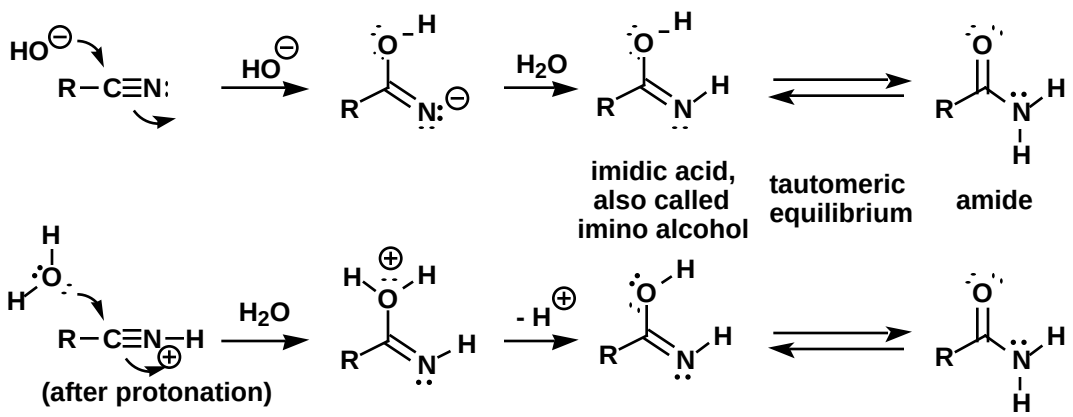
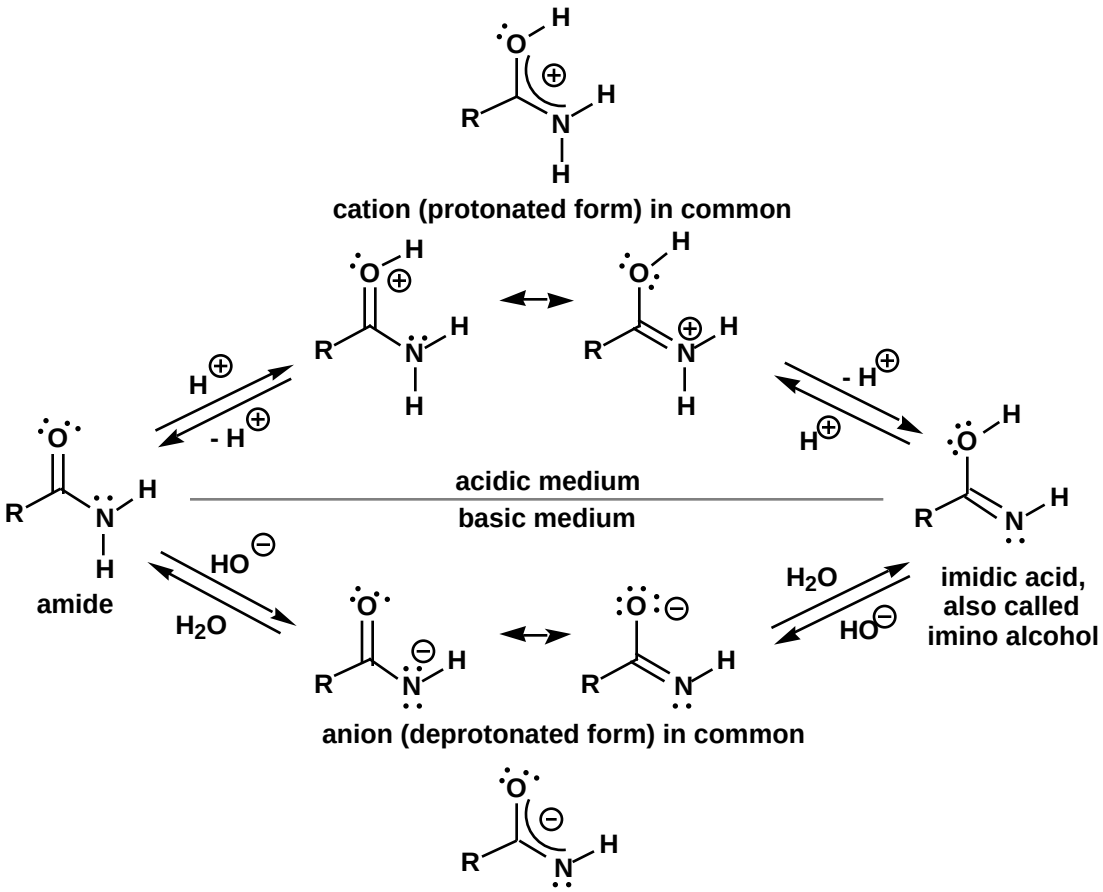
Text Related to Segment 19.07 ©2002 Claude E. Wintner

Just as the imine functionality is a carbonyl group equivalent, so too a nitrile may be attacked at carbon by nucleophiles. In the case of hydroxide ion the result, after protonation, is an imidic acid (also called an imino alcohol), the tautomer of an amide, and in general less stable than the corresponding amide. The analogous hydrolysis in acid occurs when the weaker nucleophile water interacts with a *protonated* nitrile, a species with enhanced electrophilicity:



base- and acid-catalyzed hydrolysis of nitriles to amides

The final figure reviews the concept of tautomerism, first introduced in Segment 11.04, as it applies to amides. Note that, just as was the case for ketone-enol tautomerism, amide and imidic acid tautomers are related through the delocalized anion which they have in common; correspondingly, they also share a single protonated form. An important realization to take home from the figure is that amides are not protonated at nitrogen by acids; in fact, the nitrogen atom of an amide is *not* appreciably basic, because the nitrogen electron pair is involved in a three-orbital-four-electron delocalized system.



relationship of an amide with its imidic acid tautomer

Putting these ideas together now, we see that we have rationalized the hydrolysis of nitriles to carboxylic acids, as already has been invoked, for example, in Segment 18.04. The nitrile is hydrolyzed to the amide as above, via the imidic acid, and from there onward as in Segment 19.06 to the carboxylic acid. Generally it is possible, if desired, to run the reaction so that it stops largely at the amide stage, if this outcome is desired.