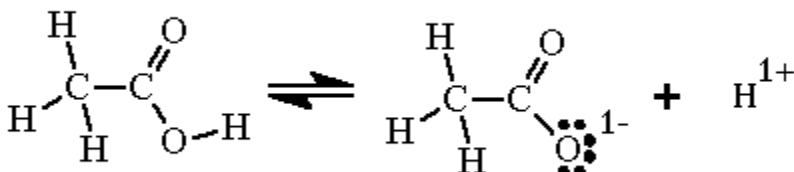


4.2 Structure and acidic properties of carboxylic acids

The OH group in a carboxylic acid is different from an OH in an alcohol. The OH group in a carboxylic acid is weakly acidic: it dissociates **reversibly** with water to form a carboxylate ion and a hydrogen ion:

dissociation of acetic acid

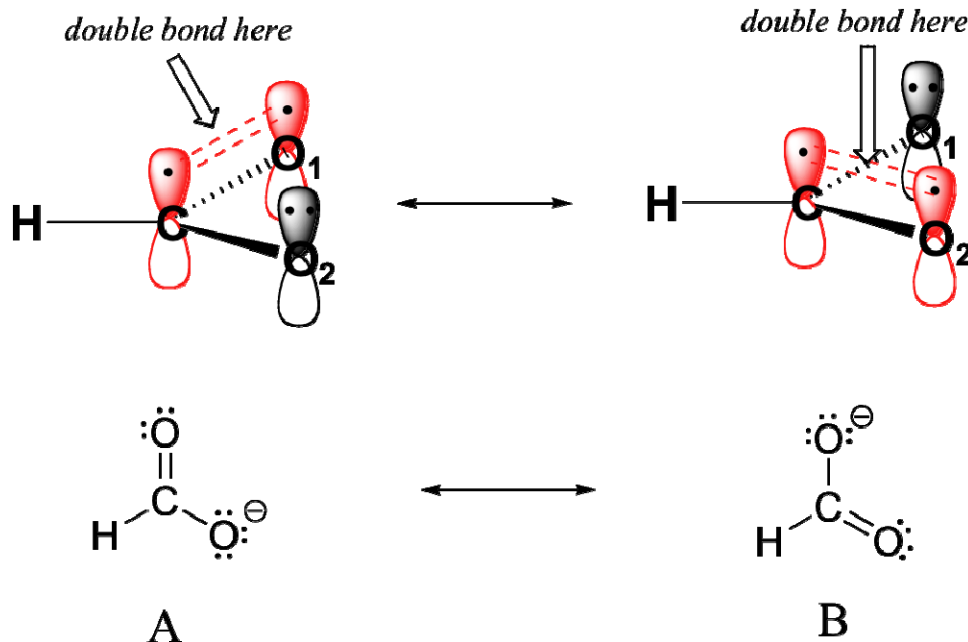


only 4 out of 100 molecules dissociate

When the bond lengths of the 2 C-O bonds of the carboxylic acid are measured experimentally the C=O is significantly shorter (and stronger) than the C-O bond of the C-O-H. However when the bond lengths of the C=O and C-O⁻¹ bonds in the **carboxylate ion** are determined, they are found to be the same, and intermediate between that expected for a C=O and a C-O bond. The explanation for this is similar to that used to explain the C-C bond lengths of benzene. In terms of **resonance** structures we have two equally possible structures for a carboxylate ion and the true molecule appears to be an intermediate between them.



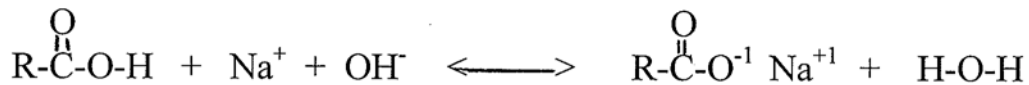
Alternatively we can look at the p orbital overlap as being shared between the C atom and **both** O atoms, similarly to the discussion with benzene.



Creative commons: Chemwiki:ucdavis

This resonance spreads the negative charge between the two O atoms of the carboxylate ion and makes the carboxylate ion more stable. Chemists use this feature to explain why the OH bond in a carboxylic acid is considerably more acidic than the OH bond in an alcohol.

Being an acid, carboxylic acids can undergo **neutralization** reactions with bases, forming water and a salt of a weak acid.



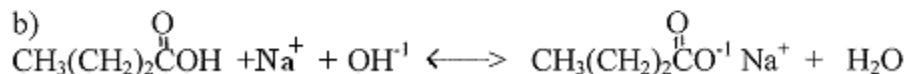
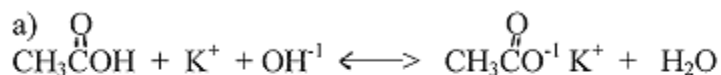
Examples:

Write the equation for the neutralization of

a) acetic acid with potassium hydroxide.

b) butyric acid with sodium hydroxide

Answers:

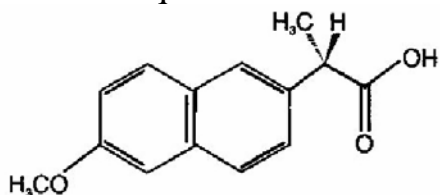


Write the equation for the neutralization of

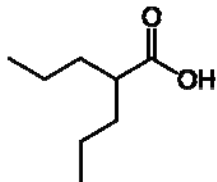
- butanoic acid with lithium hydroxide.
- propanoic acid with potassium hydroxide
- formic acid with sodium hydroxide
- Naproxen (Aleve) has the formula shown below. Circle the carboxylic acid functional group. What other functional groups are in the molecule? What is the 2 aromatic ring system called?

Naproxen is frequently administered as naproxen sodium in which the naproxen has been neutralized with sodium hydroxide, because the carboxylate is less irritating to the stomach than the carboxylic acid and it is more water soluble. In the case of drug names the positive ion is often put after the name of the negative ion: naproxen sodium.

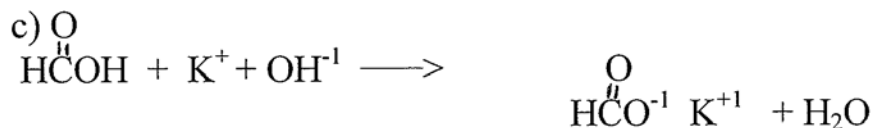
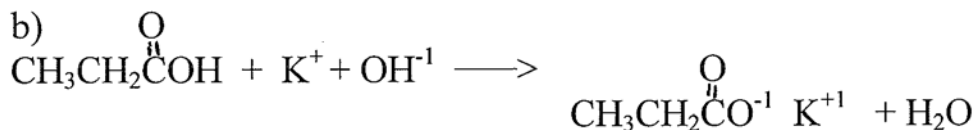
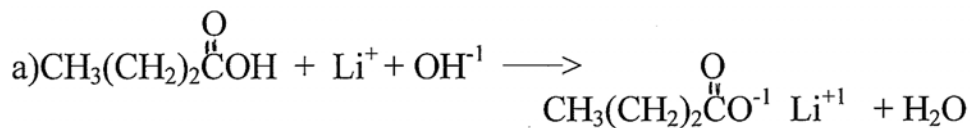
Show the equation for the neutralization with sodium hydroxide.

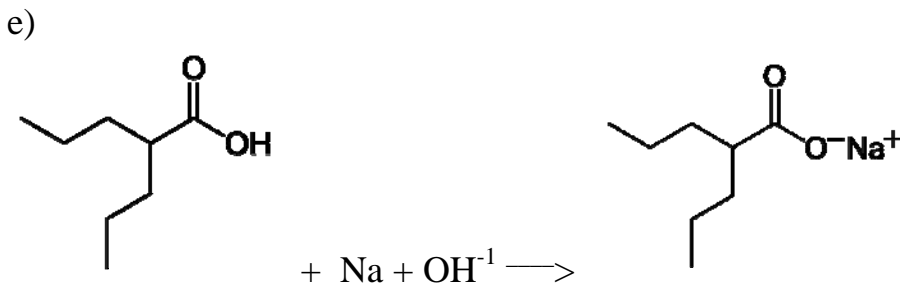
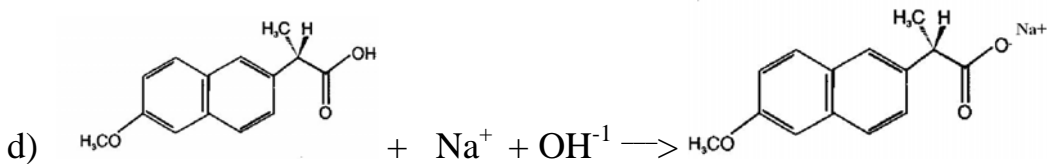


- Valproic acid is the common name for an anti-seizure medication and has the formula shown below. Give the systematic name for valproic acid. Circle the carboxylic acid functional group. It is frequently administered as valproate sodium in which the valproic acid has been neutralized with sodium hydroxide. Show the equation for the neutralization



Answers:





In most human tissues the pH is slightly alkaline (e.g. the pH in arterial blood is 7.4) and most physiologically important carboxylic acids in the body exist primarily in the carboxylate ion form rather than in the carboxylic acid form.

Many texts talk about **lactic acid** build up in the blood during anaerobic exercise when in fact most (about 99.99%) of the lactic acid exists primarily in the ionic **lactate ion** form in the blood.

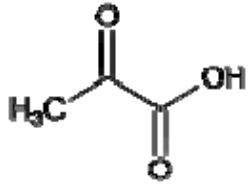


Lactic acid

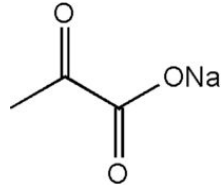
Lactate ion

Don't worry about it if you see one source refer to lactic acid and another to lactate.

Other common carboxylic acids in the body include citric acid, pyruvic acid and many others; like lactic acid they actually exist in the body primarily as carboxylate ions: citrate ions and pyruvate ions.



Pyruvic acid



pyruvate

You are likely to see both the acid and ion form names of these physiological acids and you should be comfortable switching back and forth.