

COMPARATIVE ENERGIES: THE SKI HILL

In most cases, the reactivity of carboxyloids involves converting one carboxyloid into another. This is done by replacing one heteroatom substituent with another. For example, the chloride in an acid chloride may be replaced by an alcohol or alkoxide ion to make an ester.

The fact that one carboxyloid can be converted into another suggests that there would be an equilibrium between them. The ratio of two carboxyloids at equilibrium would be determined by their relative stability, as well as the stability of other associated species in solution.

We can map out the stability of carboxyloids on a potential energy surface, as shown below. The higher energy, less stable, more reactive carboxyloids are shown at the top of the potential energy curve. The lower energy, more stable, less reactive carboxyloids are found lower down on the potential energy curve.

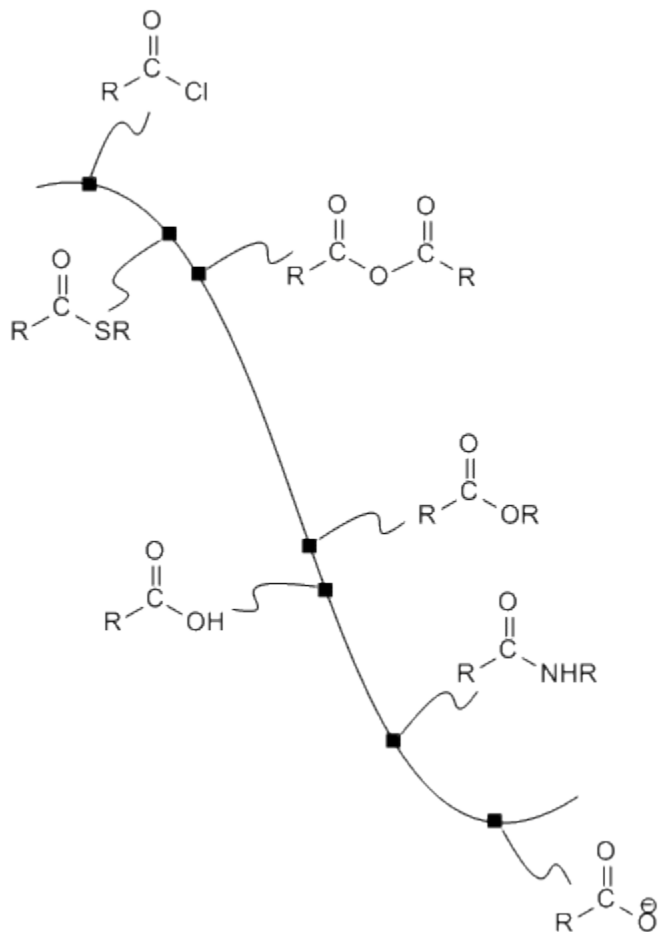
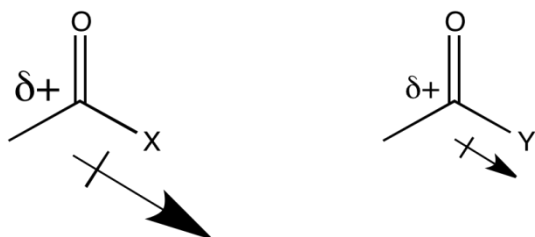
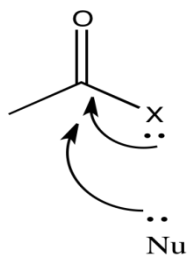


Figure CX3.1. A potential energy curve showing relative reactivity of carboxyls.

The heteroatom attached to the carbonyl in a carboxyl is always an electronegative atom with a lone pair. Either of those two features might be useful in understanding the reactivity trend illustrated above. For example, an electronegative atom would make the carbonyl carbon more positive. That carbon is already very positive because of the double bond to oxygen. Adding an additional electronegative atom should make it even more so. The amount of positive charge on the carbonyl carbon would be even greater if the atom attached to it were exceptionally electronegative.



On the other hand, a nearby lone pair might counteract the electron-attracting power of the carbonyl carbon. In a sense, we might think about that lone pair as competing with donation from a potential nucleophile.



The ability of an atom to π -donate, then, might have an influence on how strongly the carbonyl will attract nucleophiles. Of course, there is some trade-off involved in π -donation. Usually the atom that donates must take on a positive charge, since it is lending a pair of its own electrons to another atom. Factors that influence how easily this may happen could be important in determining carboxyl reactivity.

