

SOME PHYSICAL AND CHEMICAL PROPERTIES OF ALCOHOLS

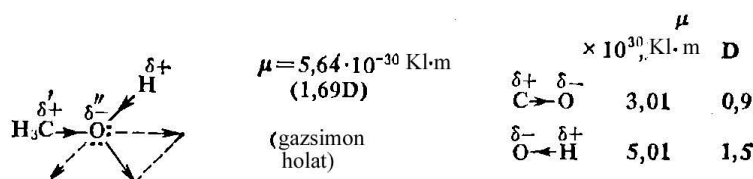
Inaqov To'lqin Qazaqovich

Professor of Medical Chemistry, Andijan State Medical Institute

Abstract: The article provides an overview of alcohols, their definition, and the issues that should be addressed.

Keywords: alkanol, dipole moment, ionization energy, association, spectrum, electrophile, alcohols.

Alkanols are polar compounds. They hold a bipolar bond in the molecule: and. The dipoles of the C - O and O - H bonds are oriented towards the oxygen atom. The sum of the dipole moments of alkanols is $5.3 - 6.0 \cdot 10^{-30} \text{ Kl} \cdot \text{m}$ ga teng ($1.6 - 1.8 \text{ D}$). The sum of dipole moments is also affected by the undistributed electron pair in the oxygen atom:



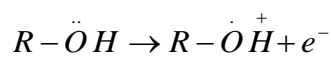
The dipole moments of the bonds indicate that the polarity of the bond O - H is higher than the polarity of the bond C - O.

Undistributed electron pairs cause alkanols to exhibit weak electron donor properties. This can be expressed by the ionization energy:

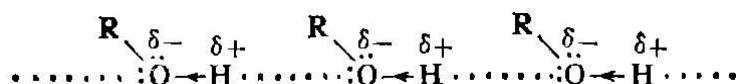
Compound	H ₂ O	CH ₃ OH	C ₂ H ₅ OH
IE, eV	12,6	10,8	10,6

The IE of alcohols is lower than that of water, the electron-donor effect of the alkyl group (+ I effect) is manifested here.

Ionization energy characterizes this process:

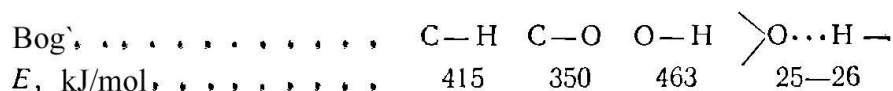


The polar O - H bond and the undistributed electron pairs determine the formation of molecular associations:



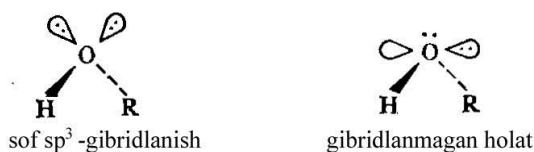
The association is mainly due to the electrostatic attraction and the overlap of the hydrogen orbitals with the orbital of the unpaired electron pair of a small amount of oxygen. This interaction is called hydrogen bonding (V. Latimer, V. Rodebush, 1920).

The energy of a hydrogen bond is less than the energy of a simple chemical bond:



Radiography and electronographic analyzes showed that in alkanols C - C and C - H bonds are normal in length and angles between bonds.

Carbon atoms are sp³-hybridized, but it is difficult to agree on the nature of the oxygen atom hybridization, that is, its undistributed electron pair. There are two possibilities: pure sp³-hybridization (both electron pairs are in the same orbitals; HOR angle is 109°28') and non-hybrid state (one electron pair is in the p-orbital and the other in the s-orbital; HOR angle is 90°):



There is no evidence that this is the case. There is only indirect information, such as valence angles, the location of the molecule in the crystal. There is every reason to believe that the nature of the undistributed electron pair of an oxygen atom depends on the nature of R, the state of the aggregate, and the intermolecular interactions (formation of hydrogen bonds).

Absorption spectra. Alkanols are "transparent" in the electronic spectra of absorption. Weak absorption is observed in the long UV region (170 - 180 nm), which is due to the passage of the undistributed pair of oxygen atoms $n \rightarrow s^*$.

In the IR spectrum, the valence oscillations characteristic of the O - H bond are observed in dilute solutions of hydrocarbons or halogenated hydrocarbons in the area of 3580 - 3650 cm⁻¹. In concentrated solutions, hydrogen bonds are formed O - H... O, so the valence oscillations of the O - H bond move in the area of 3200 - 3500 cm⁻¹.

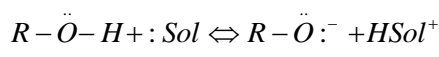
In the PMR spectra, OH group signals are observed over a wide range depending on the type of solvent and the concentration of the substance: $\delta_{\text{H}} \dots 4.5$ m.d. Signals are lost as a result of deuterium $\text{OH} \rightarrow \text{OD}$ in the presence of D_2O . Signals of H - C - O protons are observed at $\delta_{\text{H}} 3.5 - 3.8$ m.d.

Chemical properties. The chemical properties of alkanols are determined by their O - H and O - R bonds and undistributed electron pairs.

1. Reactions with the storage of an oxygen atom in an alkanol molecule.

These reactions are mainly due to the strong polarization of the O - H bond, which leads to ionization. The oxygen atom is also preserved in oxidation reactions as well as in reactions with certain electrophilic reagents.

a) Formation of alcohols and their reactions. Alkanols are weak OH acids:



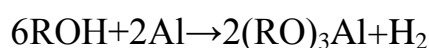
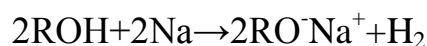
Alkanol anion is called alcohol-ion (alkoxide - or alkanolate - ion), which is a strong base. The acidity of alkanols is low:

Alkanol	CH_3OH	$\text{CH}_3\text{CH}_2\text{OH}$	$(\text{CH}_3)_2\text{CHOH}$	$(\text{CH}_3)_3\text{COH}$
pK_{a} (for aqueous solutions)	15,2	15,8	16,9	19,2

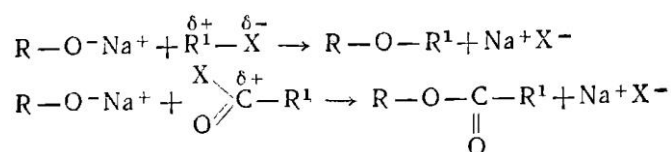
Methanol is a relatively strong acid. Its acidity is almost equal to the acidity of water ($\text{pK}_{\text{a}} = 15.7$ for water in aqueous solution). Tertiary alcohols are the weakest acids. Here there is a donor effect (+ I - effect), which increases the electron density in the oxygen atom of alkyl groups. Anions of tertiary alcohols are the strongest bases.

In aqueous solutions, the acidic properties of alcohols are weak. Only partial ionization of alcohols is observed in concentrated solutions of alkalis with $\text{pH} > 14$ (for example, in a 15% aqueous solution of KOH is $\text{pH} 15$). When MOH is dissolved in alcohols, small amounts of alcohol may be formed.

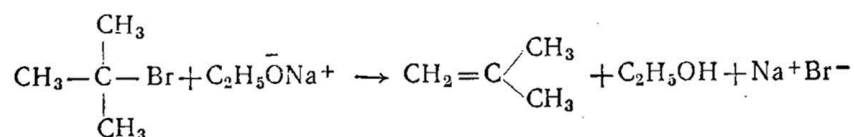
Typically, the reaction of active metals with an anhydrous solution of alcohols is used to obtain alcohols:



Alcohols are not only strong bases, but also strong nucleophilic reagents. They are easily alkylated to form simple and complex esters (Williamson reaction) and acylated:

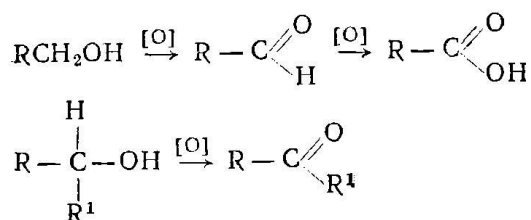


Alcohols are used as strong bases for the accumulation of carbonyls and other anions in condensation reactions, as well as for the separation of double and triple bonds of hydrogen halides, for example:

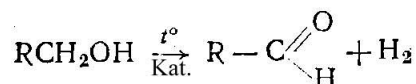


Here, the S_N reaction is inhibited by spatial factors, so the alcohol is not a nucleophile, but acts as a proton-separating base from the methyl group.

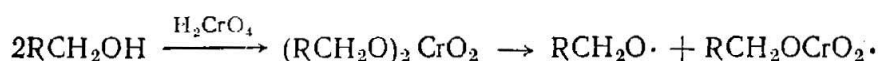
b) Oxidation. Primary and secondary alcohols are oxidized. Oxidation produces aldehydes or ketones, carbonic acids:



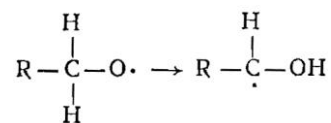
Oxidation is oxidized with oxygen in the presence of catalysts (Cu, CuO) or with various inorganic oxidizers (KMnO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$, CrO_3 , etc.). Oxygen-free catalytic dehydrogenation of alcohols in the presence of Cu, Pt or Pd is also carried out:



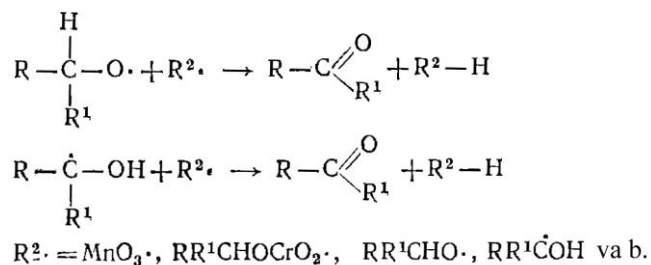
Oxidation is a homolytic process in which free radicals are formed. It is assumed that the oxidation of permanganate or chromate in acidic conditions as a by-product forms esters of suitable acids, which decompose homolytically and cause a chain process of oxidation:



The intermediate product is alkoxy radical $\text{RCH}_2\text{O}\cdot$, which is easily regrouped to the hydroxyalkyl radical:



Free radicals react with other free radicals to form carbonyl compounds:



Tertiary alcohols are oxidized only in acidic environments. Tertiary alcohol forms easily oxidizing alkenes.

Alkanols are colorless liquids or crystalline substances with a characteristic odor. The first members of the homologous series of alkanols have a pleasant odor, butanol and pentanol have a sharp and unpleasant odor. High alkanols have a pleasant odor.

Alcohols have a specific high boiling point. Although the molecular weight of alkanols is low, the boiling point is higher than that of corresponding alkanes. This is due to the intermolecular interaction - the association of molecules.

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