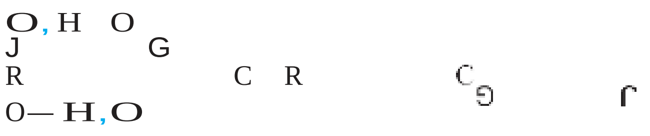
Physical Properties of Acids

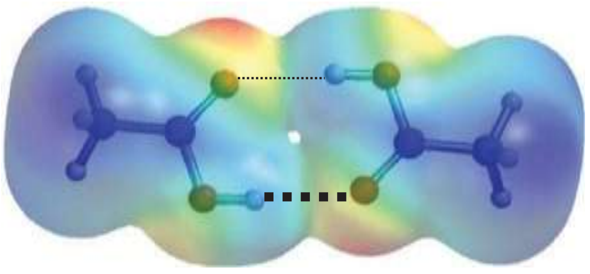
The first members of the carboxylic acid series are colorless liquids with sharp or unpleasant odors. Acetic acid, which constitutes about 4% to 5% of vinegar, provides the characteristic odor and flavor. Butyric acid gives rancid butter its disagreeable odor, and the goat acids (caproic, caprylic, and capric in Table 10.1) smell like goats. 3-Methyl-2-hexenoic acid, produced by bacteria, is responsible for the offensive odor of human armpits. Table 10.3 lists some physical properties of selected carboxylic acids.

Carboxylic acids are polar. Like alcohols, they form hydrogen bonds with themselves or with other molecules (Sec. 7.4). Therefore, they have high boiling points for their molecular weights—higher even than those of comparable alcohols. For example, acetic acid and propyl alcohol, which have the same formula weights (60 g/mol), boil at 118°C and 97°C, respectively. Carboxylic acids form dimers, with the individual units neatly held together by *two* hydrogen bonds between the electron- rich oxygens and the electron-poor hydrogens (see Sec. 7.4).

Table 3 **Physical Properties of Some CarboxylicAcids**

Name	**bp, °C**	**mp, °C**	**Solubility, g/100 g H_2O at 25°C**
formic acid	101	8	e (∞)
acetic acid	118	17	
propanoic acid	141	222	
butanoic acid	164	28	
hexanoic acid	205	21.5	1.0
octanoic acid	240	17	0.06
decanoic acid	270	31	0.01
benzoic acid	249	122	0.4 (but 6.8 at 95°C)



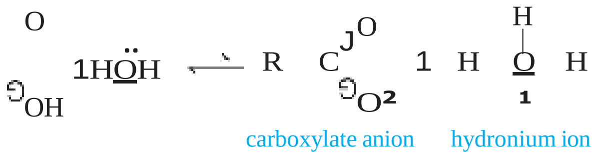


Hydrogen bonding also explains the water solubility of the lower molecular weight carboxylic acids.

Acidity and Acidity Constants

Carboxylic acids ($\mathrm{RCO_2H}$) dissociate in water, yielding a carboxylate anion ($\mathrm{RCO}\,{}^{2}_{2}$) and a hydronium ion.

R C^{J}



Their acidity constants K_a in water are given by the expression

2

$$K_a\ 5\ \frac{\begin{array}{c}\mathrm{RCO}^{2}\ 4\ 3\mathrm{H_3O}^{1}\ 4\\ 3 \qquad\qquad 4\end{array}}{\mathrm{RCO_2H}}$$

(Before proceeding further, it would be a good idea for you to review Secs. 7.5 and 7.6.)

Table 10.4 lists the acidity constants for some carboxylic and other acids. In comparing data in this table, remember that the larger the value of K_a or the smaller the value of pK_a, the stronger the acid.

EXAMPLE

Which is the stronger acid, formic or acetic, and by how much?

Solution Formic acid is stronger; it has the larger K_a. The ratio of acidities is

$$\frac{\begin{array}{c}2.1 \qquad 10^{24}\\ 1\end{array}}{1.8\ 3\ 10^{25}}\ 5\ 1.17\ 3\ 10^{3}\ 5\ 11.7$$

This means that formic acid is 11.7 times stronger than acetic acid.

PROBLEM Using the data given in Table 4, determine which is the stronger acid, acetic or dichloroacetic, and by how much.

Before we can explain the acidity differences in Table 4, we must examine the structural features that make carboxylic acids acidic.

Table 4 The Ionization Constants of Some Acids

Name	Formula	K_a	pK_a
formic acid	HCOOH	$2.1\ 3\ 10^{24}$	3.68
acetic acid	CH_3COOH	$1.8\ 3\ 10^{25}$	4.74
propanoic acid	CH_3CH_2COOH	$1.4\ 3\ 10^{25}$	4.85
butanoic acid	$CH_3CH_2CH_2COOH$	$1.6\ 3\ 10^{25}$	4.80
chloroacetic acid	$ClCH_2COOH$	$1.5\ 3\ 10^{23}$	2.82
dichloroacetic acid	$Cl_2CHCOOH$	$5.0\ 3\ 10^{22}$	1.30
trichloroacetic acid	Cl_3CCOOH	$2.0\ 3\ 10^{21}$	0.70
2-chlorobutanoic acid	$CH_3CH_2CHClCOOH$	$1.4\ 3\ 10^{23}$	2.85
3-chlorobutanoic acid	$CH_3CHClCH_2COOH$	$8.9\ 3\ 10^{25}$	4.05
benzoic acid	C_6H_5COOH	$6.6\ 3\ 10^{25}$	4.18
o-chlorobenzoic acid	*o*-Cl!C_6H_4COOH	$12.5\ 3\ 10^{24}$	2.90
m-chlorobenzoic acid	*m*-Cl!C_6H_4COOH	$1.6\ 3\ 10^{24}$	3.80
p-chlorobenzoic acid	*p*-Cl!C_6H_4COOH	$1.0\ 3\ 10^{24}$	4.00
p-nitrobenzoic acid	*p*-NO_2!C_6H_4COOH	$4.0\ 3\ 10^{24}$	3.40
phenol	C_6H_5OH	$1.0\ 310^{210}$	10.00
ethanol	CH_3CH_2OH	$1.0\ 310^{216}$	16.00
water	HOH	$1.8\ 310^{216}$	15.74

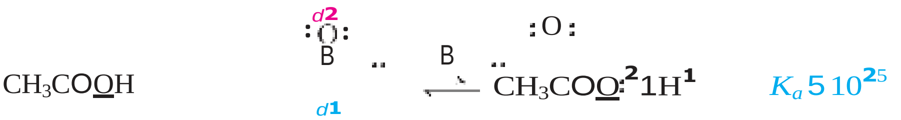
What Makes Carboxylic Acids Acidic?

You might wonder why carboxylic acids are so much more acidic than alcohols, since each class ionizes by losing H^1 from a hydroxyl group. There are two reasons, which can best be illustrated with a specific example.

From Table 10.4, we see that acetic acid is approximately 10^{11}, or 100,000 million, times stronger an acid than ethanol.

$$CH_3CH_2\ddot{\underline{O}}H \rightleftharpoons CH_3CH_2\ddot{\underline{O}}{:}^{2} 1 H^{1} \qquad K_a\,5\,10^{216}$$

ethoxide ion

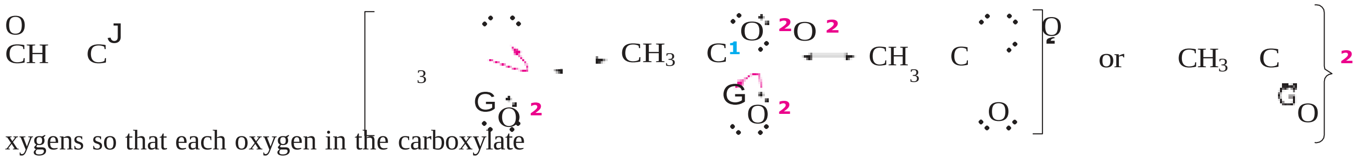


$$CH_3C\overset{:O:}{\overset{\|}{}}\underline{O}H \rightleftharpoons CH_3C\overset{:O:}{\overset{\|}{}}O\underline{O}{:}^{2} 1 H^{1} \qquad K_a\,5\,10^{25}$$

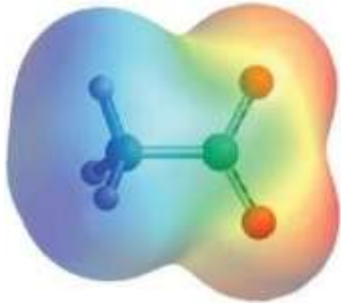
acetate ion

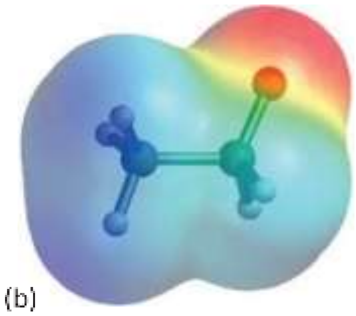
The only difference between the structures of acetic acid and ethanol is the replacement of a CH_2 group (in ethanol) by a carbonyl group (in acetic acid). But we saw (Sec. 9.5) that a carbonyl carbon atom carries a substantial *positive* charge (*d*1). This charge makes it much easier to place a *negative* charge on the adjacent oxygen atom, which is exactly what happens when we ionize a proton from the hydroxyl group.

In ethoxide ion, *the negative charge is localized on a single oxygen atom*. In acetate ion, on the other hand, *the negative charge can be delocalized through resonance*.



The negative charge is spread *equally* over the two oxygens so that each oxygen in the carboxylate ion carries only half the negative charge (Figure 10.1). The acetate ion is stabilized by resonance compared to the ethoxide ion, and this stabilization helps to drive the equilibrium more to the right in eq. 10.4 than in eq. 10.3. Consequently, more H^{1} is formed from acetic acid than from ethanol.





For both these reasons, the positive charge on the carbonyl carbon and delocalization of the carboxylate ion, carboxylic acids are much more acidic than alcohols.

EXAMPLE 2

Phenoxide ions are also stabilized by resonance (Sec. 7.6). Why are phenols weaker acids than carboxylic acids?

Solution First, the carbon atom to which the hydroxyl group is attached in a phenol is not as positive as a carbonyl carbon. Second, charge delocalization is not as great in phenoxide ions as in carboxylate ions because the contributors to the resonance hybrid are not equivalent. Some of them put the negative charge on carbon instead of on oxygen and disruptaromaticity.

PROBLEM Write two resonance structures for the benzoate ion ($C_6H_5CO_2^{2}$) that show how the negative charge is delocalized over the two oxygens. Can the negative charge in the benzoate ion be delocalized into the aromatic ring?

Physical data support the importance of resonance in carboxylate ions. In formic acid molecules, the two carbon–oxygen bonds have different lengths. But in sodium formate, both carbon–oxygen bonds of the formate ion are identical, and their length is between those of normal double and single carbon–oxygen bonds.

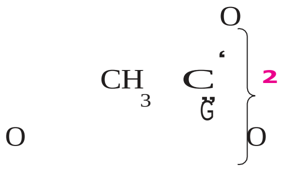
formic acid sodium formate

Effect of Structure on Acidity; the Inductive Effect Revisited

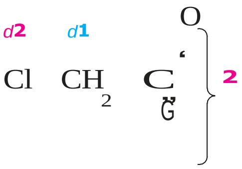
The data in Table 10.4 show that even among carboxylic acids (where the ionizing functional group is kept constant), acidities can vary depending on what other groups are attached to the molecule. Compare, for example, the K_a of acetic acid with those of mono-, di-, and trichloroacetic acids, and note that the acidity varies by a factor of 10,000.

The most important factor operating here is the inductive effect of the groups close to the carboxyl group. This effect relays charge through bonds, by displacing bonding electrons toward electronegative atoms, or away from electropositive atoms. Recallthat *electron-withdrawinggroupsenhanceacidity, andelectron-releasinggroups reduce acidity* (see Sec. 7.6).

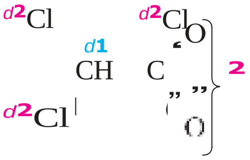
Let us examine the carboxylate ions formed when acetic acid and its chloro derivatives ionize:



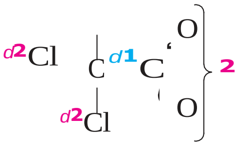
acetate



chloroacetate



dichloroacetate



trichloroacetate

Because chlorine is more electronegative than carbon, the C!Cl bond is polarized with the chlorine partially negative and the carbon partially positive. Thus, electrons are pulled away from the carboxylate end of the ion toward the chlorine. The effect tends to spread the negative charge over more atoms than in acetate ion itself and thus stabilizes the ion. The more chlorines, the greater the effect and the greater the strength of the acid.

EXAMPLE

Explain the acidity order in Table 4 for butanoic acid and its 2- and 3-chloro derivatives.

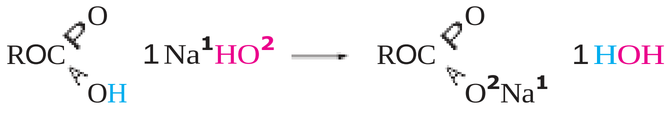
Solution The 2-chloro substituent increases the acidity of butanoic acid substantially, due to its inductive effect. In fact, the effect is about the same as for chloroacetic and acetic acids. The 3-chloro substituent exerts a similar *but much smaller* effect, because the C!Cl bond is now farther away from the carboxylate group. *Inductive effects fall off rapidly with distance.*

PROBLEM Account for the relative acidities of benzoic acid and its *ortho*, *meta*, and *para* chloro derivatives (Table 4).

We saw in Example 1 that formic acid is a substantially stronger acid than ace- tic acid. This suggests that the methyl group is more electron-releasing (hence anion-destabilizing and acidity-reducing) than hydrogen. This observation is consistent with what we have already learned about carbocation stabilities—that alkyl groups are more effective than hydrogen atoms at releasing electrons to, and therefore stabilizing, a positive carbon atom (see Sec. 3.10). A similar effect was seen for the relative acidity of ethanol and *t*-butanol in water (see Sec.7.6).

Conversion of Acids to Salts

Carboxylic acids, when treated with a strong base, form carboxylate salts. For example,



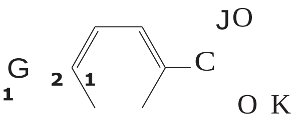
$$RCOOH + Na^+HO^- \longrightarrow RCOO^-Na^+ + HOH$$

carboxylic acid pK_a 3–5 | strong base | a sodium carboxylate (weak base) | water pK_a 16

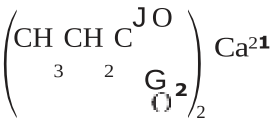
The salt can be isolated by evaporating the water. As we will see in Chapter 15, carboxylate salts of certain acids are useful as soaps and detergents.

Carboxylate salts are named as shown in the following examples:

sodium acetate
(sodium ethanoate)



potassium benzoate

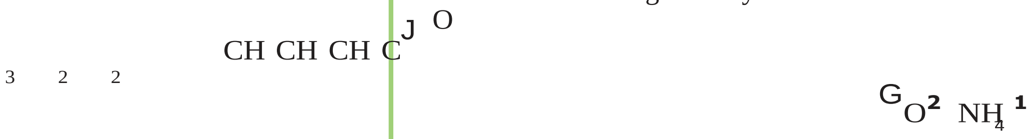


calcium propanoate

The cation is named first, followed by the name of the carboxylate ion, which is obtained by changing the *-ic* ending of the acid to *-ate*.

EXAMPLE

Name the following carboxylate salt:



$$CH_3CH_2CH_2C(=O)O^-\ NH_4^+$$

Solution The salt is ammonium butanoate (IUPAC) or ammonium butyrate (common).

PROBLEM 10.9 Write an equation, analogous to eq. 10.5, for the preparation of potassium 3-bromooctanoate from the corresponding acid.

Preparation of Acids

Organic acids can be prepared in many ways, four of which are described here: (1) oxidation of primary alcohols or aldehydes, (2) oxidation of alkyl side chains on aromatic rings, (3) reaction of Grignard reagents with carbon dioxide, and (4) hydrolysis of alkyl cyanides (nitriles).

7 Oxidation of Primary Alcohols and Aldehydes

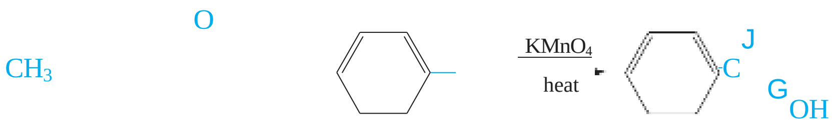
The oxidation of primary alcohols (Sec. 7.12) and aldehydes (Sec. 9.13) to carboxylic acids has already been mentioned. It is easy to see that these are oxidation reactions because going from an alcohol to an aldehyde to an acid requires replacement of $C{-}H$ bonds by $C{-}O$ bonds.

alcohol (one C—O bond) aldehyde (two C—O bonds) acid (three C—O bonds)

The most commonly used oxidizing agents for these purposes are potassium permanganate ($KMnO_4$), chromic acid anhydride (CrO_3), nitric acid (HNO_3), and, with aldehydes only, silver oxide (Ag_2O). For specific examples, see eqs. 7.37, 9.37, 9.38, and 9.41.

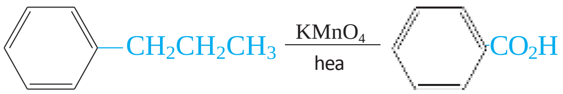
7aOxidation of Aromatic Side Chains

Aromatic acids can be prepared by oxidizing an alkyl side chain on an aromatic ring.



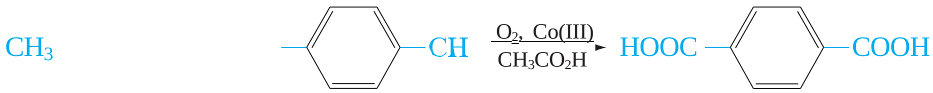
toluene benzoic acid

This reaction illustrates the striking stability of aromatic rings; it is the alkane-like methyl group, not the aromatic ring, that is oxidized. The reaction involves attack of the oxidant at a C!H bond adjacent to the benzene ring. Longer side chains are also oxidized to a carboxyl group.



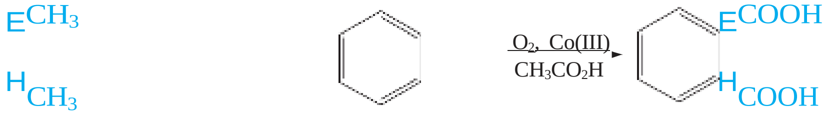
If no C!H bond is in the benzylic position, however, the aromatic ring is oxidized, although only under severe reaction conditions.

With oxidants other than potassium permanganate, this reaction is commercially important. For example, terephthalic acid (Sec. 10.1), one of the two raw materials needed to manufacture Dacron, is produced in this way, using a cobalt catalyst and air for the oxidation.



p-xylene terephthalic acid

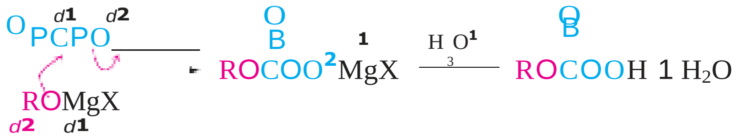
Phthalic acid, used for making plasticizers, resins, and dyestuffs, is manufactured by similar oxidations, starting with *o*-xylene.



o-xylene phthalic acid

7.a Reaction of Grignard Reagents with Carbon Dioxide

As we saw previously, Grignard reagents add to the carbonyl groups of aldehydes or ketones to give alcohols. In a similar way, they add irreversibly to the carbonyl group of carbon dioxide to give acids, after protonation of the intermediate carboxylate salt with a mineral acid like aqueous HCl.



$$\overset{d1\ \ d2}{OPCPO} + \underset{d2\ \ d1}{ROMgX} \longrightarrow RO\overset{O}{\overset{B}{C}}OO^{2}\overset{1}{M}gX \xrightarrow{H_3O^1} RO\overset{O}{\overset{B}{C}}OOH\ 1\ H_2O \qquad \textbf{(10.12)}$$

This reaction gives good yields and is an excellent laboratory method for preparing both aliphatic and aromatic acids. Note that the acid obtained has one more carbon atom than the alkyl or aryl halide from which the Grignard reagent is prepared, so the reaction provides a way to increase the length of a carbon chain.

EXAMPLE

Show how $(CH_3)_3CBr$ can be converted to $(CH_3)_3CCO_2H$.

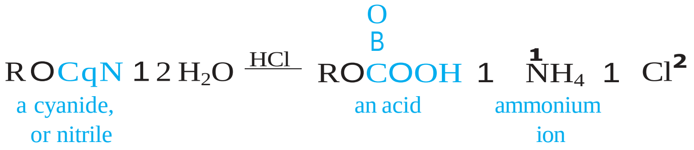
Solution $(CH_3)_3CBr \xrightarrow[\text{ether}]{Mg} (C\underline{H}_3)_3CMgBr \xrightarrow[2.\ H_3O^1]{1.\ CO_2} (CH_3)_3CCO_2H$

PROBLEM 10.10 Show how 4-methylcyclohexyl chloride can be converted to 4-methylcyclohexanecarboxylic acid.

PROBLEM 10.11 Devise a synthesis of butanoic acid ($CH_3CH_2CH_2CO_2H$) from 1-propanol ($CH_3CH_2CH_2OH$).

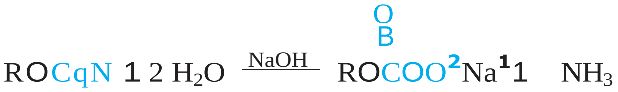
7.a Hydrolysis of Cyanides (Nitriles)

The carbon–nitrogen triple bond of organic cyanides can be hydrolyzed to a carboxyl group. The reaction requires either acid or base. In acid, the nitrogen atom of the cyanide is converted to an ammonium ion.



$$ROCqN\ 1\ 2\,H_2O \xrightarrow{HCl} RO\overset{O}{\overset{B}{C}}OOH\ 1\ \overset{1}{N}H_4\ 1\ Cl^{2}$$

In base, the nitrogen is converted to ammonia and the organic product is the carboxylate salt, which must be neutralized in a separate step to give the acid.



$$ROCqN\ 1\ 2\,H_2O \xrightarrow{NaOH} RO\overset{O}{\overset{B}{C}}OO^{2}Na^{1}1\ \ NH_3$$

a carboxylate salt ammonia
H1

O
B

ROCOOH