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Modern Ideas About the Mechanisms of Homogeneous and Heterogeneous Acid Catalysis: Similarities and Differences

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The modern ideas about the nature of the protonated states in aqueous solutions in non-polar solvents and on the surfaces of heterogeneous oxide catalysts of the acid type are examined. It is concluded that in heterogeneous systems mechanisms analogous to the mechanism of homogeneous acid catalysis in aqueous solutions operate only in catalytic reactions of polar molecules. Owing to the absence of solvation effects, the catalytic reactions of hydrocarbons take place, contrary to the widely held view, via intermediate covalent and not ionic structures. On the other hand, the properties of carbenium ions are characteristic of transition states, which in many instances also possess features resembling those of adsorbed carbenes of surface ylides. The role of synchronous or concerted mechanisms in heterogeneous acid catalysis is discussed.
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I. INTRODUCTION

The phenomenon of acid catalysis consists in the acceleration of chemical reactions in the presence of liquid (homogeneous acid catalysis) or solid (heterogeneous acid catalysis) acids. Individual examples of acid catalysis were known very long ago, as early as the end of the XVIIIth century. They include, for example, the esterification of alcohols, the hydration of olefins, etc.

Heterogeneous acid catalysis, with the aid of which the majority of the reactions in petrochemistry and petroleum processing (cracking and skeletal isomerisation of paraffins and olefins, the migration of the double bond in olefins, their oligomerisation, the alkylation of aromatic compounds, etc.) are nowadays carried out, has found the widest practical applications. The explanation is that heterogeneous acid catalytic reactions can be carried out over a wide temperature range, up to 700–800 K, which naturally extends the range of thermodynamically feasible catalytic reactions. Furthermore, heterogeneous catalysis is more susceptible to technological formulation, since it is easier to achieve on its basis continuous chemical manufacturing processes in which there is no stage involving the separation of the catalyst from the initial reactants and the final products.

The examples of the practical use of homogeneous acid catalysis are much more modest. Perhaps the most important of these is the alkylation, on a large industrial scale, of isoparaffins by olefins, and the hydration of ethylene in the presence of sulphuric acid. Despite

this, the ideas about the mechanisms of acid catalysis were formulated as early as the late 1920's precisely for homogeneous catalysis. We shall therefore begin the consideration of the mechanism of acid catalytic reactions with homogeneous catalysis.

II. HOMOGENEOUS ACID CATALYSIS

1. Catalysis in Aqueous Solutions. The Brønsted Relation

The theory of homogeneous acid catalysis in aqueous solutions, formulated in 1924 by Brønsted,[1,2] is based on the idea of the intermediate protolytic interaction of the reactants with the undissociated acid molecules (general acid catalysis) or with hydroxonium ions (specific acid catalysis). It is suggested that this entails the transfer of a proton to the substrate molecule with formation of positively charged protonated forms which exhibit an increased reactivity:

$$\begin{aligned} AH + B &\rightarrow BH^+ + A^- \text{ (general acid catalysis),} \\ H_3O^+ + B &\rightarrow BH^+ + H_2O \text{ (specific acid catalysis).} \end{aligned} \quad (1)$$

Their secondary reactions followed by decomposition lead to the regeneration of the catalyst and the formation of the final product. Here it is postulated that the protonated intermediate species have specific chemical properties which determine the selectivity of the acid catalysis. For example, it has come to be assumed that the acid-catalytic reactions of hydrocarbons are based on chemical reactions of the carbenium ions formed on proton transfer. On the other hand, the intermediate formation by secondary reactions of alkoxonium ions, etc. is characteristic of the reactions of alcohols.

If it is assumed, after Brønsted, that the proton transfer stage is rate-limiting, then the familiar correlation, which has come to be known as the Brønsted relation, should hold between the rate constants for the acid-catalytic reactions and the strength of the acids used as catalysts:

$$k = aK^{\alpha}, \quad 0 < \alpha < 1 \quad (2a)$$

or in the logarithmic form

$$\lg k = \alpha \lg K + C. \quad (2b)$$

These equations follow from the analogy between the proton transfer to water molecules, which is characterised by the acid dissociation constant K, and the proton transfer to the substrate molecules.

Eqns.(2) have been tested by Brønsted and his school for various acid-catalytic reactions, for example, for the decomposition of diazocompounds, the hydrolysis of esters, the enolisation of ketones, etc.[5] It was shown, within the limits of chemically similar groups of substances and acids, that the corresponding linear correlations do indeed hold between the logarithms of the equilibrium constants and the reaction rates, the proportionality coefficients C and α varying somewhat on passing from one group of substances to another. On the other hand, when the acid strength is varied within very wide limits, appreciable deviations from Eqns.(2) are usually observed. It must also be emphasised that Brønsted's reasoning is not sufficiently rigorous, because the analogy between the proton transfer to water molecules and the corresponding transfer to substrate molecules actually leads to a linear relation between the logarithms of the corresponding equilibrium constants, and not between the equilibrium acid dissociation constants themselves, and the rate constant for the proton transfer to a substrate molecule. In other words, Eqns.(2) presuppose the existence of a linear relation between the equilibrium constants and the rate of formation of the protonated form of the substrate.

Frequent attempts have been made to justify theoretically the existence of such a relation. Among them, the familiar model of intersecting unperturbed potential curves for the protonated states of the acid and substrate, proposed by Horiuti and Polanyi, merits most attention, its development having led subsequently to the creation of the theory of absolute reaction rates.[3,4] This model is not, however, confirmed by modern spectroscopic data, from which it follows that, for a sufficiently strong interaction beween an acid and a base, the form of the potential energy curve for proton vibrations is significantly perturbed (see Section III, subsection 4). Thus the Brønsted equation must be regarded as an empirical relation applicable to fairly narrow groups of substances and reactions rather than a rigorously theoretically justified relation.

2. Modern Ideas about the State of the Proton in Aqueous Solution

It is generally accepted that electrolytic dissociation in aqueous solutions is possible only as a result of solvation effects. Its contribution to the overall process energetics is decisive. For example, the heterolytic dissociation of the water molecule in the gas phase into the H^+ and OH^- ions is associated with an enormous energy expenditure, which is approximately 17 eV (1630 kJ mol^{-1}). However, in the liquid phase this energy is almost completely compensated by the sum of the hydration energies of the proton and the hydroxide ion. The endothermicity of the heterolytic dissociation of liquid water is therefore characterised by only 0.6 eV (or 60 kJ mol^{-1}), while the dissociation constant of this reaction is 1.8×10^{-16} g-ion litre^{-1}.

We shall consider the make up of the heat of hydration of the proton in liquid water. The affinity of the proton for the first water molecule is 7.4 eV ($\sim$710 kJ mol^{-1}). When the second and subsequent water molecules are added, the solvation energy decreases monotonically in the following sequence (the corresponding heats of hydration are given in brackets):

$$\begin{aligned} &H_3O^+ + H_2O \rightarrow H_5O_2^+ \quad (134 \text{ kJ mol}^{-1}), \\ &H_5O_2^+ + H_2O \rightarrow H_7O_3^+ \quad (96 \text{ kJ mol}^{-1}), \\ &H_7O_3^+ + H_2O \rightarrow H_9O_4^+ \quad (72 \text{ kJ mol}^{-1}), \\ &H_9O_4^+ + nH_2O \rightarrow H_9O_4^+ \cdot nH_2O \quad (79 \text{ kJ mol}^{-1}). \end{aligned} \quad (3)$$

Thus the overall proton hydration energy is 1100 kJ mol^{-1}. On the other hand, the heat of hydration of the hydroxide ion is smaller by approximately a factor of 2 and amounts to $\sim$500 kJ mol^{-1}.[5]

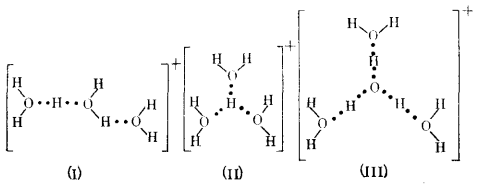
The exceptionally fine energy balance between the electrolytic dissociation processes in liquid water must be specially emphasised. The corresponding heat change represents the difference between two very large quantities—the energy of the heterolytic dissociation of the OH bond and the sum of the heats of solvation of the proton and the acid residues formed in this process. Although each of these quantities is approximately 1600 kJ mol^{-1}, the dissociation process is almost thermally neutral overall. Therefore, even very

slight changes in the energy of the abstraction of a proton from the acid molecule or in the heat of hydration of the proton in the acid residue have a marked influence on the character of the electrolytic dissociation. We shall return to this question below in the discussion of proton transfer to molecules with different basic properties in heterogeneous systems.

The main information about the real structure and geometry of the different hydrated forms of the proton in liquid water has been obtained from IR spectroscopic data, on the basis of quantum-chemical calculations, and with the aid of the results of other physicochemical measurements. Such information reduces to the following findings.[5]

The simplest stable state of the hydrated proton in liquid water is the hydroxonium ion H_3O^+ and the symmetrical very slightly polarised ion $O_2H_5^+$.[6-8] Regardless of the nature of the initial acid, it is characterised by a continuous absorption in the IR in the range $1000-3500$ cm^{-1}. In this structure the proton is not localised in the vicinity of one of the oxygen atoms but oscillates between them; this agrees with the estimated average lifetime of the H_3O^+ ion in liquid water (2×10^{-13} s).[5] For a theoretical interpretation of the continuous absorption, two approaches have been suggested: in one of them account is taken of the inter-relation between the proton transitions and the phonon spectrum of the medium,[9] while in the other account is taken of the inter-relation between the proton transitions and the vibrations of the hydrogen bond.[10,11] In both cases, a satisfactory agreement with experiment is achieved.

Of the two versions of the addition of yet another water molecule to the $O_2H_5^+$ ion that which leads to the linear structure (I) is preferred, because the structure (II), which has C_{3v} symmetry and the trigonal configuration, is less stable owing to the strong electrostatic repulsion between the negatively charged oxygen atoms.



(I) (II) (III)

The linear structure (I) is also very slightly polarised, because even the smallest distortion of the geometry leads to the localisation of a proton on the right- or left-hand side of the chain of water molecules.

As can be seen from Eqns.(3), further hydration of the $O_3H_7^+$ ion also produces a considerable energy gain, which agrees with the finding that the most stable structure and therefore the structure which predominates in aqueous solutions is the symmetrical trigonal $O_4H_9^+$ (III). It can be assumed that the proton in the structure (II) oscillates continuously between two neighbouring oxygen atoms, i.e. it forms part of the composition of the continuously migrating simplest species $O_2H_5^+$. The ease of its formation and decomposition in the oscillations of the water molecules linked by hydrogen bond network does explain the high mobility of the proton in aqueous solutions. In other words, the familiar Grotthus relay mechanism of proton migration in liquid water is a consequence of the high polarisability of the simplest solvated $O_2H_5^+$ fragments.

3. Proton Transfer in Non-aqueous Media

Certain details of the mechanism of proton transfer from acid molecules to solvent or substrate molecules can be more readily traced in non-aqueous solutions, since the IR spectra do not then show the broad lines due to the hydroxy-groups linked by the hydrogen bond network. This makes it possible to investigate the influence of the successive addition of several molecules on the protonation. Such measurements by IR spectroscopy have been carried out recently by ourselves for the interaction of HCl and HBr with the molecules of water, methyl, ethyl, and isopropyl alcohols, and diethyl ether in CCl_4, CH_2Cl_2, and nitromethane.[12,13] The dilute solutions used in these studies contained an acid ($0.02-0.2$ M) and the substrate ($0.01-0.5$ M).

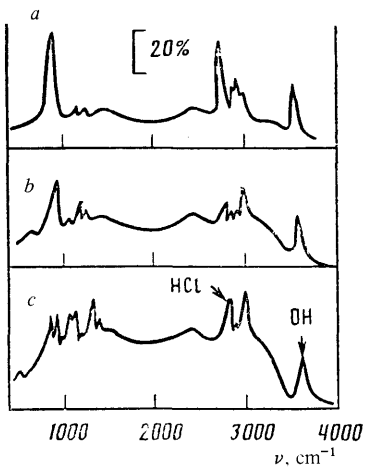
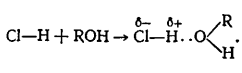


Figure 1. IR absorption spectra of the complexes of methyl alcohol (a), ethyl alcohol (b), and isopropyl alcohol (c) with HCl in CCl_4. Alcohol concentration 5×10^{-2} M; acid concentration 3×10^{-2} to 6×10^{-2} M.[12]

Fig.1 presents typical IR spectra of the complexes of HCl with methyl, ethyl, and isopropyl alcohols in CCl_4. Narrow lines due to the stretching vibrations of the H—Cl, C—H, and O—H bonds are observed against the background of the broad bands due to the HCl molecules perturbed by a hydrogen bond. In addition there is also a continuous absorption analogous to that observed previously for $O_2H_5^+$ ions in aqueous solutions,[6,7] i.e. the absorption induced by the oscillations of protons between two oxygen atoms. The measurements carried out for different ratios of the acid and alcohols showed that the intensity of the broad lines near 2400 cm^{-1}, due to the presence of HCl molecules perturbed by the hydrogen bond, increases linearly with increasing alcohol concentration. On the other hand, the narrow line associated with the free HCl molecules at 2820 cm^{-1} diminishes linearly. This result was explained by the

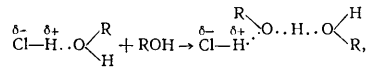
formation of 1 : 1 complexes between acid and alcohol molecules via a strong hydrogen bond:



(4)

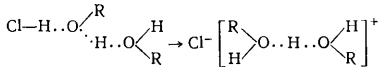
In contrast to this, the intensity of the continuous absorption, measured at 2000 cm^{-1}, increased in proportion to the square of the concentration of the alcohol or water molecules, which made it possible to attribute the composition HCl.2ROH to the alcohol complexes. Apparently, even in the case of a strong acid such as HCl, complete proton transfer occurs immediately to only two alcohol molecules. This entails the formation of complexes, resembling the $O_2H_5^+$ ions in aqueous solutions, in which the proton oscillates between two oxygen atoms. This in fact leads to the appearance of the analogous continuous absorption in the IR spectrum. On the other hand, the proton affinity of one alcohol molecule is sufficient only for the formation of complexes with a strong hydrogen bond.

The mechanism of proton transfer to two alcohol molecules may be analogous to the mechanism of the relay transfer in liquid water. Yet another hydrogen bond is formed initially with participation of a second alcohol molecule:



(5)

and this is followed by the vibrational excitation of such an associated species, which leads to complete proton transfer:



(6)

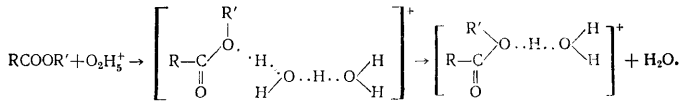
The proton is also apparently transferred via the same mechanism to two water molecules, while the interaction with one water molecule also results in the formation of a complex with only a moderately strong hydrogen bond. The HCl stretching vibration band then shifts from 2820 and 2500 cm^{-1}. We may also note that the shifts of the vibration frequency of the hydrogen bond-perturbed acid molecules in the 1 : 1 complexes and the intensity of the continuous absorption of the 1 : 2 complexes agree well with the substrate basicity series (H_2O < CH_3OH < C_2H_5OH < C_3H_7OH) and the acid strength series (HBr > HCl). In the case of aqueous solutions, the conclusion that a proton is transferred to two water molecules at once was reached also in relation to films of polyfluorosulphonic acid[6] and sulphuric acid solutions.[14,15]

The proton transfer in non-polar solvents from a wide range of weak and strong acids to the molecule of a strong base (pyridine) has been investigated.[16] The protonated forms were detected only after the interaction with very strong acids (HNO_3, HCl, HBr, $HClO_4$). Weaker acids form only hydrogen-bonded complexes whose stability varies within wide limits. These data also evidently indicate only a weak tendency towards proton transfer only in non-polar solvents. The reduced tendency towards proton transfer and the absence of solvation effects have likewise been observed in the gas phase[17] and in inert gas matrices.[18]

4. Modern Ideas about the Mechanism of Homogeneous Acid Catalysis

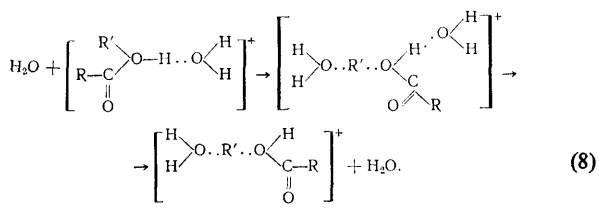
The results described above indicate a decisive role for the interaction of the acid with several water or substrate molecules in the transfer of a proton to the latter. Therefore, in discussing the mechanism of homogeneous acid catalysis in aqueous solutions, it is evidently insufficient to consider only the interaction of the reacting molecules with hydroxonium ions or with undissociated acid molecules alone and account must be taken also of the possibility of the formation of more complex solvated complexes including several water molecules. This conclusion agrees with the results obtained in a study of the kinetics of the hydrolysis of esters in aqueous solutions of strong acids:[14,15] it was shown that the activated complex involves the $O_2H_5^+$ ion and not the hydroxonium ion H_3O^+. We shall consider the possible mechanism of this reaction in greater detail.

It appears likely that its first stage is proton transfer from the $O_2H_5^+$ ion to the ester molecule, which is analogous to the proton transfer via a chain of hydrogen-bonded water molecules:



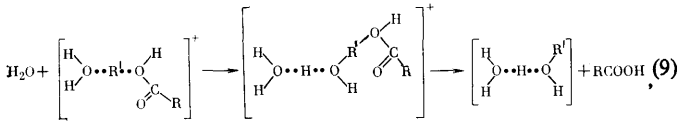
(7)

The positively charged ion of the protonated ester is then solvated by yet another water molecule, which results in the localisation of the positive charge on the R′ fragment:

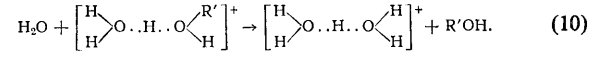


(8)

The decomposition of this complex (also with participation of a water molecule) then leads to the formation of an acid and the protonated alcohol, which loses its proton as a result of yet another reaction involving a water molecule:



(9)



(10)

Thus water participates in all the intermediate stages of the catalytic reaction. Its driving force is the high polarisability of the complexes incorporating a solvated proton, which are readily formed and decomposed under the influence of the vibrations of the solvent molecules surrounding them. This entails a "switchover", as it were, from the dissociating bonds to the newly formed bonds induced by the proton migration along the hydrogen-bonded chain of molecules.

This mechanism differs from that considered in the literature,[14,15] but we believe that it agrees better with modern data concerning the state of the hydrated proton in aqueous solutions and concerning the mechanism of proton transfer in liquid water. It also confirms the idea of "bond redistribution chains" developed for enzyme catalysis[19,20] and the mechanisms of proton transfer in biological systems discussed in a number of studies.[21-23]

III. HETEROGENEOUS ACID CATALYSIS

The ideas about the mechanisms of heteogeneous-catalytic reactions of hydrocarbons were formulated much later than for the the homogeneous acid catalysis—not until the end of the 1940's and the beginning of the 1950's. At that time, a number of workers put forward independently the hypothesis of the carbenium ion mechanism of the reactions in question[24-28] based on purely chemical analogies with low-temperature reactions of hydrocarbons in the presence of strong acids (the higher reactivity of olefins compared with paraffins, the high reactivity of compounds with a tertiary carbon atom, the selective formation of isoparaffins under the catalytic conditions, the occurrence of olefin isomerisation, hydrogen transfer, and hydrogen isotope exchange reactions, etc.).

The next important step was the experimental demonstration of the acidity of amorphous aluminosilicates and certain other oxide catalysts based on the use of the absorption of ammonia and Hammett indicators.[29,30] These studies led to the widespread adoption of the idea that adsorbed carbenium ions exist on the surfaces of oxide catalysts and that they play a decisive role in the mechanisms of the catalytic reactions of hydrocarbons, although this hypothesis was never in fact subsequently confirmed by direct spectroscopic methods.

Multistage schemes, analogous to those for general acid catalysis in solutions, are usually postulated for the mechanisms of heterogeneous-catalytic reactions of hydrocarbons.[31-34] For example, for the catalytic reactions of olefins, it is suggested that the adsorbed molecules are initially linked by strong hydrogen bonds to the acid hydroxyls. Complete proton transfer then takes place with formation of adsorbed carbenium ions. It is also assumed that such protonated intermediate forms exhibit an enhanced specific reactivity, which explains the selectivity of the corresponding heterogeneous-catalytic reactions. For example, the reverse abstraction of a proton from them leads to the migration of the double bond in the olefin molecules. Linear carbenium ions can isomerise to branched ions, which induces the skeletal isomerisation of the hydrocarbons. The occurrence of cracking, etc. is explained by the splitting off of carbenium ions from olefin molecules. In particular, the fairly typical mechanism of the heterogeneous-catalytic reactions of but-1-ene can be represented as follows in accordance with these ideas:

$$\begin{aligned} &CH_2{=}CH{-}CH_2{-}CH_3 + H^+ \rightarrow CH_3{-}\overset{+}{C}H{-}CH_2{-}CH_3 \rightarrow \\ &\rightarrow CH_3{-}CH{=}CH{-}CH_3 + H^+ \text{ (migration of the double bond)}, \\ &\rightarrow CH_3{-}\overset{CH_3}{\overset{|}{\underset{+}{C}}}{-}CH_3 \rightarrow CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_3 + H^+ \text{ (skeletal isomerisation)}, \\ &\rightarrow CH_2{=}CH_2 + C_2H_5^+ \rightarrow 2C_2H_4 + H^+ \text{ (cracking)}. \end{aligned} \qquad (11)$$

Although such schemes have come to be widely adopted in the literature and they describe satisfactorily the composition of the products of heterogeneous-catalytic reactions of hydrocarbons, from our point of view they are no longer consistent with the significance which is nowadays attributed to the concepts of the mechanism of catalytic reactions. Indeed, carbenium ions are not in fact free but are adsorbed on the catalyst surfaces. Therefore, depending on the strength of the acid centres or on the nature of the basic centres to which the carbenium ions are bound during adsorption, their chemical properties can vary within extremely wide limits. For example, it is known that the migration of the double bond in olefins takes place on weaker acid centres than their skeletal isomerisation.[34] This difference is not, however, taken into account by Scheme (11). It also fails to reveal the driving forces of various elementary reactions on the adsorbed carbenium ions. Furthermore, these processes have come to be part of the order of the day by virtue of the results obtained in the study of proton transfer by modern spectroscopic methods and the results of quantum-chemical calculations. Their discussion is the main aim of the present article.

1. Spectroscopic Data on the Protic Acid Centres on the Surfaces of Oxide Catalysts

Among acid catalysts, amorphous and crystalline aluminosilicates (zeolites), alumina, aluminium phosphate, phosphoric acid on silica gel, etc. have come to be most widely used. Their active centres are acid hydroxy-groups, which are formed on the surfaces of the oxides on partial hydrolysis of the metal–oxygen bonds (the so called terminal OH groups) or when the protons compensate the excess local negative charge on the surface fragments (the so called structural OH groups). The number of these groups, determined from the intensity of the proton resonance spectra or by the method involving isotope exchange with molecular deuterium, usually corresponds to only a few per cent of the monolayer coverage. If such hydroxy-groups have fairly pronounced acid properties, then they do play the role of the active centres in heterogeneous acid catalysis.

Brønsted centres of both types have been studied in detail by IR spectroscopy[35,36] and NMR,[37,38] which made it possible to obtain detailed information about their geometry, the energy barriers to the rotation of the $M\diagup^{O}\diagdown H$ fragment, and certain other parameters characterising such centres. In particular, it has been demonstrated by IR spectroscopy that the number of different hydroxy-groups on the zinc oxide surface is three, while on the surface of nickel(II) oxide it is four. There are OH groups of five different types on the surface of alumina. The discrete character of the distribution of the hydroxy-groups is characteristic also of the hydrogen-forms of the zeolites.

A systematic treatment has been proposed[39,40] for the surface hydroxy-groups based on the hypothesis that the frequency of their stretching vibrations depends primarily on the coordination number of the oxygen atoms in relation to the surrounding cations. In other words, it was assumed that the nature of the OH bond is determined mainly by the character of the hybridisation of the orbitals of the oxygen atom. On the other hand, there exists the view that the stretching vibration frequency of the hydroxy-groups depends predominantly on the acid–base properties.[41] This is based on the fact that stretching vibration frequencies of 3839 and 2955 cm^{-1} are characteristic of the free OH^- ion and the OH^+ ion respectively.[42] Thus the lower-frequency hydroxy-groups have acid properties and the higher-frequency groups have basic properties.

However, the stretching vibration frequency of the hydroxy-groups can also be influenced by a number of other factors. It is therefore extremely desirable to measure not only the fundamental frequency

of the stretching vibrations of the OH bond but also other parameters characterising it.

This can be done with the aid of the diffuse scattering IR spectroscopy, the great possibilities of which have been demonstrated in a number of studies.[43-49] This method makes it possible to extend greatly the range of spectroscopic measurements, including the frequencies of the first and second overtones of the stretching vibrations of the surface OH groups, and to calculate from these data the energies of their homolytic dissociation and the parameters of the Morse functions ω_e and x for the OH bond. The results obtained indicate that the vibrations of the OH groups, which virtually do not interact with the vibrations of the oxide lattices, are highly characteristic. It was also found that the frequencies of the deformation vibrations of the surface hydroxy-groups contain most information as regards the nature and geometry of such groups. They are difficult to measure directly owing to the marked absorption of light by the oxide lattice in the range $800-1500$ cm^{-1}, but it is possible to obtain them as differences between the frequencies of the combination stretching-deformation vibrations and the frequencies of the stretching vibrations. The lowest deformation vibration frequency ($\sim 700-800$ cm^{-1}) is that of terminal OH groups. On passing to bridging hydroxy-groups, whose oxygen is linked to two cations of the oxide lattice, the deformation vibration frequency increases to $1000-1100$ cm^{-1}. This can be explained by the increase in the rigidity of the M⟨OH⟩M fragment when oxygen is coordinated to the second cation. For hydroxy-groups with a still higher oxygen coordination number, the combination stretching plus deformation vibrations frequencies are usually not observed at all, so that the number of bands in the fundamental region of their IR spectrum is greater than in the combination region. The results of these measurements make it possible to refine and test the conclusions concerning the nature and geometry of the surface hydroxy-groups reached from the analysis of the fundamental stretching vibrations frequencies alone.

IR spectroscopy is used widely also in quantitative measurements of the acid strength of the surface hydroxy-groups. The bathochromic shifts of the stretching vibration frequencies, induced by the formation of hydrogen bonds with the molecules of different bases, are usually employed for this purpose. These shifts are linearly correlated both the with acidity of the OH groups and with the basicity of the molecules interacting with them:[50,51]

$$\Delta\nu_{OH}/\nu_{OH} = a - b\Delta pK_a, \qquad (12)$$

where $\Delta pK_a = pK_a^{ac} - pK_a^{bas}$, ν_{OH} and $\Delta\nu_{OH}$ are the stretching vibration frequency of the OH group and its shifts induced by interaction with the molecules of bases, pK_a^{ac} is the logarithm of the acid dissociation constant, and pK_a^{bas} the logarithms of the basicity constants of the corresponding bases.

Thus pK_a^{ac} for the OH surface groups on any one oxide can be determined from a series of shifts induced by the adsorption on it of several weak bases characterised by different pK_a^{bas} values. On the other hand, the frequency shifts, induced by the adsorption of the same base, for example, benzene or carbon monoxide, on the surfaces of different oxides, are usually measured to compare the acidities of their hydroxy-groups. Studies involving the use of IR spectroscopy of the acid–base properties of oxides have been surveyed in a review.[52]

2. Quantum-chemical Cluster Models of the Surface Hydroxy-groups and the Nature of Their Acidity

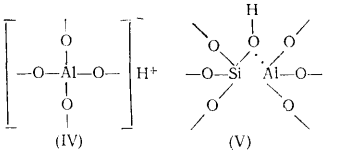
The nature of the acidity of the OH groups can also be analysed with the aid of quantum-chemical calculations performed using the so called "cluster" models.[53-58] The simplest model of an OH acid is the A–O–H molecule, where A is a hydrogen-like atom, whose ionisation potential can be varied within wide limits. If it is equal to 13.6 eV, as for the hydrogen atom, then a structure of this kind models the neutral water molecule. Lower ionisation potentials correspond to alkali metals, whereupon the hydroxy-groups are negatively charged and acquire basic properties. On the other hand, higher ionisation potentials correspond to ions with a high positive charge such as N^{5+}, P^{5+}, S^{6+}, etc. The electron density then shifts to the A atom, imparting acid properties to the hydroxy-groups.

These effects can be described more rigorously using clusters taking into account the real structure of the oxide surfaces. For example, in the case of terminal hydroxy-groups on the silica surface, one frequently considers the $Si(OH)_4$ or $SiOH(OA)_3$ clusters, where A are hydrogen-like atoms, as for the simplest clusters.

It follows from the foregoing that one of the causes of the formation of strongly acid terminal hydroxy-groups on the oxide surfaces is the polarising effect of neighbouring highly charged cations. Accordingly, the surfaces of partly hydrolysed alkali and alkaline earth metal oxides have basic properties, while the terminal groups on the TiO_2, V_2O_5, and MoO_3, or WO_3 surfaces have acid properties. The strength of the centres then increases with increasing positive charge on the cations. With the exception of WO_3, these oxides are not, however, used in heterogeneous acid catalysis because, at a high temperature in the presence of hydrocarbons or other reductants they readily pass to lower valence states.

Mixed oxides, among which crystalline skeletal aluminosilicates (zeolites) and amorphous aluminosilicates are most important, are much more significant for acid catalysis. They are characterised by the presence of structural bridging hydroxo-groups in which the coordination number of oxygen in relation to the cations is two.

The crystal lattice of aluminosilicates is constructed of oxygen tetrahedra at the centres of which are silicon or aluminium atoms. When it is described in terms of the ionic model, the aluminium-occupied tetrahedra carry a single excess negative charge, which is compensated by the charges of the adjoining cations or protons with which the Brønsted acidity of the aluminosilicates [structure (IV)] is in fact associated:



(IV) (V)

Within the framework of the covalent model (V), the acid centre may consist of a terminal silanol group, whose oxygen is linked by a coordinate bond to an adjoining aluminium atom (a Lewis acid centre). The combination of the Brønsted and Lewis acid centres shifts the electron density from oxygen to aluminium, diminishes the negative charge on the OH group, and enhances its acid properties.

In amorphous aluminosilicates, the number of such bridging acid groups is small and only a small proportion of the entire aluminium content corresponds to them. On the other hand, the vast majority

of the hydroxy-groups formed on hydrolysis of the surfaces are terminal OH groups with weakly acid properties.[36]

The situation is different in the hydrogen-forms of zeolites—aluminosilicates with a strictly regular crystal structure. Ideally the number of acid hydroxy-groups is in this instance identical with the number of aluminium atoms present in the lattice, i.e. it is many times greater than in amorphous aluminosilicates. This in fact explains the high catalytic activity of zeolites.[59,60]

Quantum-chemical cluster models of hydroxy-groups in zeolites have been developed,[61] and the calculations performed have shown that, with increase in the number of neighbouring aluminium atoms, the acidity of the hydroxy-groups diminishes monotonically; this can be inferred from the decrease in the positive charge on the proton and from the increase in the energy of its abstraction from the corresponding clusters. It has also been concluded that a characteristic feature of crystalline aluminosilicates with a definite silicon : aluminium ratio is the presence of hydroxy-groups with a constant number of nearest aluminium atoms. For example, in high-silica zeolites, the bridging hydroxy-groups are surrounded solely by silicon atoms. They are therefore characterised by identical Brønsted acid centres of identical strength.[62] With increase in the number of aluminium atoms in the crystal lattice, for example in the case of faujasites, hydroxy-groups having two or three neighbouring aluminium atoms appear and the character of the Brønsted acidity changes, which has in fact been confirmed experimentally.[34]

Thus quantum-chemical cluster models permit an atomic-molecular description of the structure of the acid centres in zeolites and explains satisfactorily the discrete character of the variation of the acidity in specimens with different aluminium contents in the lattice.[63,64] It is no less significant also that, with their aid, one can carry out fairly well-founded quantitative calculations of the intermediate structures in heterogeneous acid-catalytic reactions, which will be discussed below.

Analogous atomic-molecular models have also been used to treat systematically the hydroxy-groups on the surfaces of other oxides, for example, alumina.[41] There is no doubt that in the future this approach will permit a rational systematic treatment of the surface OH groups on oxides with a wide variety of different acid–base properties.

3. The Nature of the Protonated Intermediate States on the Surfaces of Oxide Catalysts

As already stated above, heterolytic dissociation in solution is possible only in the presence of solvation effects, whose contribution to the process energetics is decisive. Therefore proton transfer on the surfaces of heterogeneous oxide catalysts during high-temperature gas-phase reactions in the absence of polar solvents differs radically from the protonation in aqueous solutions.

Under the conditions of heterogeneous acid catalysis, the situation approaches more closely to the proton transfer in non-polar solvents discussed above where the solvation effects are minimal and the protonation of the substrate is associated with additional energy expenditure. For the majority of adsorbed molecules, the proton transfer is therefore significantly endothermic. It becomes energetically favourable in the interaction of very acid hydroxy-groups with strong bases such as ammonia, pyridine etc. These molecules are in fact usually employed as indicators for strongly acid surface OH groups. However, in this connection the fact has been overlooked that, even if adsorbed ammonium or pyridinium ions are actually formed from them on the surfaces of acid type catalysts, this by no means implies that analogous ionic intermediate compounds arise also in the adsorption of olefins or even paraffins, whose proton affinity is much smaller than those of ammonia or pyridine. In fact, in the interaction of hydrocarbons even with very strongly acid Brønsted centres, either complexes with a short hydrogen bond or highly polarised covalent structures are produced. Thus the intermediate active forms in heterogeneous acid catalysis differ significantly from the protonated ionic states in aqueous solutions and other polar sovlents and resemble more closely the complexes formed in the interaction of strong acids with weak bases or of weak acids with strong bases in non-polar solvents.

In this connection, it is appropriate to recall that the concept of carbonium ion mechanisms arose in organic chemistry exclusively on the basis of indirect kinetic and stereochemical data and also as a result of studies on the final products of the corresponding reactions. Carbonium ions are then regarded as short-lived species which cannot be observed directly by physical methods.[65] On the other hand, in heterogeneous catalysis the formation of adsorbed carbonium or carbenium ions is frequently understood too literally, as the solid catalysts are not superacids and solvation effects, stabilising the intermediate structures, are absent in the catalytic reactions of hydrocarbons.

Indeed, surface esters and not ion pairs are formed in the interaction of Brønsted acid centres with olefins or alcohols. These are known to be covalent compounds, as is confirmed by their dipole moments and by the comparatively small low-field chemical shifts in the ^{13}C NMR spectra involving the α-carbon atoms of the alkyl substituents, which do not differ from the chemical shifts in the corresponding alcohols and are in the range 50–70 p.p.m.[66] On the other hand, the shifts for stable carbenium ions in superacid solutions, where the positive charge on the carbon is much higher, reach 300–350 p.p.m. For example, the chemical shift for the central atom in the $(CH_3)_3C^+$ is 335.7 p.p.m. and that for the carbon atom in the $(C_2H_5)_3C^+$ ion is 331.8 p.p.m.[70]

The covalent nature of the C–O bond in the surface esters has also been confirmed by quantum-chemical calculations. Thus it has been shown[67] that the interaction of ethylene with the bridging hydroxy-group of a high-silica zeolite leads to the formation of a surface ethoxy-fragment carrying a comparatively low positive charge of +0.26 e, and not a carbenium ion, while the interaction of an ammonia molecule with the same hydroxy-group results in the formation of an ammonium ion, whose charge is +0.71 e.[68] On the other hand, it follows from quantum-chemical calculations that the tendency towards an increase in the amount of ionic character of the C–O bond in esters increases with increase in its length or on vibrational excitiation.[69] Thus the carbenium ion properties of the alkyl substituents are manifested not in the ground states of the corresponding intermediates but in their transition stages.

The complete rejection of the mechanisms involving adsorbed carbenium ions, which are nowadays generally accepted, does not by any means follow from the foregoing. We merely wish to emphasise yet again that the concept of carbenium ions refers more to transition states than to intermediate compounds. On the other hand the very concept of the "adsorbed carbenium ion" may have a completely different significance in each specific case. From our point of view, it should be understood not as the real existence of contact ion pairs on the surfaces of catalysts but rather as implying the presence of intermediate compounds resembling carbenium ions in the liquid phase as regards their reactivity.

4. Spectroscopic Studies on the Elementary Proton Transfer Stage on the Surfaces of Oxide Catalysts

The reduced tendency towards the formation of ionic structures in the proton transfer from acid hydroxy-groups to molecules adsorbed on the surfaces of heterogeneous catalysts has been confirmed also by spectroscopic data. Above it was already stated that the bathochromic shifts of the stretching vibrations of the OH groups, induced by the formation of a hydrogen bond with the adsorbed molecules, are widely used for the measurement of the strength of the Brønsted acid centres on the surfaces of oxides. The possibilities of IR spectroscopy in the study of the proton transfer mechanism are not, however, exhausted by this. It has been suggested[43,48,71–75] that, together with the shifts of the fundamental stretching vibration frequency, one should also measure the bathochromic shifts of the overtones of the stretching vibrations. These data make it possible to reconstruct the lowest sections of the potential curves for the OH bond in the surface complexes preceding the proton transfer and to calculate the height of the potential barrier in this elementary stage.

Indeed it is well known that the potential energy curve for a diatomic molecule can be constructed from the positions of any two of its vibrational levels. It has been shown[43,44] that, as a consequence of the characteristic nature of the stretching vibrations, the surface OH groups can also be regarded as diatomic fragments which hardly interact with the lattice vibrations of the oxide. Therefore the lowest sections of the potential curves for the OH bond in the free hydroxy-groups and in the hydrogen-bonded complexes can be plotted from the fundamental frequencies and overtones of the OH group vibrations. On the other hand, for the reconstruction of the complete potential energy profile of the elementary proton transfer stage, one can assume to a first approximation that the stage corresponds to an increase in the length of the OH bond by approximately 0.05 nm, which follows from the considerations described above.

It is known that the lengths of the strong hydrogen bonds in a wide variety of complexes are in the range 0.24–0.26 nm.[76] On the other hand, the equilibrium O–H distance in the initial hydroxy-groups is approximately 0.1 nm. Similar values are characteristic also of the length of the C–H (0.109 nm), N–H (0.101 nm), and other bonds formed in protonated intermediate compounds. The extension of the O–H bond by approximately 0.05 nm therefore corresponds to proton transfer to adsorbed molecules and a somewhat smaller increase in its length corresponds to the apex of the potential proton transfer barrier. As regards the complete potential energy profile for the elementary proton transfer stage, the latter can be obtained by positioning the potential curve for the OH bond, calculated from spectroscopic data, and the potential curve for the bond newly formed in the protonated compound in such a way that the distance between their minima is 0.05 nm.

Fig.2 presents the potential energy profiles constructed in this way for the exothermic and endothermic proton transfer stages.[73–75] In the former case, the transfer requires virtually no activation energy. On the other hand, for the endothermic stages the formation of the stable intermediate protonated compounds is possible only provided that the energy expenditure on the proton transfer does not exceed approximately 100 kJ mol^{-1}. Otherwise, the local minimum on the potential curve corresponding to the formation of the protonated state is either absent or its depth is so small that the protonated state is metastable and decomposes even after a few vibrations. This is caused by the comparatively large width of the lowest section of the potential curve for the OH bond and the slight increase in its length on complete proton transfer in its surface complexes. In this respect, heterogeneous acid catalysis differs significantly from homogeneous acid catalysis in aqueous solutions, where the proton transfer reaction coordinate does not have the significance of a simple increase in the length of the OH bond and is accompanied by a rearrangement of many solvent molecules, resulting in the separation of cations and anions in space. Therefore, in aqueous solutions protonated states can really exist even if proton transfer is significantly endothermic.

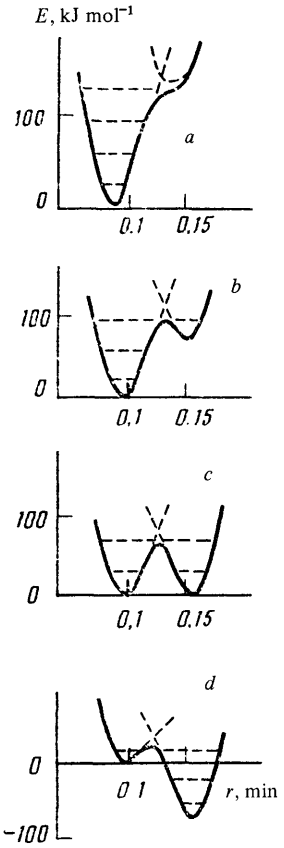


Figure 2. The potential energy profiles for the elementary proton transfer stage constructed on the basis of spectroscopic data:[73,74] (a) process endothermicity 150 kJ mol^{-1}; (b) process endothermicity 100 kJ mol^{-1}; (c) thermally neutral process; (d) process exothermicity 50 kJ mol^{-1}.

It is possible to formulate several spectroscopic criteria for the determination of the real tendency towards proton transfer to the adsorbed molecules. The most clear-cut of these is the increase in the anharmonicity of the potential curve for the OH bond on formation of surface complexes. To use a picturesque phase, the anharmonicity makes it possible to analyse the response of the acid hydroxy-group to the extension of the OH bond and to the

approach of the adsorbed molecule by the proton. The increase in anharmonicity indicates the attraction of the proton to the substrate and its decrease indicates the repulsion.[77]

The isotope effect, i.e. the ratio of the vibration frequencies of the light and heavy hydroxy-groups perturbed by hydrogen bond formation, may be used as another criterion of the positive tendency towards the formation of protonated states (the ratio diminishes with increase in anharmonicity and in positive tendency towards proton transfer). Furthermore, the tendency towards proton transfer is manifested by the absence of strong perturbation of the first overtone and in the large bathochromic shifts of the stretching vibrations in the spectra of hydrogen-bonded complexes (400 – 600 cm^{-1} and above).

The application of these criteria to the analysis of the IR spectra of the complexes of hydroxy-groups with various molecules also indicates merely a moderate tendency towards the formation of ionic intermediate structures under the conditions of heterogeneous catalysis. For example, in the benzene complexes with acid hydroxy-groups of the hydrogen-form of the type Y zeolite, the decrease in the fundamental stretching vibration frequency is approximately 350 cm^{-1}. This, however, is insufficient for the complete proton transfer to benzene molecules. The anharmonicity coefficient also increases only up to 4×10^{-2}, i.e. by a factor of approximately two. Approximately the same bathochromic shifts are observed likewise in the interaction of acid hydroxy-groups of the type HY zeolite with ethylene.[78]

The proton affinities of certain molecules.[80]

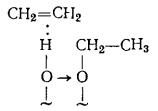
Molecule	Proton affinity, eV	Molecule	Proton affinity, eV
H_2	4,4	C_4H_8	7,8
CH_4	5,1	CH_3OH	7,8
C_2H_6	5,6	C_3H_6	7,9
C_3H_8	6,1	CH_3CHO	8,0
C_2H_4	6,9	CH_3CN	8,1
H_2O	7,1	C_2H_5OH	8,1—8,4
C_6H_6	7,5	CH_3OCH_3	8,5
cyclo-C_6H_{10}	7,7	NH_3	9
CH_3NO_2	7,7—7,8	CH_3NH_2	9,2

The formation of ion pairs hardly occurs even in the interaction of ethylene with the very highly acid hydroxy-groups of the high-silica zeolites of type ZSM-5. This is indicated both by the moderate shifts of the OH vibration frequencies in the spectra of the hydrogen-bonded complexes and by the linear structure of the ethylene oligomers formed at room temperature, which cannot be explained by steric effects, because the polymerisation of propene on the same catalysts leads to the formation of branched structures in their channels.[79] Apparently, in conformity with the quantum-chemical calculations already discussed above, the interaction of ethylene with such centres entails the formation of highly polarised covalent structures and not ion pairs. Thus spectroscopic data also demonstrate that the concept of carbenium ions is too simplified when applied to heterogeneous systems.

We may note that the transition from the hydrogen-bonded complexes to polarised covalent structures and further to surface contact ion pairs depends very markedly on the energetics of the elementary stage of proton transfer. For example, the benzene is not protonated in its interaction with the acid OH groups of a type Y zeolite (the proton affinity of benzene is 7.5 eV—see Table), but contact ion pairs are undoubtedly formed in the interaction of these groups with ammonia (the proton affinity is 9 eV [80]). Thus the proton transfer and the formation of contact ion pairs require an additional energy of only approximately 1.5 eV. There is nothing surprising in this, because a free energy change of 5.7 kJ mol^{-1} corresponds to one unit on the pK_a scale in aqueous solutions and a free energy change of approximately 120 kJ mol^{-1} or 1.2 eV corresponds to the transition from a weak acid with $pK_a = +10$ to superacids with $pK_a = -10$. Solvation in fact makes good this deficiency in the formation of intermediate ionic states and contributes to the energy balance of the acid – base interaction in aqueous solutions. On the other hand, in the high-temperature catalytic reactions of hydrocarbons, this source of additional energy is absent. It cannot be replaced by the activation energy either, because, as already mentioned above, in the case where the proton transfer stages are insufficiently endothermic minima corresponding to protonated ionic structures are missing from the potential energy surface.

5. The Reaction Coordinate in Heterogeneous Acid Catalysis. Synchronous Mechanisms of Acid Catalytic Reactions

In constructing the energy profiles, discussed in the previous Section, for the elementary proton transfer stage, no account is taken of the additional energy gain associated with the optimisation of the geometry of the protonated state. For example, the conversion of a π-complex of ethylene into the ethoxy-fragment actually involves, apart from the extension of the OH bond as the proton approaches the ethylene molecule, also an increase in the length of the C=C bond when it is converted into a single bond, a change in the hybridisation and in the valence angles in the CH_2 and CH_3 groups, and the orientation of the adsorbed molecule relative to the catalyst surface:



(13)

In other words, the vibrational excitation of the OH bond and the associated increase in length by no means always constitute the optimum coordinate of the elementary protonation stage.

Depending on the relative contributions of various factors, there is a possibility of a wide variety of situations in this instance. For example, the role of relaxation in the formation of the ammonium ion from adsorbed ammonia is minimal. On the other hand, in the example involving the formation of the ethoxy-fragment just discussed, the optimisation of the geometry is extremely significant and the reaction coordinate corresponds to only a very slight extent to an increase in the length of the OH bond. In similar cases we shall henceforth speak of a synchronous mechanism of heterogeneous catalytic reactions involving the simultaneous activation and rearrangement of many chemical bonds in the adsorbed molecules or intermediate complexes.

The advantage of these mechanisms under the conditions of acid – base homogeneous catalysis compared with the multistage consecutive protonation-deprotonation of the substrate molecules was noted as early as the end of the 1950's by Syrkin.[81–83] It was

concluded in this connection that there is a possibility of the formation of cyclic five-, six-, and seven-membered transition states and their role in hydrolytic, esterification, Friedel–Crafts, etc. reactions was discussed.[84–86] In relation to heterogeneous catalysis, the important role of synchronous or joint mechanisms in heterogeneous catalysis has been discussed by Boreskov mainly in relation to catalytic oxidation reactions.[87]

The pre-exponential factors in the rate constants for such complex elementary stages are naturally smaller than the stretching vibration frequency of the OH bond because a concerted change in a large number of different coordinates takes place at once in the transition state or many vibrations are found to be in phase. This more complex reaction pathway is associated, however, with a lower energy barrier to the formation of the intermediate protonated state. This more than makes up for the lower activation entropy for the protonation stage and ensures a high rate of the catalytic reaction.[88]

The limiting case in such synchronous mechanisms in acid catalysis involves reactions where the intermediate protonated forms are not formed at all. This is apparently typical of molecules with a low proton affinity, for example, for hydrogen or the paraffins. Since the formation of the intermediate protonated state is unfavourable in this instance, a new bond between the molecule or its fragment and the catalyst surface is formed simultaneously with proton transfer which apparently at least partly compensates for the energy of the abstraction of the proton from the acid centre. For example, in heteroisotope exchange reactions, the proton transfer to the acid centre of the substrate is accompanied by the simultaneous reverse reaction involving the abstraction of another proton from the activated complex. On the other hand, the energy involved in binding the second proton compensates for the difficulty of transferring the first proton to the substrate molecule analogously to the promotion of proton transfer in aqueous solutions by solvation. Specific examples of similar and other synchronous reactions will be discussed below.

6. The Principal Types of Mechanisms of Acid Heterogeneous-catalytic Reactions

Since a great variety of mechanisms of acid heterogeneous-catalytic reactions follows from the foregoing, it is useful to discuss them, having combined them into individual groups, as a function of the presence or absence of solvation effects and as a function of the proton affinity of the reacting molecules. Our aim here is not to provide an exhaustive survey of the literature, because this is impossible within the framework of the present review, and we shall consider only certain most typical examples.

(a) Low-temperature Catalytic Reactions with Participation of Polar Molecules

The mechanism of low-temperature heterogeneous-catalytic reactions involving polar molecules, for example, the hydration of olefins to alcohols, the esterification of alcohols, the hydrolysis of esters, etc., is closest to the mechanism of homogeneous acid catalysis. If the reaction temperature is not too high and there is a possibility of the formation of associated species comprising several molecules, then effects analogous to the solvation effects with participation of polar molecules in solutions come into force and the protonated forms of the substrate play the role of the active intermediates in catalytic reactions. This situation resembles very strongly homogeneous catalysis in aqueous solutions, where solvation effects make a decisive contribution to the formation of protonated states and to proton transfer to the adsorbed molecules. More precisely, this is two-dimensional homogeneous catalysis in a thin liquid film condensed on the surface of the heterogeneous catalyst. In particular, the possibility of the operation of such a mechanism in the olefin hydration reaction has been demonstrated by Chirkov, Vinnik, and co-workers.[89]

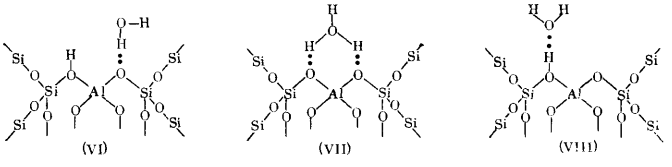
Apparently an analogous mechanism also obtains in enzyme catalysis. Here, however, the specificity of the interaction of the water or substrate molecules with the polar groups on the biopolymer surface is manifested. This leads to structure formation in the adsorbed film, which affects both the solvation energy and the proton transfer mechanism.[21–23] This factor does not, however, alter the main features—the real existence of intermediate protonated states in these systems.

(b) Heteroisotope Deuterium Exchange Reactions

Another limiting case is that of catalytic reactions involving nonpolar molecules having a minimal proton affinity. As can be seen from the Table, these include molecular hydrogen and the paraffins. Since the solvation effects are virtually absent here and the proton affinity is low, the formation of intermediate protonated states is extremely unfavourable. At the same time different versions of synchronous or joint mechanisms operate.

For a series of heteroisotope exchange reactions, their possibility has been confirmed by quantum-chemical calculations carried out using the cluster models of Brønsted acid centres examined above. In particular, synchronous heteroisotope exchange between terminal silanol groups on the silica surface and molecular deuterium can proceed via a symmetrical tetragonal transition state.[54]

The advantage of such synchronous mechanisms in the heteroisotope exchange reaction with water molecules, which have a much higher proton affinity (~7 eV), was more unexpected.[90,91] Quantum-chemical calculations have been performed for the adsorption of water and the mechanism of the heteroisotope exchange between the acid bridging hydroxy-groups in the hydrogen-forms of zeolites and water.[91] Among the three versions of the adsorption of H_2O molecules examined [structures (VI)–(VIII)], the highest heat was obtained for the interaction of water with the basic oxygen of the aluminium–oxygen tetrahedron [70 kJ mol^{-1}, structure (VI)], while the lowest heat was found for its two-point adsorption [40 kJ mol^{-1}, structure (VII)]. The heat of adsorption of water on the proton of the bridging hydroxy-group proved to have an intermediate value [46 kJ mol^{-1}, structure (VIII)].



Bearing in mind that the highest heat of adsorption corresponds to the structure (VI), one may conclude that the rate-limiting stage in the hetero-exchange is most likely to be the desorption of water from the surface. On the other hand, the reaction itself apparently proceeds via a synchronous mechanism, in the transition state (VII)

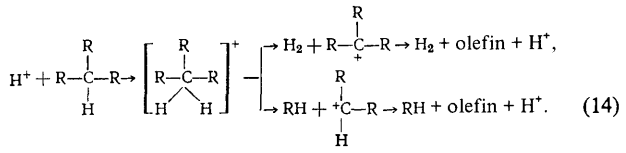
of which there is simultaneous proton transfer from the acid bridging hydroxy-group to the adsorbed water and the abstraction from it of a second proton, which is transferred to a neighbouring basic oxygen atom.

A synchronous mechanism has also been proposed for the heteroisotope exchange between surface hydroxy-groups and acetylene.[92] However, this mechanism is unlikely in the heteroisotope exchange with ethylene, whose rate is much lower.[93,94]

(c) The Cracking of Paraffins

Paraffins constitute another class of compounds in the reactions of which the formation of intermediate protonated states is unlikely because of the low proton affinity. Until recently, it was assumed that their acid-catalytic cracking proceeds via a chain mechanism and that chain transfer is achieved via the transfer of a hydride ion from the paraffin molecule to the adsorbed carbenium ions. It has been suggested that the source of the latter is olefins, which are either present in the starting material as an impurity or are formed in the dehydrogenation of the paraffins.[32]

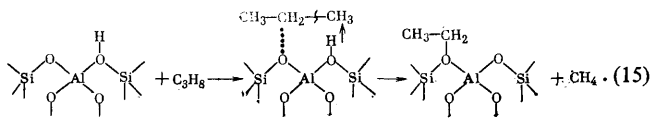
Apart from this classical cracking mechanism, which is valid at relatively low temperatures and high pressures of the hydrocarbons, there is a possibility also of protolytic cracking with participation of non-classical carbenium ions containing pentacoordinate carbon atoms:[95]



(14)

Its distinctive features are the rapid deuterium–hydrogen exchange involving the paraffins without their skeletal isomerisation and the presence of molecular hydrogen and of light C_1 and C_2 paraffins in the cracking products.

However, in conformity with what has been said above, the formation of non-classical carbonium ions as stable intermediates hardly occurs owing to the low proton affinity of the paraffins. It is sufficient to state that non-classical carbonium ions cannot be observed even in the interaction of paraffins with superacids.[70] From our point of view, an alternative synchronous cracking mechanism, involving a six-membered transition state with simultaneous proton transfer to the CH_3 group, the dissociation of a C–C bond in the paraffin molecule, and the formation of a new carbon–oxygen bond is more probable:

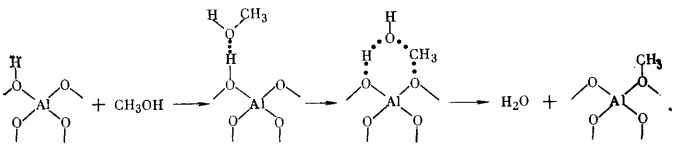


(15)

In this case the activated complex does not indeed resemble the non-classical carbenium ion but it is not a stable intermediate structure which really exists.

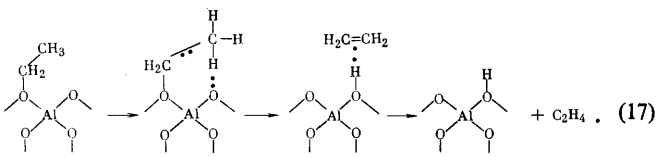
(d) High-temperature Catalytic Reactions of Alcohols

Esterification reactions, dehydration reactions with formation of olefins, alkylation of olefins and aromatic compounds by alcohols, and the synthesis of higher hydrocarbons from alcohols are characteristic high-temperature acid-catalytic reactions of alcohols. There is no doubt that, under the conditions of heteogeneous acid catalysis, the first stage in all these reactions is the formation of surface alkoxy-structures. The mechanism of this elementary stage can be treated, by analogy with heteroisotope exchange reactions between highly acid hydroxy-groups and water molecules, as a synchronous substitution reaction with participation of neighbouring basic centres and involving the inversion of the methyl group in the transition state similarly to what happens in the thoroughly investigated S_N2 nucleophilic substitution reactions



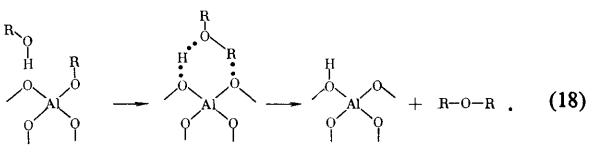
(16)

In the case of higher alcohols, the decomposition of surface alkoxy-fragments leads to the desorption of olefins from the surface:



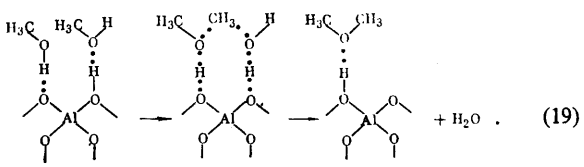
(17)

and their interaction with a second alcohol molecule results in esterification:



(18)

Another bimolecular synchronous mechanism, involving the formation of an eight-membered cyclic transition state, has also been discussed for this reaction:[90,96]



(19)

The low energy barriers in these elementary stages can be explained by the synchronous nature of the dissociation of old and the formation of new bonds in the activated complexes arising by the interaction of alcohol molecules with the surface acid–base pairs.

The establishment of the mechanism of the reactions involving the alkylation of olefins and the aromatic compounds by alcohols and also the synthesis of higher hydrocarbons from alcohols constitute a

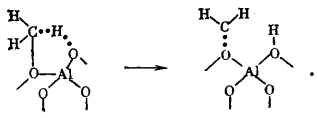
more complex problem. We shall discuss these questions below in relation to the catalytic reactions of methanol on high-silica type ZSM-5 zeolites.

Much attention has been devoted recently to the synthesis of hydrocarbons from methanol (see, for example, the relevant reviews[97,98]). The most difficult question is that of the mechanism of the formation of ethylene from methanol and of the appearance of the primary C–C bond. A wide variety of schemes involving the formation of oxonium ions, ylides, free radicals, and carbenes have been discussed in the literature,[99] the greatest preference being given to carbenes. For example, it has been suggested[32] that the methanol adsorbed on the zeolite surface loses water with formation of adsorbed carbenoid species, which then polymerise to olefins:

$$HCH_2{-}OH \rightarrow H_2O + {:}CH_2,$$
$$n{:}CH_2 \rightarrow (CH_2)_n. \qquad (20)$$

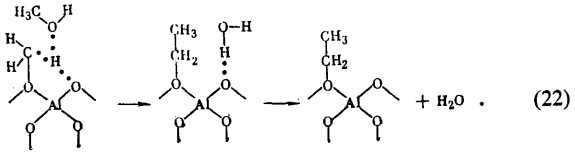
Similar mechanisms have been examined also in other investigations.[100–102]

Quantum-chemical calculations have thrown some light on this question.[69,103,104] It has been found that the properties of the surface methoxy-structures themselves are dual to some extent, combining the features of both adsorbed carbenium ions and carbenes. This is caused by the presence of a bond between one of the hydrogen atoms of the methoxy-group and the neighbouring basic oxygen atom, which undoubtedly indicates the possibility of proton transfer to the latter. This tendency increases with increase in the length of the ether bond. Although, according to calculations by the MNDO method and non-empirical calculations in terms of the STO-3G basis set there is a deficiency of approximately 1.5 eV of energy for the complete proton transfer with formation of an adsorbed carbene species and an acid hydroxy-group, i.e.



(21)

the formation of a carbene-like transition state may be significantly facilitated by the interaction with a second methanol molecule, similarly to the situation arising when the interaction with a second water or alcohol molecule favours proton transfer and the formation of ion pairs in homogeneous systems. Such transition state is then converted into a surface ethoxy-group and an adsorbed water molecule:



(22)

The ethoxy-fragment can then be alkylated by further methanol molecules via an analogous mechanism, affording the isopropoxy- or t-butoxy-structure or decomposing with desorption of ethylene.

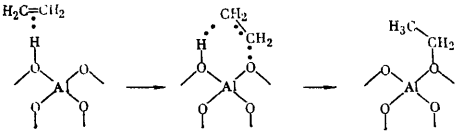
This mechanism is also synchronous, because the abstraction of a proton from the methoxy-group takes place simultaneously with formation of a new bond in the water molecule, while the dissociation of the C–O bond in the methanol molecule is compensated by the formation of a carbon–carbon bond in the alkoxy-fragment. It too has features in common with simultaneous proton transfer to two water or alcohol molecules in homogeneous systems with the sole difference that the additional energy source is in this instance not the heat of solvation of the intermediate protonated state but the energy evolved as a result of the chemical alkylation reaction.

The carbene-like properties of methoxy-groups on the surfaces of high-silica zeolites has been confirmed experimentally.[105] It was found that the interaction of the surfaces of previously methoxylated ZSM-5 zeolites with benzene, ethane, and propane, entails the incorporation of methylcarbene fragments into these molecules, which leads to the formation of toluene, propane, and butane.

(e) Catalytic Reactions of Olefins

Double bond migration, skeletal isomerisation, polymerisation, and cracking reactions are characteristic catalytic reactions of olefins in the presence of heterogeneous catalysts of the acid type. Adsorbed carbenium ions are traditionally considered as the active intermediate structures in all these reactions. In conformity with the foregoing, it is more correct, however, to speak of the formation of surface alkoxy-fragments or esters, whose carbenium ion properties are manifested only in transition states with extended or vibrationally excited C–O bonds.

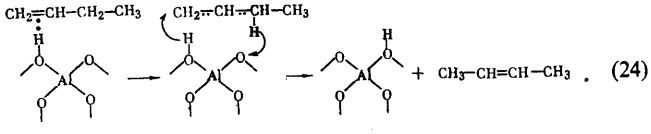
In the interaction of olefins with acid hydroxy-groups, hydrogen-bonded complexes are formed initially. This is followed by the two-point adsorption of the olefin, which, to coin a phrase, "creeps off" to a neighbouring basic centre, being converted into a surface alkoxy-group:



(23)

The reverse process leads to the desorption of olefins. The migration of the double bond in olefins and deuterium exchange involving them can also be explained by the reversibility of reaction (23).

Such multistage (but concerted as regards the elementary proton transfer step) mechanism does not, however, rule out the possibility of the migration of the double bond also via a synchronous mechanism without the formation of stable intermediate protonated states:[62]



(24)

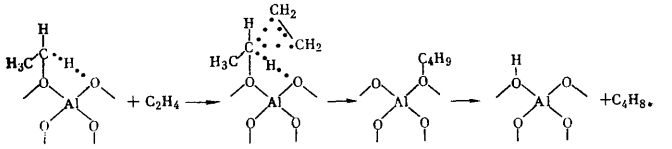
A concerted mechanism of the isomerisation of olefins is more probable for reactions involving moderately acid hydroxy-groups, while the multistage mechanism is preferable in the case of highly acid Brønsted centres.

We shall now discuss the mechanism of the oligomerisation of olefins. It is generally accepted that this reaction proceeds with the participation of adsorbed carbenium ions, which are readily formed from branched olefins but not from ethylene.[34] From our point of

view, this claim must be understood in the sense that the ease of formation of carbenium ion transition states from covalent alkoxy-structures increases with increase in the degree of their branching.

This tendency has been traced[106] with the aid of quantum-chemical calculations for methyl, ethyl, and isopropyl fragments adsorbed on the surfaces of high-silica zeolites. It was found that, although their positive charges are virtually identical, the tendency towards heterolytic dissociation diminishes on passing from the isopropyl to the ethyl substituent. The carbenium ion mechanism, which is characteristic of the oligomerisation of higher olefins, is ineffective in the case of ethylene.

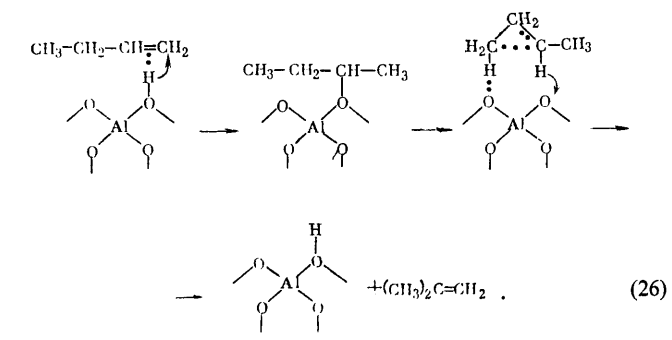
If, on the other hand, account is taken, by analogy with the previously discussed Scheme (21), of the fact that the abstraction of α-protons from the ethyl fragments imparts properties of adsorbed ethylcarbenes to the latter, presumably the oligomerisation of ethylene can also proceed via the "carbene" mechanism in certain cases:[107,108]



(25)

The transition state resembles in this instance cyclopropane or its derivatives. On the other hand, the source of the additional energy compensating for the difficulty forming the carbene-like activated complex is, as in the reactions of methanol discussed above, a chemical reaction, and in this case it is the oligomerisation reaction and not the alkylation reaction. The reverse reaction leads to the cracking of olefins.

It may be that the skeletal isomerisation of olefins proceeds also via an analogous "cyclopropane" transition state formed when γ-protons are split off from the surface alkoxy-groups:



(26)

Thus the generally accepted mechanism of the carbenium ion reactions of olefins under the conditions of heterogeneous acid catalysis can be usefully supplemented by two new elementary reactions which take into account the dual carbenium ion and ylide nature of the transition states formed from covalent alkoxy-structures:

(1) The elimination of a proton from the α-carbon atom, which leads to the possibility of alkylation and oligomerisation reactions via the ylide mechanism, which is an alternative to the carbenium ion mechanism.

(2) The elimination of a proton from the γ-carbon atom, which leads to the skeletal isomerisation and cracking of olefins.

Since the cracking and skeletal isomerisation proceed via the same cyclic cyclopropane transition state, these reactions should take place under similar conditions and on the same active centres.

The conclusions concerning the composition of the products of the corresponding catalytic reactions, made on the basis of the ideas developed above, hardly differ from those which follow from the chemistry of carbenium ions. At the same time, the schemes which we have proposed are much more realistic than those discussed in the literature, because they take into account the interaction of the active intermediate species with the surface. Furthermore, they make it possible to understand what are the driving forces and causes of the selectivity or relative ease of particular elementary stages of heterogeneous acid-catalytic reactions.

IV. CONCLUSION

The results described show that, apart from the analogies between homogeneous and heterogeneous acid catalysis frequently discussed in the literature, there are also significant differences between these types of catalytic action. The main one is the absence of solvation effects in high-temperature catalytic reactions of hydrocarbons. For this reason, many heterogeneous acid-catalytic reactions do not proceed via ionic intermediate compounds, which are energetically unfavourable under these conditions, but via a synchronous mechanism which makes it possible to avoid their formation. Thus the main disadvantage of the modern ideas about the mechanisms of heterogeneous-catalytic reactions is the formal description of these mechanisms within the framework of a single multistage ionic scheme. In fact, depending on the proton affinity of the reacting molecules and also on the presence or absence of solvation effects, a broad range of different mechanisms operate. Their range extends from homogeneous catalysis in thin liquid films condensed on the surfaces of heterogeneous catalysts to a synchronous reaction with the participation of acid-base pairs, where stable intermediate protonated states are not produced.

Another disadvantage of modern theoretical ideas in the field of heterogeneous acid catalysis is the failure to take into account the interaction of protonated intermediate structures with the catalyst surface. The contribution of this factor to the energetics of proton transfer is in fact very significant and in many cases decisive. The interaction of weakly basic organic molecules with Brønsted acid centres therefore leads to the formation in most instances of covalent surface intermediate compounds and not of quasi-free carbenium ions. On the other hand, the properties of carbenium ions are manifested in transition states where the carbon–basic oxygen bond on the catalyst surface is partly dissociated (extended or vibrationally excited).

Finally yet another feature of heterogeneous acid catalysis is the bifunctional nature of its active centres, the acid part of which is a proton donor while the basic part either stabilises the intermediate protonated compounds or promotes the elimination of a proton from the transition states in the synchronous reaction mechanisms. Deprotonation can impart also the features of adsorbed carbenes or ylides to the activated complexes. Allowance for this factor permits a more natural explanation of the mechanisms of the reactions involving the alkylation, cracking, and skeletal isomerisation of olefins. Incidentally, all that has been said applies equally and in general to electrophilic reactions in organic chemistry, while allowance for the interaction of intermediate protonated structures with

counterions is also an essential condition for the correct interpretation of the reaction mechanisms. However, the discussion of these questions is outside the framework of the present review.

The ideas developed above should not be regarded as a criticism of the concept of carbenium and carbonium ions in heterogeneous acid catalysis. The aim is rather to deepen and update this concept. Naturally, many of the mechanisms discussed are so far debatable and their confirmation requires further quantum-chemical calculations for detailed kinetic and spectroscopic studies.

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