

# INTRODUCTION TO ORGANIC CHEMISTRY

FOURTH EDITION

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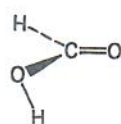
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| Bond Lengths, Å |       | Bond Angles, deg |       |
|-----------------|-------|------------------|-------|
| C=O             | 1.202 | H—C=O            | 124.1 |
| C—O             | 1.343 | O—C=O            | 124.9 |
| C—H             | 1.097 | H—C—O            | 111.0 |
| O—H             | 0.972 | H—O—C            | 106.3 |

FIGURE 18.1 Structure of formic acid.

For formic acid in the vapor phase,  $\Delta H^\circ$  for the dimerization has been determined to be  $-14 \text{ kcal mole}^{-1}$ .

## 18.2 Nomenclature

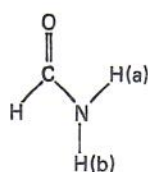
Two systems of nomenclature are currently in use for carboxylic acids, and the student should be acquainted with both. Since many of the simpler acids are naturally occurring and were discovered early in the history of organic chemistry, they have well-entrenched common names. At the 1892 Geneva Congress it was agreed to derive the name of a carboxylic acid systematically from that of the normal alkane having the same number of carbon atoms by dropping the ending **-e** and adding the suffix **-oic acid**. The common and IUPAC names for the first ten straight-chain acids, as well as other selected examples, are given in Table 18.1. The name used by *Chemical Abstracts* in indexing is printed in bold type.

Past caproic acid, the even-numbered carboxylic acids are the more important because only the even-numbered acids occur in nature. Carboxylic acids are biosynthesized by the combination of two-carbon units related to acetic acid. **Biosynthesis** is the synthesis from small precursor molecules in reactions catalyzed by the multiple enzyme systems found in living organisms. Because they are built up from acetic acid, most of the naturally occurring acids have an even number of carbon atoms in the chain.

When naming a substituted carboxylic acid in the IUPAC system, the longest carbon chain *containing the carboxy group* is numbered from 1 to  $n$ , beginning with the carboxy

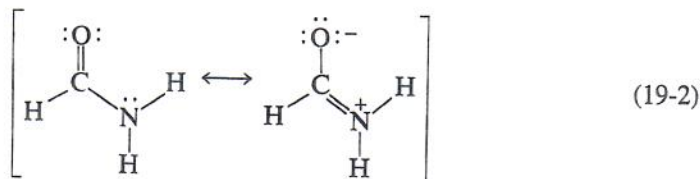
TABLE 18.1 Nomenclature of Carboxylic Acids

| Compound                                              | Common Name        | IUPAC Name                |
|-------------------------------------------------------|--------------------|---------------------------|
| HCOOH                                                 | <b>formic acid</b> | methanoic acid            |
| CH <sub>3</sub> COOH                                  | <b>acetic acid</b> | ethanoic acid             |
| CH <sub>3</sub> CH <sub>2</sub> COOH                  | propionic acid     | <b>propanoic acid</b>     |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH  | butyric acid       | <b>butanoic acid</b>      |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOH  | valeric acid       | <b>pentanoic acid</b>     |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOH  | caproic acid       | <b>hexanoic acid</b>      |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> COOH  | enanthic acid      | <b>heptanoic acid</b>     |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> COOH  | caprylic acid      | <b>octanoic acid</b>      |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> COOH  | pelargonic acid    | <b>nonanoic acid</b>      |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOH  | capric acid        | <b>decanoic acid</b>      |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> COOH | lauric acid        | <b>dodecanoic acid</b>    |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> COOH | myristic acid      | <b>tetradecanoic acid</b> |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOH | palmitic acid      | <b>hexadecanoic acid</b>  |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH | stearic acid       | <b>octadecanoic acid</b>  |

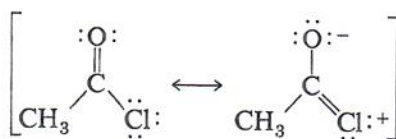


| Bond Lengths, Å |       | Bond Angles, deg |        |
|-----------------|-------|------------------|--------|
| C=O             | 1.193 | H-C=O            | 122.97 |
| C-N             | 1.376 | H-C-N            | 113.23 |
| C-H             | 1.102 | N-C=O            | 123.80 |
| N-H(a)          | 1.014 | C-N-H(a)         | 117.15 |
| N-H(b)          | 1.002 | C-N-H(b)         | 120.62 |
|                 |       | H-N-H            | 118.88 |

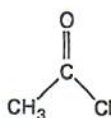
FIGURE 19.2 Structure of formamide.



Since the simplest acyl chloride, formyl chloride, is not stable at temperatures above  $-60^{\circ}\text{C}$ , its structural parameters have not been measured. However, the bond lengths and bond angles have been determined for acetyl chloride (Figure 19.3). The carbon-chlorine bond is not appreciably shorter than the analogous bond in methyl chloride ( $1.784\text{ Å}$ ), suggesting that dipolar resonance structures are not particularly important in the case of acyl halides.



**EXERCISE 19.1** For methylamine, dimethyl ether, and methyl fluoride, the  $\text{CH}_3\text{—X}$  distances are  $1.47\text{ Å}$ ,  $1.42\text{ Å}$ , and  $1.38\text{ Å}$ , respectively. For acetamide, methyl acetate, and acetyl fluoride, the analogous distances are  $1.36\text{ Å}$ ,  $1.36\text{ Å}$ , and  $1.37\text{ Å}$ , respectively. Use the differences in  $\text{C—X}$  distances to evaluate the relative importance of dipolar resonance structures in the three carboxylic acid derivatives. Is there a correlation between the importance of the dipolar resonance structure and the relative basicity of  $\text{F}^-$ ,  $\text{OH}^-$ , and  $\text{NH}_2^-$ ?

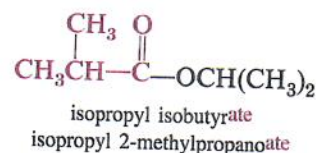
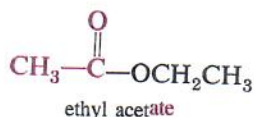
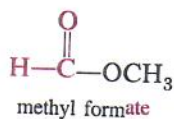


| Bond Lengths, Å |       | Bond Angles, deg |        |
|-----------------|-------|------------------|--------|
| C=O             | 1.192 | C-C=O            | 127.08 |
| C-C             | 1.499 | C-C-Cl           | 112.66 |
| C-Cl            | 1.789 | O=C-Cl           | 120.26 |
| C-H             | 1.083 |                  |        |

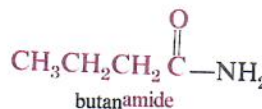
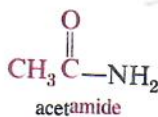
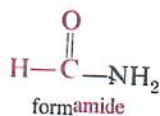
FIGURE 19.3 Structure of acetyl chloride.

## 19.2 Nomenclature

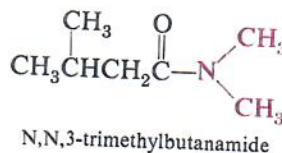
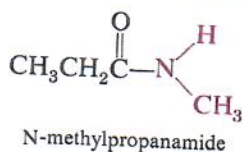
Esters are named in the following way. The first word of the name is the stem name of the alkyl group attached to oxygen. The second word of the name is the name of the parent acid with the suffix **-ic** replaced by **-ate**. This nomenclature applies for both common and IUPAC names of acids.



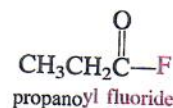
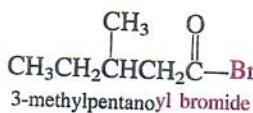
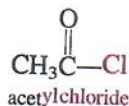
Amides are named by dropping the suffix **-ic** or **-oic** from the name of the parent acid and adding the suffix **-amide**.



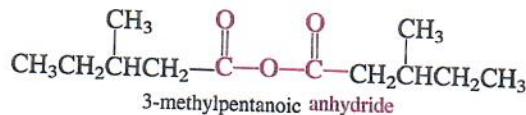
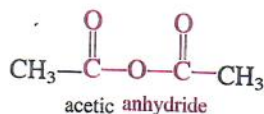
A substituted nitrogen is indicated by prefixing the name of the simple amide by **N-**, followed by the name of the substituent group.



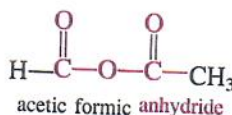
Acyl halides are named in a similar manner. In this case the suffix **-ic** is replaced by the suffix **-yl**, and the halide name is added as a second word. (Note that for acyl halides, the "o" of the ending **oic** is retained.)



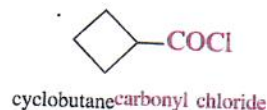
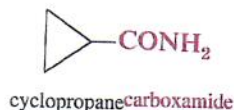
Anhydrides are named by adding **anhydride** to the name of the corresponding carboxylic acid.



For mixed anhydrides, the parent name of each acid is given, followed by the word **anhydride**.



For functional derivatives of carboxylic acids that are named as alkanecarboxylic acids (page 483) the suffix **-carboxylic acid** is replaced by **-carboxamide** or **-carbonyl halide**.



Occasionally it is necessary to name an acid derivative function as a derivative of some other functional stem. The group names for the various radicals as prefixes are given in Table 19.1.