Carboxylic Acid Derivatives

1. Background and Properties

The important classes of organic compounds known as alcohols, phenols, ethers, amines and halides consist of alkyl and/or aryl groups bonded to hydroxyl, alkoxyl, amino and halo substituents respectively. If these same functional groups are attached to an **acyl group** (RCO–) their properties are substantially changed, and they are designated as **carboxylic acid derivatives**. Carboxylic acids have a hydroxyl group bonded to an acyl group, and their functional derivatives are prepared by replacement of the hydroxyl group with substituents, such as halo, alkoxyl, amino and acyloxy. Some examples of these functional derivatives were displayed earlier.

The following table lists some representative derivatives and their boiling points. An aldehyde and ketone of equivalent molecular weight are also listed for comparison. Boiling points are given for 760 torr (atmospheric pressure), and those listed as a range are estimated from values obtained at lower pressures. As noted earlier, the relatively high boiling point of carboxylic acids is due to extensive hydrogen bonded dimerization. Similar hydrogen bonding occurs between molecules of 1º and 2º-amides (amides having at least one N–H bond), and the first three compounds in the table serve as hydrogen bonding examples.

Physical Properties of Some Carboxylic Acid Derivatives

Formula	**IUPAC Name**	**Molecular Weight**	**Boiling Point**	**Water Solubility**
$CH_3(CH_2)_2CO_2H$	butanoic acid	88	164 ºC	very soluble
$CH_3(CH_2)_2CONH_2$	butanamide	87	216-220 ºC	soluble

$CH_3CH_2CONHCH_3$	N-methylpropanamide	87	205 -210 ºC	soluble
$CH_3CON(CH_3)_2$	N,N-dimethylethanamide	87	166 ºC	very soluble
$HCON(CH_3)CH_2CH_3$	N-ethyl, N-methylmethanamide	87	170-180 ºC	very soluble
$CH_3(CH_2)_3CN$	pentanenitrile	83	141 ºC	slightly soluble
CH_3CO_2CHO	ethanoic methanoic anhydride	88	105-112 ºC	reacts with water
$CH_3CH_2CO_2CH_3$	methyl propanoate	88	80 ºC	slightly soluble
$CH_3CO_2C_2H_5$	ethyl ethanoate	88	77 ºC	moderately soluble
CH_3CH_2COCl	propanoyl chloride	92.5	80 ºC	reacts with water
$CH_3(CH_2)_3CHO$	pentanal	86	103 ºC	slightly soluble
$CH_3(CH_2)_2COCH_3$	2-pentanone	86	102 ºC	slightly soluble

The last nine entries in the above table cannot function as hydrogen bond donors, so hydrogen bonded dimers and aggregates are not possible. The relatively high boiling points of equivalent 3º-amides and nitriles are probably due to the high polarity of these functions. Indeed, if hydrogen bonding is not present, the boiling points of comparable sized compounds correlate reasonably well with their dipole moments.

2. Nomenclature

Three examples of acyl groups having specific names were noted earlier. These are often used in common names of compounds. In the following examples the IUPAC names are color coded, and common names are given in parentheses.

- **Esters:** The alkyl group is named first, followed by a derived name for the acyl group, the oic or ic suffix in the acid name is replaced by ate.

  e.g. $CH_3(CH_2)_2CO_2C_2H_5$ is ethyl butanoate (or ethyl butyrate).

  Cyclic esters are called lactones. A Greek letter identifies the location of the alkyl oxygen relative to the carboxyl carbonyl group.

- **Acid Halides:** The acyl group is named first, followed by the halogen name as a separate word.

  e.g. CH_3CH_2COCl is propanoyl chloride (or propionyl chloride).

- **Anhydrides:** The name of the related acid(s) is used first, followed by the separate word "anhydride".

  e.g. $(CH_3(CH_2)_2CO)_2O$ is butanoic anhydride & $CH_3COOCOCH_2CH_3$ is ethanoic propanoic anhydride (or acetic propionic anhydride).

- **Amides:** The name of the related acid is used first and the oic acid or ic acid suffix is replaced by amide (only for 1º-amides).

  e.g. CH_3CONH_2 is ethanamide (or acetamide).

  2º & 3º-amides have alkyl substituents on the nitrogen atom. These are designated by "N-alkyl" term(s) at the beginning of the name.

  e.g. $CH_3(CH_2)_2CONHC_2H_5$ is N-ethylbutanamide; & $HCON(CH_3)_2$ is N,N-dimethylmethanamide (or N,N-dimethylformamide).

  Cyclic amides are called lactams. A Greek letter identifies the location of the nitrogen on the alkyl chain relative to the carboxyl carbonyl group.

- **Nitriles:** Simple acyclic nitriles are named by adding nitrile as a suffix to the name of the corresponding alkane (same number of carbon atoms).

  Chain numbering begins with the nitrile carbon . Commonly, the oic acid or ic acid ending of the corresponding carboxylic acid is replaced by onitrile.

  A nitrile substituent, e.g. on a ring, is named carbonitrile.

  e.g. $(CH_3)_2CHCH_2C\equiv N$ is 3-methylbutanenitrile (or isovaleronitrile).

Source : http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/crbacid2.htm#nomen