a_{H_2SO_4}$ for the dehydration reaction of β-hydroxy-β-phenylpropionic acid is greater than in more concentrated solutions, which can be explained by the contribution of yet another reaction pathway. As noted above, the influence of the medium on k_{dehydr} for 1-*p*-nitrophenylethanol and k_{hydr} for *p*-nitrostyrene[22] may be caused by the operation of two pathways: via the formation of an RC with $a_\delta = a_{H_2SO_4}$ and an RC with $a_\delta = a_{H_2SO_4}a_{H_2O}$. the latter variant was first examined by Osipova et al.[50] In this case, the following equation should hold:

$$k_{dehydr} = k_{dehydr}^{HA.H_2O} a_{H_2SO_4} a_{H_2O} + k_{dehydr}^{HA} a_{H_2SO_4}.$$

Table 8. Kinetics of the hydration of $C_6H_5C(CF_3)=CH_2$ and the dehydration of the corresponding alcohol [the values of k_{dehydr} (min^{-1}) and k_{hydr} (min^{-1}) were taken from Koshy et al.[49]].

$[H_2SO_4]$, wt.%	$\lg k_{dehydr}$	$\lg k_{hydr}$	$\lg(k_{dehydr}/a^2_{H_2SO_4})$
87.1	−1.27	−1.83	−18.53
87.1	−1.23	−1.79	−18.48
84.9	−1.92	−2.28	−18.62
83.6	−2.14	−2.43	−18.43
80.9	−2.94	−3.01	−18.48
79.9	−3.30	−3.28	−18.52

The dehydration of β-hydroxy-β-(*p*-methoxyphenyl)propionic acid also proceeds via two pathways. This follows from data in a communication[48] in which the values of k_{dehydr} at 45 °C for 1.0−24.85% H_2SO_4 solutions and at 25 °C for 24.18−47% H_2SO_4 solutions are presented. In experiments with relatively low acid concentrations, it was seen that, with increase in the H_2SO_4 concentration, the main reaction pathway becomes the second one. Table 9 shows that, in the H_2SO_4 concentration range 1.0−18.7%, the quantity $k_{dehydr}/h_0a_{H_2O}$ is practically constant. This permits the assumption that in such solutions the reaction proceeds via only one pathway—via the formation of an RC with $a_\delta = h_0a_{H_2O}$ and that

$$\lg(k_{dehydr}/h_0\,a_{H_2O}) = \lg(k_{true}/K_i^{ROH})_{H_2O_2^+} = -1.60 \pm 0.08.$$

In more concentrated solutions, the quantity $\lg(k_{dehydr}/h_0a_{H_2O})$ increases but the data are insufficient for a quantitative estimation of the contribution by the second pathway. At 25 °C the experiments were performed in more concentrated solutions, which made it possible to calculate the rate constants for the first and second pathways with the aid of the equation

$$k_{dehydr} = k_{dehydr}^{H_5O_2^+} h_0 a_{H_2O} + k_{dehydr}^{HA} a_{H_2SO_4}.$$

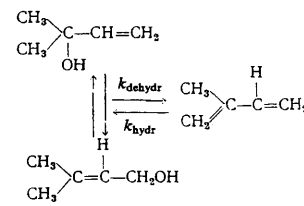
Thus at 25 °C we have

$$\lg(k_{true}/K_i^{ROH})_{H_5O_2^+} = -3.77; \quad \lg \left.\frac{k_{true}}{K_i^{ROH}}\right|_{HA} = -2.44.$$

Table 9. Kinetics of the dehydration of β-hydroxy-β-(*p*-methoxyphenyl)propionic acid at 45 °C [the values of k_{dehydr} (min^{-1}) were taken from Noyce et al.[48]].

$[H_2SO_4]$, wt.%	$\lg k_{dehydr}$	$\lg(k_{dehydr}/h_0a_{H_2O})$
1.0	−2.59	−1.56
4.8	−1.68	−1.66
9.25	−1.41	−1.52
16.2	−0.81	−1.55
18.7	−0.69	−1.60
20.6	−0.62	−1.47
22.3	−0.39	−1.42
24.85	−0.18	−1.45

The dehydration reactions in sulphuric acid solutions of an equilibrium mixture of dimethylvinylmethanol and dimethylallyl alcohol and the hydration reaction of isoprene (Table 10)[50] proceed via two pathways: via the formation of an RC with $a_\delta = h_0a_{H_2O}$ and with $a_\delta = a_{H_2SO_4}a_{H_2O}$:



When the composition of the medium is varied, k_{dehydr} changes in accordance with the equation

$$k_{dehydr} = k_{dehydr}^{H_5O_2^+} h_0 a_{H_2O} + k_{dehydr}^{HA.H_2O} a_{H_2SO_4} a_{H_2O}.$$

The linearity of the relation presented in Fig. 1, where $k_{dehydr}/h_0\,a_{H_2O}$ is plotted against $a_{H_2SO_4}/h_0$, confirms the applicability of this equation in the given instance.

The quantity k_{dehydr} for the highest (in the range investigated) H_2SO_4 concentration of 35.11% proved to be significantly lower than expected according to the experimental data for less concentrated acid solutions. This can be explained by the conversion of a large proportion of the unsaturated alcohols into the ionised form.

As noted above, Eqns. (7) and (9) were derived for the case where the degrees of conversion of the ROH and the UC into the ionised form and the RC are low. If the degree of their ionisation is significant, then, provided that only one reaction pathway is retained, these formulae must be supplemented by a multiplier taking into account the concentration of the ionised forms: $1/(1 + \sum a_\delta/K_\delta^i)$, where K_δ^i denotes the equilibrium constants of the formation reactions of the ionised forms.

Table 10. Kinetics of the dehydration of the equilibrium mixture of dimethylvinylmethanol and dimethylallyl alcohol and the hydration of isoprene [the values of k_{hydr} (min^{-1}) and k_{dehydr} (min^{-1}) were taken from Osipova et al.[50]].

$[H_2SO_4]$, wt.%	$\lg k_{hydr}$	$\lg k_{dehydr}$	$c^\infty_{ROH}/c^\infty_{UC}$
4.3	−2.82	−4.02	15.8
7.05	−2.70	−3.89	15.4
10.08	−2.29	−3.48	15.4
15.0	−1.88	−3.05	14.9
15.0	−1.95	−3.12	14.9
19.6	−1.44	−2.59	14.3
20.0	−1.46	−2.62	14.3
20.0	−1.43	−2.58	14.3
24.9	−1.05	−2.15	13.2
27.46	−0.86	−1.96	12.8
30.02	−0.64	−1.72	12.1
32.47	−0.41	−1.47	11.3
35.11	−0.15	−1.18	10.8

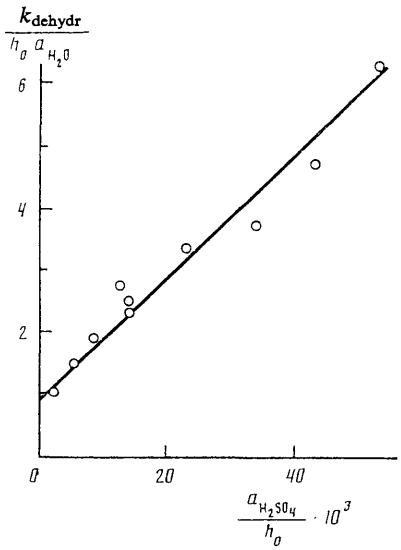


Figure 1. The influence of the H_2SO_4 concentration on k_{dehydr} for the equilibrium mixture of dimethylvinylmethanol and dimethylallyl alcohol (according to the data of Osipova et al.[50]).

The examples presented naturally do not cover all the possible mechanisms of the alcohol dehydration and UC hydration reactions. An illustration may be provided by the dehydration of β-hydroxyketones in acid solutions. Investigators have drawn attention to the fact that substituents in the benzene ring have little influence on the rate of dehydration of β-hydroxyketones.[51] On these grounds, they concluded that the atoms of the benzene ring remote from the reaction centre participate in the rate-limiting stage of the dehydration of these substances and that in certain cases the rate-limiting stage is enolisation. The dependence of k_{dehydr} on the acid concentration in aqueous solution confirms this hypothesis. It has been shown[52] that, when the acid concentration is varied, the enolisation rate constants k_{eff} for acetone varies in accordance with the equation

$$k_{eff} = k_1 c_{H_5O_2^+} + k_2 c_{H_5O_2^+} c_{A^-}, \quad (19)$$

where k_1 and k_2 are respectively the rate constants for pathways with participation of the $H_5O_2^+$ ion and with participation of $H_5O_2^+ + A^-$.

Eqn. (19) is applicable also to the description of the influence of the medium on k_{dehydr} for certain β-hydroxyketones. For example, only the second pathway operates in the dehydration of 4-hydroxy-4-(*p*-nitrophenyl)-2-butanone (Table 11) in the H_2SO_4 concentration range 22.1 − 51.0%. The RC concentration is determined by that of the ions $H_5O_2^+$ and HSO_4^-, so that in this reaction $k_1 = 0$ and $a_\delta = c_{H_5O_2^+} c_{A^-}$.

Table 11. Kinetics of the dehydration of 4-hydroxy-4-(*p*-nitrophenyl)-2-butanone at 25 °C (the values of k_{dehydr} were taken from Noyce and Reed[51]).

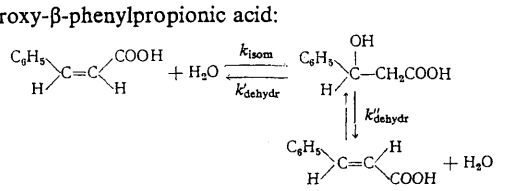
$[H_2SO_4]$, wt.%	$[H_2SO_4]$, M	$10^3\, k_{dehydr}$, min^{-1}	$10^4(k_{dehydr}/c_{H_5O_2^+} c_{A^-})$, litre^2 mol^{-2} min^{-1}
9.45	1.02	0.095	9.2
22.1	2.59	0.36	5.4
36.25	3.75	0.74	5.3
41.7	5.61	1.70	5.4
51.0	7.30	3.46	6.5

Note. The degree of dissociation of the HSO_4^- anions may be neglected in the experimental range. In the calculation, it was assumed that c_{A^-} and $c_{H_5O_2^+}$ are numerically equal to the analytical molar concentration of the acid, since the dissociation constant of the HSO_4^- ions is 1.2×10^{-2} [Dobos (Ref. 53, p. 131)].

Judging from the experimental data,[51] when the nitro-group in the *para*-position in the benzene ring is replaced by the methoxy-group, the reaction mechanism changes and the influence of the medium on k_{dehydr} is determined by the functions $a_\delta = a_{H_5O_2^+} = h_0 a_{H_2O}$ and $a_\delta = a_{H_2SO_4} a_{H_2O}$.

In the determination of the reaction mechanism from the dependence of the effective rate constant on the function a_δ, characterising the ionising capacity of the medium, account must be taken of the fact that in the experimental acid concentration range it is possible to select several functions a_δ varying in the same way. This hinders the choice of the reaction mechanism. In order to solve the problem, it is essential to measure the rate constants over wider acid concentration and temperature ranges and to determine the influence of the medium on the activity coefficients of the UC and the corresponding alcohol. If even these experiments do not provide an unambiguous answer, it is necessary to select such a function and hence the reaction mechanism which agrees best with results obtained by other methods. As an example, we shall

examine the isomerisation of *cis*-cinnamic acid in H_2SO_4 at 45 °C to *trans*-cinnamic acid.[54] In this reaction, the intermediate is β-hydroxy-β-phenylpropionic acid:



The rate-limiting stage of the isomerisation reaction is the hydration of *cis*-cinnamic acid, since the rate constant for the hydration of β-hydroxy-β-phenyl-propionic acid is much greater than k_{isom}. Consequently k_{isom} is the rate constant for the hydration of *cis*-cinnamic acid. The data in Table 12 show that in the range 38.43–69.88% H_2SO_4 the quantity $\lg(k_{isom}/a_{H_2SO_4}a_{H_2O})$ is constant within the limits of the error of the measurements, while $\lg(k_{isom}/h_0)$ varies, albeit only slightly. In order to solve the problem of the composition of the RC in this reaction, it is essential to have information about the dependence of f_{UC}/f_{ROH} on the concentration of the catalyst in solution. Unfortunately, such data were not provided in the above study.[54] If it is found that the ratio f_{UC}/f_{ROH} does not change, it will be necessary to conclude that the RC in the given instance is a complex consisting of a molecule of β-hydroxy-β-phenylpropionic acid and a molecule of H_2SO_4 (or *cis*-cinnamic acid, H_2SO_4, and H_2O). On the other hand, if the ratio $(f_{UC}/f_{ROH})a_{H_2O}$ is constant, this will imply that the RC is formed from a molecule of β-hydroxy-β-phenylpropionic acid and the ion pair $H_3O^+.HSO_4^-$.

Table 12. Kinetics of the isomerisation of *cis*-cinnamic acid in aqueous H_2SO_4 solutions at 45 °C [the values of k_{isom} (min^{-1}) were taken from Noyce et al.[54]].

$[H_2SO_4]$, wt.%	$\lg k_{isom}$	$\lg a_{H_2SO_4}$	H_0	$\lg a_{H_2O}$	$\lg(k_{isom}/h_0)$	$\lg(k_{isom}/a_{H_2SO_4}a_{H_2O})$
38.43	−4.84	0.89	−2.21	−0.22	−7.05	−5.51
46.84	−4.10	1.90	−2.89	−0.37	−6.89	−5.63
51.87	−3.55	2.53	−3.30	−0.49	−6.85	−5.59
58.05	−3.01	3.40	−3.90	−0.68	−6.91	−5.73
62.80	−2.44	4.11	−4.45	−0.88	−6.89	−5.67
67.92	−1.87	4.88	−5.18	−1.13	−7.05	−5.62
69.00	−1.71	5.03	−5.33	−1.20	−7.04	−5.54
69.88	−1.59	5.16	−5.47	−1.24	−7.06	−5.51
75.95	−0.82	6.10	−6.40	−1.76	−7.22	−5.16

IV. The mechanism of the exchange of the oxygen atom in alcohols and of the racemisation of optically active alcohols

In order to derive an equation in which account is taken of the influence of the medium on the rate w_{exch} and the rate constants k_{exch} for the exchange of the oxygen atom in alcohols, we express the activity of the RC in terms of the equilibrium constant of its formation reaction, the ROH concentration, and the functions a_δ, as was done above [Eqns. (7) and (8)]:

$$w_{exch} = k_{true}^{exch}\frac{a_{ROH}\,a_\delta}{f^*} = \frac{k_{true}^{exch}}{K_i^{exch}}c_{ROH}a_\delta\frac{f_{ROH}}{f^*};$$

$$k_{exch} = \frac{k_{true}^{exch}}{K_i^{exch}}a_\delta\frac{f_{ROH}}{f^*};\quad K_i^{exch} = \frac{a_{ROH}\,a_\delta}{a_{ROH.\delta}},$$

where k_{true}^{exch} is the elementary rate constant, K_i^{exch} the equilibrium formation constant, expressed in terms of activities, of the RC in the reaction involving the exchange of the oxygen atom. We believe that, after a correct choice of the function a_δ, the multiplier f_{ROH}/f^* is independent of the acid concentration in the aqueous solution and that

$$k_{exch} = (k_{true}^{exch}/K_i^{exch})a_\delta.$$

An equation of this type can also be used to take into account the influence of the medium on the rate constant for the racemisation of optically active alcohols k_{rac}.

Unfortunately, there are few literature data concerning the dependence of k_{exch} and k_{rac} on the acid concentration in aqueous solution, but on the basis of their analysis one can nevertheless reach conclusions about the mechanism of the catalytic action of acids in these reactions.

Measurements have been made[33] of the constants k_{exch} for methanol at 67.2 °C in sulphuric (20.1–69.3%) and perchloric (26.3–59.9%) acids. The methanol concentration in solution was ~0.3 M. The addition of such amounts of the alcohol to the aqueous acid solution has little effect on the degree of protonation of indicators of the nitroaniline series.[55] However, it has been shown[52] that the basicity of the alcohol itself is independent of its concentration in the mixture with water. Therefore, in analysing the above kinetic data,[33] one can use the values of H_0 and a_{H_2O} for aqueous solutions with the same acid concentration (molar ratio).[52]

The influence of the medium on k_{exch} is determined by the function $a_\delta = h_0 a_{H_2O}^2$, since, according to experimental data[33] $k_{exch}h_0a_{H_2O}^2 = \text{const}$. (Tables 13 and 14). This means that the activity of the RC can be expressed either in terms of the product of the activities of the non-protonated CH_3OH, the $H_5O_2^+$ ion, and

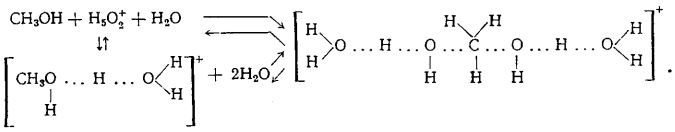
Table 13. Kinetics of the exchange of ^{18}O for ^{16}O in methanol in aqueous H_2SO_4 solutions at 67.2 °C [the values of k_{exch} (min^{-1}) were taken from McClellend[33]].

$[H_2SO_4]$, wt.%	$\lg k_{exch}$	H_0	$\lg a_{H_2O}$	$\lg(k_{exch}/h_0a_{H_2O}^2)$
20.1	−5.99	−0.96	−0.06	−6.83
30.1	−5.47	−1.57	−0.12	−6.80
40.5	−5.07	−2.31	−0.22	−6.94
51.0	−4.63	−3.62	−0.40	−6.85
60.9	−4.26	−4.05	−0.71	−6.89
69.3	−3.93	−5.06	−1.12	−6.75

Table 14. Kinetics of the exchange of ^{18}O for ^{16}O in methanol in aqueous $HClO_4$ solutions at 67.2 °C [the values of k_{exch} (min^{-1}) were taken from McClellend[33]].

$[HClO_4]$, wt.%	$\lg k_{exch}$	H_0	$\lg a_{H_2O}$	$\lg(k_{exch}/h_0a_{H_2O}^2)$
26.3	−5.64	−1.30	−0.09	−6.76
42.1	−4.92	−2.46	−0.26	−6.86
50.5	−4.47	−3.20	−0.44	−6.79
59.9	−3.95	−4.63	−0.89	−6.80

water (with a power exponent of unity) or in terms of the product of the activity of the protonated CH_3OH and the square of the activity of water. The equation of the formation reaction of such RC is



The participation of two water molecules is essential for the intermediate (RC) to have a symmetrical structure. In this RC, the carbon atom is bound covalently to three hydrogen atoms and two water molecules are coordinated to it on either side.

In sulphuric and perchloric acids, the ratios $\lg(k_{exch}/h_0 a_{H_2O}^2)$ are respectively -6.84 ± 0.1 and -6.80 ± 0.06. The similarity of the values of $k_{true}^{exch}/k_i^{exch}$ in these acids constitutes additional confirmation of the reaction mechanism described.

There exist examples of the racemisation of optically active alcohols via this mechanism. For example, the rate constant for the racemisation of 1-methyl-3-phenyl-allyl alcohol in perchloric acid at 25 °C varies in proportion to h_0.[45] The activity of water in solutions with $HClO_4$ concentrations in the range 0.0225–0.333 M is almost constant.

The catalytic action of an acid in alcohol racemisation and oxygen atom exchange reactions is not determined solely by the formation of an RC with $a_\delta = h_0 a_{H_2O}^2$ as in the case of CH_3OH. Thus the influence of the medium on k_{rac} for (+)-β-hydroxy-phenyl-propionic acid in sulphuric acid[47] can be described on the assumption that $a_\delta = a_{H_2SO_4} a_{H_2O}$ (Table 15). In this reaction the activity of the RC should be expressed in terms of the activity of the ROH, the acid, and water with an exponent of unity. The intermediate reactive complex has a symmetrical structure:

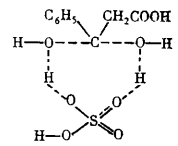


Table 15. Kinetics of the racemisation of (+)-β-hydroxy-β-phenyl-propionic acid in sulphuric acid at 25 °C [the values of k_{rac} (min^{-1}) were taken from Noyce and Lane[47]].

$[H_2SO_4]$, wt.%	$\lg k_{rac}$	$\lg(k_{rac}/a_{H_2SO_4}a_{H_2O})$
39.77	−2.97	−4.24
47.70	−2.17	−4.21
52.03	−1.56	−4.24
58.84	−0.72	−4.18
58.84	−0.72	−4.16
58.84	−0.74	−4.20

The values of $\lg k_{rac}$ at 45 °C have been published.[47] They amount to −1.87 and −1.13 in 39.77% and 47% H_2SO_4 solutions (the k_{rac} are expressed in min^{-1}). Calculation shows that $\lg(k_{rac}/a_{H_2SO_4}a_{H_2O}) = -2.69 \pm 0.01$ at 45 °C and -4.20 ± 0.04 at 25 °C; the temperature dependence of k_{true}^{rac}/K_i^{rac} is characterised by the quantity 137 J mol^{-1}.

In the oxygen atom exchange and 1-phenylethanol racemisation reactions in perchloric acid,[56] the pathways with $a_\delta = h_0 a_{H_2O}^2$ and $a_\delta = a_{HClO_4} a_{H_2O}$ have been observed. The values of k_{rac} for 1-phenylethanol at 30.4 °C in the $HClO_4$ concentration range 0.0172–1.00 M have been published;[56] in 0.0472 and 0.0826 M $HClO_4$ solutions, the ratios k_{exch}/k_{rac} are respectively 0.84 and 0.82. In the concentration range 0.02–0.47 M, the constants k_{rac} in hydrochloric, hydrobromic, and perchloric acids are almost identical. In the acid concentration range 0.0172–1.0 M, k_{rac} is described by the equation

$$k_{rac} = \left(\frac{k_{true}^{rac}}{K_i^{rac}}\right)_{h_0} h_0 a_{H_2O}^2 + \left(\frac{k_{true}^{rac}}{K_i^{rac}}\right)_{HA.H_2O} a_{HClO_4} a_{H_2O}. \qquad (20)$$

Fig. 2 presents experimental data for the influence of the medium on the rate constant for the racemisation of 1-phenylethanol.[56]

It follows from the analysis of the kinetic data described that the alkene hydration and alcohol dehydration reactions proceed via a synchronous mechanism without the particpation of "classical" carbonium ions.

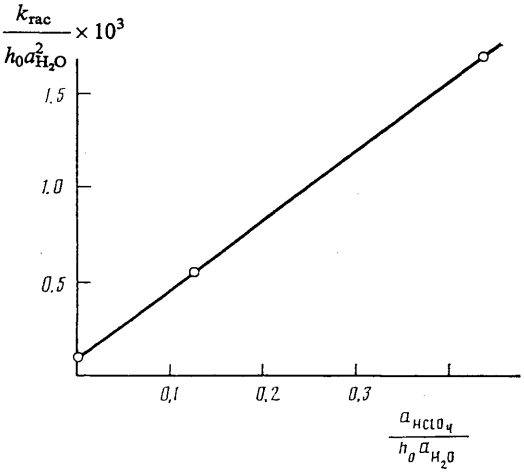


Figure 2. The application of Eqn. (20) to describe the influence of the medium on k_{rac} for 1-phenylethanol (according to the data of Grunwald et al.[56]).

In order to increase the solubility of the reactants, ethanol was added to the acid solution in a number of investigations (see, for example, the studies of Noyce and co-workers[57–59]). The acid concentration and the composition of the mixed water–ethanol solvent (the alcohol/water molar ratio) were varied simultaneously. In the present review, such data are not analysed because it is impossible to take into account the influence of the alcohol on the ionising properties of the solution.

In the analysis of kinetic data, we used the known values of H_0 for sulphuric acid,[60] concentrated perchloric acid solutions at 25 °C,[61] and dilute solutions of perchloric acid[62] and nitric acid at 20 °C.[63] The acitivities $a_{H_2SO_4}$ of concentrated sulphuric acid solutions at 25 °C were taken from Giauque et al.,[64] the activities of dilute sulphuric acid solutions (up to 30 wt.%) were calculated using the values of $\gamma_\pm$ from Dobos,[53] and the activities a_{H_2O} in sulphuric acid were taken from Giauque et al.[64] The activities $a_{H_2SO_4}$ in solutions with acid concentrations up to 60 wt.% at 45 °C were

calculated from the values of $\gamma_{\pm}$ at this temperature, which were found using the relation $\lg \gamma_{\pm} = f(1/T)$ for the range 25–60 °C, quoted by Dobos.[53] The activities a_{H_2O} in perchloric acid at 25 °C were taken from Landolt and Börnstein.[65]

V. Conclusion

The above analysis of kinetic data shows convincingly that, for the determination of the detailed mechanism of the hydration of alkenes in aqueous solutions of acids, it is necessary to know not only the values of k_{hydr} for the alkene but also those of k_{dehydr} for the corresponding alcohol over a wide range of acid concentrations. The composition of the RC in the alcohol dehydration reactions and in the hydration reactions of the corresponding alkenes can be found from the dependence of k_{dehydr} on the parameters of the medium characterising the ionising capacity of the solution. If the ratio of the equilibrium concentrations of the alcohol and the alkene ($c^{\infty}_{ROH}/c^{\infty}_{UC}$) varies with the acid concentration, then the influence of the medium on k_{hydr} can be determined from the values of k_{dehydr} and the experimental equilibrium concentrations c^{∞}_{ROH} and c^{∞}_{UC}. If this ratio remains unaltered at different acid concentrations in solution then the detailed mechanism can be determined using the dependence of k_{dehydr} and k_{hydr} on the parameters of the ionising capacity of the medium.

When the acid concentration is varied within wide limits, the alkene hydration and alcohol dehydration reactions can proceed via several pathways. Therefore, when account is taken of the influence of substituents on the reactivity of substances in concentrated acid solutions, one must be completely certain that the reactions of these substances proceed via identical mechanisms.

In concentrated aqueous acid solutions, catalysis is effected not only by solvated protons, but also by dissociated acid molecules as well as acid hydrates. Kinetic data for the hydration of UC, the dehydration and racemisation of ROH, and the exchange of the oxygen atom in alcohols are susceptible to a quantitative description on the assumption that in these reactions the RC are complexes of the reactant with the above ions and species in the aqueous acid solution.

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