Because of their polarities, aldehydes and ketones have higher boiling points than alkenes or alkanes with similar molecular masses and shapes. But because aldehydes and ketones are not hydrogen-bond donors, their boiling points are considerably lower than those of the corresponding alcohols.

Aldehydes and ketones with four or fewer carbons have considerable solubilities in water because they can accept hydrogen bonds from water at the carbonyl oxygen.

Acetaldehyde and acetone are miscible with water (that is, soluble in all proportions). The water solubility of aldehydes and ketones along a series diminishes rapidly with increasing molecular mass.

Acetone and 2-butanone are especially valued as solvents because they dissolve not only water but also a wide variety of organic compounds. These solvents have sufficiently low boiling points that they can be easily separated from other less volatile compounds. Acetone, with a dielectric constant of 21, is a polar aprotic solvent and is often used as a solvent or co-solvent for nucleophilic substitution reactions.

### 19.3 SPECTROSCOPY OF ALDEHYDES AND KETONES

#### A. IR Spectroscopy

The principal infrared absorption of aldehydes and ketones is the C=O stretching absorption, a strong absorption that occurs in the vicinity of 1700 cm⁻¹. In fact, this is one of the most important of all infrared absorptions. Because the C=O bond is stronger than the C=C bond, the stretching frequency of the C=O bond is greater.
The position of the C==O stretching absorption varies predictably for different types of carbonyl compounds. It generally occurs at 1710–1715 cm\(^{-1}\) for simple ketones and at 1720–1725 cm\(^{-1}\) for simple aldehydes. The carbonyl absorption is clearly evident, for example, in the IR spectrum of butyraldehyde (Fig. 19.3). The stretching absorption of the carbonyl–hydrogen bond of aldehydes near 2710 cm\(^{-1}\) is another characteristic absorption; however, NMR spectroscopy provides a more reliable way to diagnose the presence of this type of hydrogen (Sec. 19.3B).

Compounds in which the carbonyl group is conjugated with aromatic rings, double bonds, or triple bonds have lower carbonyl stretching frequencies than unconjugated carbonyl compounds.

\[
\begin{align*}
\text{acetophenone} & \quad \text{3-buten-2-one} & \quad \text{1-butene} & \quad \text{2-butane}
\end{align*}
\]

\[
\begin{array}{cccc}
\text{C==O} & 1685 \text{ cm}^{-1} & 1670 \text{ cm}^{-1} & \text{—} \\
\text{C==C} & 1600 \text{ cm}^{-1} & 1613 \text{ cm}^{-1} & 1642 \text{ cm}^{-1} & \text{—} \\
\end{array}
\]

(19.2)

The carbon–carbon double-bond stretching frequencies are also lower in the conjugated molecules. These effects can be explained by the resonance structures for these compounds. Because the C==O and C==C bonds have some single-bond character, as indicated by the following resonance structures, they are somewhat weaker than ordinary double bonds, and therefore absorb in the IR at lower frequency.
19.3 SPECTROSCOPY OF ALDEHYDES AND KETONES

In cyclic ketones with rings containing fewer than six carbons, the carbonyl absorption frequency increases significantly as the ring size decreases. (See Further Exploration 19.1.)

**B. Proton NMR Spectroscopy**

The characteristic NMR absorption common to both aldehydes and ketones is that of the protons on the carbons adjacent to the carbonyl group: the \( \alpha \)-protons. This absorption is in the \( \delta 2.0–2.5 \) region of the spectrum (see also Fig. 13.4 on p. 580). This absorption is slightly farther downfield than the absorptions of allylic protons because the \( \text{C}==\text{O} \) group is more electronegative than the \( \text{C}==\text{C} \) group. In addition, the absorption of the aldehydic proton is quite distinctive, occurring in the \( \delta 9–10 \) region of the NMR spectrum, at lower field than most other NMR absorptions.

In general, aldehydic protons have very large chemical shifts. The explanation is the same as that for the large chemical shifts of protons on a carbon–carbon double bond (Sec. 13.7A). However, the carbonyl group has a greater effect on chemical shift than a carbon–carbon double bond because of the electronegativity of the carbonyl oxygen.
C. Carbon NMR Spectroscopy

The most characteristic absorption of aldehydes and ketones in $^{13}$C NMR spectroscopy is that of the carbonyl carbon, which occurs typically in the $\delta$ 190–220 range (see Fig. 13.20, p. 624). This large downfield shift is due to the induced electron circulation in the $\pi$ bond, as in alkenes (Fig. 13.14, p. 613), and to the additional chemical-shift effect of the electronegative carbonyl oxygen. Because the carbonyl carbon of a ketone bears no hydrogens, its $^{13}$C NMR absorption, like that of other quaternary carbons, is characteristically rather weak (Sec. 13.9). This effect is evident in the $^{13}$C NMR spectrum of propiophenone (Fig. 19.5).

The $\alpha$-carbon absorptions of aldehydes and ketones show modest downfield shifts, typically in the $\delta$ 30–50 range, with, as usual, greater shifts for more branched carbons. The $\alpha$-carbon shift of propiophenone, 31.7 ppm (Fig. 19.5, carbon $b$) is typical. Because shifts in this range are also observed for other functional groups, these absorptions are less useful than the carbonyl carbon resonances for identifying aldehydes and ketones.

---

PROBLEM

19.4 Deduce the structures of the following compounds.

(a) $C_4H_8O$: IR 1720, 2710 cm$^{-1}$
   NMR in Fig. 19.4

(b) $C_4H_8O$: IR 1717 cm$^{-1}$
   NMR $\delta$ 0.95 (3H, t, $J = 8$ Hz); $\delta$ 2.03 (3H, s); $\delta$ 2.38 (2H, q, $J = 8$ Hz)

(c) A compound with molecular mass = 70.1, IR absorption at 1780 cm$^{-1}$, and the following NMR spectrum: $\delta$ 2.01 (quintuplet, $J = 7$ Hz); $\delta$ 3.09 (t, $J = 7$ Hz). The integral of the $\delta$ 3.09 resonance is twice as large as that of the $\delta$ 2.01 resonance.

(d) $C_{10}H_{12}O_2$: IR 1690 cm$^{-1}$, 1612 cm$^{-1}$
   NMR $\delta$ 1.4 (3H, t, $J = 8$ Hz); $\delta$ 2.5 (3H, s); $\delta$ 4.1 (2H, q, $J = 8$ Hz); $\delta$ 6.9 (2H, d, $J = 9$ Hz); $\delta$ 7.9 (2H, d, $J = 9$ Hz)

---

Figure 19.4 The NMR spectrum for Problem 19.4(a). The relative integrals are indicated in red over their respective resonances.
D. UV Spectroscopy

The $\pi \rightarrow \pi^*$ absorptions (Sec. 15.2B) of unconjugated aldehydes and ketones occur at about 150 nm, a wavelength well below the operating range of common UV spectrometers. Simple aldehydes and ketones also have another, much weaker, absorption at higher wavelength, in the 260–290 nm region. This absorption is caused by excitation of the unshared electrons on oxygen (sometimes called the $n$ electrons). This high-wavelength absorption is usually referred to as an $n \rightarrow \pi^*$ absorption.

$$n \rightarrow \pi^* \quad 271 \text{ nm} \, (e = 16) \quad \text{(in ethanol)}$$

This absorption is easily distinguished from a $\pi \rightarrow \pi^*$ absorption because it is only $10^{-2}$ to $10^{-3}$ times as strong. However, it is strong enough that aldehydes and ketones cannot be used as solvents for UV spectroscopy.
Like conjugated dienes, the \( \pi \) electrons of compounds in which carbonyl groups are conjugated with double or triple bonds have strong absorption in the UV spectrum. The spectrum of 1-acetylcyclohexene (Fig. 19.6) is typical. The 232-nm peak is due to light absorption by the conjugated \( \pi \)-electron system and is thus a \( \pi \rightarrow \pi^* \) absorption. It has a very large extinction coefficient, much like that of a conjugated diene. The weak 308-nm absorption is an \( n \rightarrow \pi^* \) absorption.

![Figure 19.6](image)

The ultraviolet spectrum of 1-acetylcyclohexene [1-(cyclohexen-1-yl)ethanone] in methanol. The spectrum of a more concentrated solution (red) reveals the "forbidden" \( n \rightarrow \pi^* \) absorption, which is so weak that it is not apparent in the spectrum taken on a more dilute solution (black).

The \( \lambda_{\text{max}} \) of a conjugated aldehyde or ketone is governed by the same variables that affect the \( \lambda_{\text{max}} \) values of conjugated dienes: the number of conjugated double bonds, substitution on the double bond, and so on. When an aromatic ring is conjugated with a carbonyl group, the typical aromatic absorptions are more intense and shifted to higher wavelengths than those of benzene.
The $\pi \rightarrow \pi^*$ absorptions of conjugated carbonyl compounds, like those of conjugated alkenes, arise from the promotion of a $\pi$ electron from a bonding to an antibonding ($\pi^*$) molecular orbital (Sec. 15.2B). An $n \rightarrow \pi^*$ absorption arises from promotion of one of the $n$ (unshared) electrons on a carbonyl oxygen to a $\pi^*$ molecular orbital. As stated previously in this section, $n \rightarrow \pi^*$ absorptions are weak. Spectroscopists say that these absorptions are forbidden. This term refers to certain physical reasons for the very low intensity of these absorptions. The 254-nm absorption of benzene, which has a very low extinction coefficient of 212, is another example of a “forbidden” absorption.

**PROBLEMS**

19.7 Explain how the compounds within each set can be distinguished using only UV spectroscopy.

(a) 2-cyclohexenone and 3-cyclohexenone

(b) ![Chemical structure of 2-cyclohexenone and 3-cyclohexenone](image)

(c) 1-phenyl-2-propanone and $p$-methylacetophenone

19.8 In neutral alcohol solution, the UV spectra of $p$-hydroxyacetophenone and $p$-methoxyacetophenone are virtually identical. When NaOH is added to the solution, the $\lambda_{\text{max}}$ of $p$-hydroxyacetophenone increases by about 50 nm, but that of $p$-methoxyacetophenone is unaffected. Explain these observations.

19.9 Which one of the following compounds should have a $\pi \rightarrow \pi^*$ UV absorption at the greater $\lambda_{\text{max}}$ when the compound is dissolved in NaOH solution? Explain.

(a) ![Chemical structure of vanillin and isovanillin](image)

E. **Mass Spectrometry**

Important fragmentations of aldehydes and ketones are illustrated by the electron-impact (EI) mass spectrum of 5-methyl-2-hexanone (Fig. 19.7, p. 902). The three most important peaks occur at $m/z = 71$, 58, and 43. The peaks at $m/z = 71$ and $m/z = 43$ arise from cleavage of the molecular ion at the bond between the carbonyl group and an adjacent carbon atom by two mechanisms that were discussed in Sec. 12.6C: inductive cleavage and $\alpha$-cleavage. Inductive cleavage accounts for the $m/z = 71$ peak. In this cleavage, the alkyl fragment carries the charge and the carbonyl fragment carries the unpaired electron.

\[
\begin{align*}
\text{molecular ion from loss of unshared electron} & \quad \text{inductive cleavage} \\
(CH_3)_2CHCH_2CH_2(C=CH_3) & \quad (CH_3)_2CHCH_2CH_2(C=CH_3) \quad \text{inductive cleavage} \\
& \quad \text{m/z} = 71
\end{align*}
\]
\( \alpha \)-Cleavage accounts for the \( m/z = 43 \) peak. In this case the same molecular ion undergoes fragmentation in such a way that the carbonyl fragment carries the charge and the alkyl fragment carries the unpaired electron:

\[
\text{(CH}_3)_2\text{CHCH}_2\text{CH}_2 \quad \overset{\text{\( \alpha \)-cleavage}}{\longrightarrow} \quad \text{(CH}_3)_2\text{CHCH}_2\text{H}_2 + \overset{\text{:O}}{\text{:O}}\text{C} = \text{CCH}_3
\]

(19.6)

An analogous cleavage at the carbon–hydrogen bond accounts for the fact that many aldehydes show a strong \( M - 1 \) peak.

What accounts for the \( m/z = 58 \) peak? A common mechanism for the formation of odd-electron ions is hydrogen transfer followed by loss of a stable neutral molecule (p. 564). In this case, the oxygen radical in the molecular ion abstracts a hydrogen atom from a carbon five atoms away, and the resulting radical then undergoes \( \alpha \)-cleavage.

\[
\text{H}_3\text{C} = \overset{\text{\( \alpha \)-cleavage}}{\overset{+\text{H}}{\overset{\text{hydrogen transfer}}{\text{C(CH}_3)_2}}} \quad \longrightarrow \quad \text{H}_3\text{C} = \overset{\text{\( \alpha \)-cleavage}}{\overset{+\text{H}}{\overset{\text{McLafferty rearrangement}}{\text{C(CH}_3)_2}}} \quad \longrightarrow \quad \text{H}_3\text{C} = \overset{+\text{H}}{\overset{\text{m/z = 58}}{\text{C(CH}_3)_2}}
\]

(19.7)

If we count the hydrogen that is transferred, the first step occurs through a transient six-membered ring. This process is called a McLafferty rearrangement, after Professor Fred McLafferty of Cornell University, who investigated this type of fragmentation extensively. The McLafferty rearrangement and subsequent \( \alpha \)-cleavage constitute a common mechanism for the production of odd-electron fragment ions in the mass spectrometry of carbonyl compounds.

As illustrated by Fig. 19.7, the EI mass spectra of many aldehydes and ketones have weak molecular ions, because relatively stable fragment ions can be formed. However, as we’ll learn in Sec. 19.6, the carbonyl oxygen can be protonated. As a result, chemical-ionization (CI) mass spectra (Sec. 12.6D) of aldehydes and ketones show very strong \( M + 1 \) ions, from which accurate molecular masses can be determined.

**Figure 19.7** The EI mass spectrum of 5-methyl-2-hexanone. The odd-electron ion at \( m/z = 58 \) results from a McLafferty rearrangement of the molecular ion.

---

\( m/z \) stands for mass-to-charge ratio.
19.4 SYNTHESIS OF ALDEHYDES AND KETONES

Several reactions presented in previous chapters can be used for the preparation of aldehydes and ketones. The four most important of these are:

1. Oxidation of alcohols (Secs. 10.6A and 17.5A). Primary alcohols can be oxidized to aldehydes, and secondary alcohols can be oxidized to ketones.
2. Friedel–Crafts acylation (Sec. 16.4F). This reaction provides a way to synthesize aryl ketones. It also involves the formation of a carbon–carbon bond, the bond between the aryl ring and the carbonyl group.
3. Hydration of alkynes (Sec. 14.5A)
4. Hydroboration–oxidation of alkynes (Sec. 14.5B)

Two other reactions have been discussed that give aldehydes or ketones as products, but these are less important as synthetic methods:

1. Ozonolysis of alkenes (Sec. 5.5)
2. Periodate cleavage of glycols (Sec. 11.5B)

Ozonolysis and periodate cleavage are reactions that break carbon–carbon bonds. Because an important aspect of organic synthesis is the making of carbon–carbon bonds, use of these reactions in effect wastes some of the effort that goes into making the alkene or glycol starting materials. Nevertheless, these reactions can be used synthetically in certain cases.

Other important methods of preparing aldehydes and ketones start with carboxylic acid derivatives; these methods are discussed in Chapter 21. Appendix V gives a summary of all of the synthetic methods for aldehydes and ketones, arranged in the order in which they appear in the text.

19.5 INTRODUCTION TO ALDEHYDE AND KETONE REACTIONS

The reactions of aldehydes and ketones can be grouped into two categories: (1) reactions of the carbonyl group, which are considered in this chapter; and (2) reactions involving the α-carbon, which are presented in Chapter 22.

The great preponderance of carbonyl-group reactions of aldehydes and ketones fall into three categories:

1. Reactions with acids. The carbonyl oxygen is weakly basic and thus reacts with Lewis and Bronsted acids. With $E^+$ as a general electrophile, this reaction can be represented as follows:

PROBLEMS

19.10 Explain each of the following observations resulting from a comparison of the mass spectra of 2-hexanone (A) and 3,3-dimethyl-2-butanone (B).

(a) The $m/z = 57$ fragment peak is much more intense in the spectrum of B than it is in the spectrum of A.
(b) The spectrum of compound A shows a fragment at $m/z = 58$, but that of compound B does not.

19.11 Using only mass spectrometry, how would you distinguish 2-heptanone from 3-heptanone?