7.6 The Acidity of Alcohols and Phenols

Like water, alcohols and phenols are weak acids. The hydroxyl group can act as a proton donor, and dissociation occurs in a manner similar to that for water:

$$\overrightarrow{RO} - H \rightleftharpoons \overrightarrow{RO} = H^+$$
 (7.11)
alcohol alkoxide
ion

The conjugate base of an alcohol is an **alkoxide ion** (for example, *meth*oxide ion from *meth*anol, *eth*oxide ion from *eth*anol, and so on).

Table 7.2 lists pK_a values for selected alcohols and phenols.* Methanol and ethanol have nearly the same acid strength as water; bulky alcohols such as *t*-butyl alcohol are somewhat weaker because their bulk makes it difficult to solvate the corresponding alkoxide ion (see Figure 6.3).

Name	Formula	р <i>К_а</i>
water	НО—Н	15.7
nethanol	CH₃O—H	15.5
ethanol	CH ₃ CH ₂ O—H	15.9
-butyl alcohol	(CH ₃) ₃ CO—H	18
2,2,2-trifluoroethanol	CF_3CH_2O-H	12.4
phenol	—О—Н	10.0
<i>p</i> -nitrophenol	0 ₂ N-0-H	7.2
picric acid	0 ₂ N-0-H	0.25

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Phenol is a much stronger acid than ethanol. How can we explain this acidity difference between alcohols and phenols, since in both types of compounds, the proton donor is a hydroxyl group?

Phenols are stronger acids than alcohols mainly because the corresponding phenoxide ions are stabilized by resonance. The negative charge of an alkoxide ion is concentrated on the oxygen atom, but the negative charge on a phenoxide ion can be delocalized to the *ortho* and *para* ring positions through resonance.



We see in Table 7.2 that 2,2,2-trifluoroethanol is a much stronger acid than ethanol. How can we explain this effect of fluorine substitution? Again, think about the stabilities of the respective anions. Fluorine is a strongly electronegative element, so each C-Fbond is polarized, with the fluorine partially negative and the carbon partially positive.



The positive charge on the carbon is located near the negative charge on the nearby oxygen atom, where it can partially neutralize and hence stabilize it. This **inductive** effect, as it is called, is absent in ethoxide ion.

The acidity-increasing effect of fluorine seen here is not a special case, but a general phenomenon. All electron-withdrawing groups increase acidity by stabilizing the conjugate base. Electron-donating groups decrease acidity because they destabilize the conjugate base.



First, the nitrogen atom has a formal positive charge and is therefore strongly electron withdrawing. It therefore increases the acidity of *p*-nitrophenol through the inductive effect. Second, the negative charge on the oxygen of the phenoxide can be delocalized through resonance, not only to the *ortho* and *para* ring carbons, as in phenoxide itself, but to the oxygen atoms of the nitro group as well (structure IV). Both the inductive and the resonance effects of the nitro group are acid-strengthening.

Additional nitro groups on the benzene ring further increase phenolic acidity. Picric acid (2,4,6-trinitrophenol) is an even stronger acid than *p*-nitrophenol. **PROBLEM 7.10** Draw the resonance contributors for the 2,4,6-trinitrophenoxide (picrate) ion, and show that the negative charge can be delocalized to every oxygen atom.



PROBLEM 7.11 Rank the following five compounds in order of increasing acid strength: 2-chloroethanol, *p*-chlorophenol, *p*-methylphenol, ethanol, phenol.

Both alcohols are weaker acids than the three phenols. Of the alcohols, 2-chloroethanol is the stronger acid because of the electronegativity of the chlorine substituent. Among the three phenols, acidity increases with increasing electronegativity of the *para* substituent: $CH_3 < H < CI$.



Alkoxides, the conjugate bases of alcohols, are strong bases just like hydroxide ion. They are ionic compounds and are frequently used as strong bases in organic chemistry. They can be prepared by the reaction of an alcohol with sodium or potassium metal or with a metal hydride. These reactions proceed irreversibly to give the metal alkoxides that can frequently be isolated as white solids.



Ordinarily, treatment of alcohols with sodium hydroxide does not convert them to their alkoxides. This is because alkoxides are stronger bases than hydroxide ion, so the reaction goes in the reverse direction. Phenols, however, can be converted to phenoxide ions in this way.

$$ROH + Na^{+}HO^{-} \neq RO^{-}Na^{+} + H_{2}O$$
 (7.14)

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7.7 The Basicity of Alcohols and Phenols

Alcohols (and phenols) function not only as weak acids but also as weak bases. They have unshared electron pairs on the oxygen and are therefore Lewis bases. They can be protonated by strong acids. The product, analogous to the oxonium ion, H_3O^+ , is an alkyloxonium ion.

$$R - \ddot{O} - H + H^{+} \rightleftharpoons R - \overset{H}{O} - H \qquad (7.16)$$
alcohol acting alkyloxonium ion
as a base

This protonation is the first step in two important reactions of alcohols that are discussed in the following two sections: their dehydration to alkenes and their conversion to alkyl halides.

7.8 Dehydration of Alcohols to Alkenes

Alcohols can be dehydrated by heating them with a strong acid. For example, when ethanol is heated at 180°C with a small amount of concentrated sulfuric acid, a good yield of ethylene is obtained.

$$\begin{array}{c} H - CH_2CH_2 - OH \xrightarrow{H^+, 180^{\circ}C} CH_2 = CH_2 + H - OH \\ ethanol ethylene \end{array}$$
(7.17)

This type of reaction, which can be used to prepare alkenes, is the reverse of hydration (Sec. 3.7.b). It is an *elimination reaction* and can occur by either an E1 or an E2 mechanism, depending on the class of the alcohol.

Tertiary alcohols dehydrate by the E1 mechanism. *t*-Butyl alcohol is a typical example. The first step involves rapid and reversible protonation of the hydroxyl group.

H mean the alkene

Ionization (the rate-determining step), with water as the leaving group, occurs readily because the resulting carbocation is tertiary.

$$(CH_3)_3C \xrightarrow[]{O}{O} H \implies (CH_3)_3C^+ + H_2O$$

$$(7.19)$$

$$H$$

Proton loss from a carbon atom adjacent to the positive carbon completes the reaction.

$$\begin{array}{c} H & CH_3 \\ CH_2 - C^+ & \longrightarrow \\ CH_3 \end{array} \xrightarrow{CH_2} CH_2 = C \xrightarrow{CH_3} + H^+ \\ CH_3 \end{array}$$
(7.20)

The overall dehydration reaction is the sum of all three steps.



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With a primary alcohol, a primary carbocation intermediate is avoided by combining the last two steps of the mechanism. The loss of water and an adjacent proton occur simultaneously in an E2 mechanism.

$$CH_{3}CH_{2}\overset{.}{O}H + H^{+} \rightleftharpoons CH_{3}CH_{2} - \overset{+}{O}H_{H}$$
 (7.22)

$$\begin{array}{c} H \\ H \\ CH_2 - CH_2 - CH_2 - CH_2 - H \\ H \\ H \end{array} \rightarrow CH_2 = CH_2 + H^+ + H_2O$$
 (7.23)

The important things to remember about alcohol dehydrations are that (1) they all begin by protonation of the hydroxyl group (that is, the alcohol acts as a base) and (2) the ease of alcohol dehydration is $3^{\circ} > 2^{\circ} > 1^{\circ}$ (the same as the order of carbocation stability).

Sometimes a single alcohol gives two or more alkenes because the proton lost during dehydration can come from any carbon atom that is directly attached to the hydroxyl-bearing carbon. For example, 2-methyl-2-butanol can give two alkenes.



In these cases, *the alkene with the most substituted double bond usually predominates*. By "most substituted", we mean the alkene with the greatest number of alkyl groups on the doubly bonded carbons. Thus, in the example shown, the major product is 2-methyl-2-butene.

PROBLEM 7.14 Write the structure for all possible dehydration products of



Write the structure of the alcohol, and consider products with a double bond between the hydroxyl-bearing carbon and each adjacent carbon that also have at least one hydrogen attached.



The predominant product is generally the alkene with the most substituted double bond. In part a, the products with trisubstituted double bonds should predominate over the disubstituted product. To predict more precisely is not possible. In part b, the product with the double bond in the ring (1-methylcyclohexene) is trisubstituted and will predominate.

7.9 The Reaction of Alcohols with Hydrogen Halides

Alcohols react with hydrogen halides (HCl, HBr, and HI) to give alkyl halides (chlorides, bromides, and iodides).

$$R - OH + H - X \longrightarrow R - X + H - OH$$
alcohol
(7.25)
alkyl halide

This substitution reaction provides a useful general route to alkyl halides. Because halide ions are good nucleophiles, we obtain mainly substitution products instead of dehydration. Once again, the reaction rate and mechanism depend on the class of alcohol (tertiary, secondary, or primary).

Tertiary alcohols react the fastest. For example, we can convert *t*-butyl alcohol to *t*-butyl chloride simply by shaking it for a few minutes at room temperature (rt) with concentrated hydrochloric acid.

 $(CH_3)_3COH + H - Cl \xrightarrow{rt} (CH_3)_3C - Cl + H - OH$ (7.26) *t*-butyl alcohol *t*-butyl chloride The reaction occurs by an S_N1 mechanism and involves a carbocation intermediate. The first two steps in the mechanism are identical to those shown in eqs. 7.18 and 7.19. The final step involves capture of the *t*-butyl carbocation by chloride ion.

$$(CH_3)_3C^+ + Cl^- \xrightarrow{\text{fast}} (CH_3)_3CCl$$
 (7.27)

On the other hand, 1-butanol, a primary alcohol, reacts slowly and must be heated for several hours with a mixture of concentrated hydrochloric acid and a Lewis acid catalyst such as zinc chloride to accomplish the same type of reaction.

$$CH_{3}CH_{2}CH_{2}CH_{2}OH + H - Cl \xrightarrow{heat, ZnCl_{2}} CH_{3}CH_{2}CH_{2}CH_{2} - Cl + H - OH$$
(7.28)
1-butanol 1-chlorobutane

The reaction occurs by an S_N^2 mechanism. In the first step, the alcohol is protonated by the acid.

$$CH_{3}CH_{2}CH_{2}CH_{2}-\overset{.}{O}H + H^{+} \Longrightarrow CH_{3}CH_{2}CH_{2}CH_{2}-\overset{.}{O}H$$
 (7.29



$$CH_{3}CH_{2}CH_{2}$$

$$CI^{-} \xrightarrow{H} C \xrightarrow{H} O - H \longrightarrow CH_{3}CH_{2}CH_{2}CH_{2}CI + H_{2}O$$
(7.30)

Secondary alcohols react at intermediate rates by both S_N1 and S_N2 mechanisms.





7.10 Other Ways to Prepare Alkyl Halides from Alcohols

Since alkyl halides are extremely useful in synthesis, it is not surprising that chemists have devised several ways to prepare them from alcohols. For example, **thionyl chloride** (eq. 7.31) reacts with alcohols to give alkyl chlorides. The alcohol is first converted to a chlorosulfite ester intermediate, a step that converts the hydroxyl group into a good leaving group. This is followed by a nucleophilic substitution whose mechanism (S_N1 or S_N2) depends on whether the alcohol is primary, secondary, or tertiary.

$$R - OH + Cl - S - Cl \xrightarrow{heat} \begin{bmatrix} Cl - H^+ \\ R - O - S - Cl \end{bmatrix} \longrightarrow R - Cl + S^{\dagger} + HCl^{\dagger}$$
(7.31)
thionyl chloride intermediate

One advantage of this method is that two of the reaction products, hydrogen chloride and sulfur dioxide, are gases and evolve from the reaction mixture (indicated by the upward pointing arrows), leaving behind only the desired alkyl chloride. The method is not effective, however, for preparing low-boiling alkyl chlorides (in which R has only a few carbon atoms), because they easily boil out of the reaction mixture with the gaseous products. Phosphorus halides (eq. 7.32) also convert alcohols to alkyl halides.

 $3 \text{ ROH} + PX_3 \longrightarrow 3 \text{ RX} + H_3 PO_3 (X = Cl \text{ or } Br)$ (7.32) phosphorus halide

In this case, the other reaction product, phosphorous acid, has a rather high boiling point. Thus, the alkyl halide is usually the lowest boiling component of the reaction mixture and can be isolated by distillation.

Both of these methods are used mainly with primary and secondary alcohols, whose reaction with hydrogen halides is slow.

PROBLEM 7.17 Write balanced equations for the preparation of the following alkyl halides from the corresponding alcohol and either SOCl₂, PCl₃ or PBr₃.

a.

CH₂Br

b.



Complete the following reaction!



.

.

7.11 A Comparison of Alcohols and Phenols

Because they have the same functional group, alcohols and phenols have many similar properties. But whereas it is relatively easy, with acid catalysis, to break the C—OH bond of alcohols, this bond is difficult to break in phenols. Protonation of the phenolic hydroxyl group can occur, but loss of a water molecule would give a phenyl cation.



With only two attached groups, the positive carbon in a phenyl cation should be *sp*hybridized and linear. But this geometry is prevented by the structure of the benzene ring, so *phenyl cations are energetically unstable and are exceedingly difficult to form*. Consequently, phenols cannot undergo replacement of the hydroxyl group by an S_N1 mechanism. Neither can phenols undergo displacement by the S_N2 mechanism. (The geometry of the ring makes the usual inversion mechanism impossible.) Therefore, hydrogen halides, phosphorus halides, or thionyl halides cannot readily cause replacement of the hydroxyl group by halogens in phenols. **PROBLEM 7.18** Compare the reactions of cyclopentanol and phenol with a. HBr. b. H₂SO₄, heat.



- 7.12 Oxidation of Alcohols
 - Oxidation of Primary Alcohols to Aldehydes
 - A primary alcohol can be oxidized to an aldehyde or a carboxylic acid
 - The oxidation is difficult to stop at the aldehyde stage and usually proceeds to the carboxylic acid



A reagent which stops the oxidation at the aldehyde stage is pyridinium chlorochromate (PCC)

- PCC is made from chromium trioxide under acidic conditions
- It is used in organic solvents such as methylene chloride (CH₂Cl₂)



Oxidation of Primary Alcohols to Carboxylic Acids

- Potassium permanganate (KMnO₄) is a typical reagent used for oxidation of a primary alcohol to a carboxylic acid
 - The reaction is generally carried out in aqueous solution; a brown precipitate of MnO_2 indicates that oxidation has taken place

$$R - CH_{2}OH + KMnO_{4} \xrightarrow[heat]{OH^{-}} RCO_{2}^{-}K^{+} + MnO_{2}$$

$$\downarrow H_{3}O^{+}$$

$$RCO_{2}H$$

Oxidation of Secondary Alcohols to Ketones

- Oxidation of a secondary alcohol stops at the ketone
 - Many oxidizing agents can be used, including chromic acid (H₂CrO₄) and Jones reagent (CrO₃ in acetone)



7. CrO_3 in H_2SO_4/H_2O will <u>fail</u> to give a positive test with which of these compounds?



20. What is the predominant product from the reaction of 2-hexanol with H₂CrO₄?
A) CH₃CO₂H
B) CH₃(CH₂)₃CO₂H
C) 0
CH₃ (CH₂) 3CCH₃
D) CH₃(CH₂)₄CO₂H
E) A) and B)

45. Which reaction is an oxidation?

- A) RCHO \longrightarrow RCO₂H
- B) $RCH_2OH \longrightarrow RCHO$
- C) $RCH_2OH \longrightarrow RCO_2H$
- D) Two of these
- E) All of these

7.14 Aromatic Substitution in Phenols – Bromination

• The hydroxyl group is a powerful ortho, meta director and usually the tribromide is obtained



Nitration

- Nitration produces *o* and *p*-nitrophenol
 - Low yields occur because of competing oxidation of the ring





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