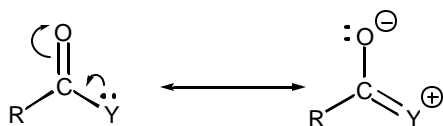


ELECTRONIC STRUCTURE OF CARBOXYLIC ACID DERIVATIVES

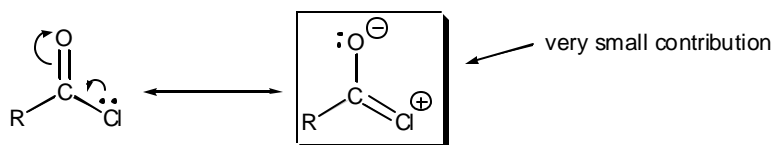
1. Conjugation and Resonance in Acid Halides, Anhydrides, Esters and Amides.

Each of these derivatives can be represented by a generalized structure as follows:

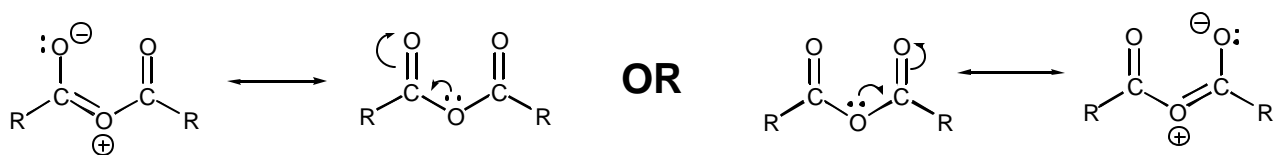


Y is the atom directly connected to the acyl unit RCO (in other words oxygen or nitrogen, or halogen). They all have unshared electron pairs, thus making possible another resonance structure, as indicated above. In terms of orbitals, this is equivalent to the overlap of *p*-orbitals at each of the three centers. This resonance contribution (or conjugation) leads to: 1) Partial double bond character of the C – Y bond and 2) Reduced partial positive charge at the carbonyl carbon. The particular extent of the effect depends on the type of derivative.

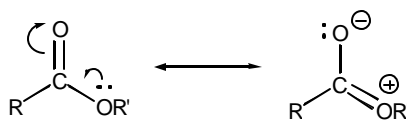
- A. Acid Halides – halogens have considerable electronegativity. Plus, their *p*-orbitals are *3p*, *4p*, etc. The carbon *p*-orbital is *2p*. This mismatch will lead to a relatively poor overlap. All in all the resonance contribution (overlap) from halogens is weakest. This would mean that in acyl halides the carbonyl carbon would have the largest positive charge.



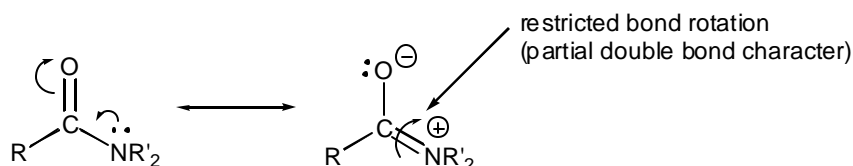
- B. Acid Anhydrides – the central oxygen makes a resonance contribution, but the effect is shared between TWO acyl moieties, so each carbonyl carbon experiences only half of the overall stabilization.



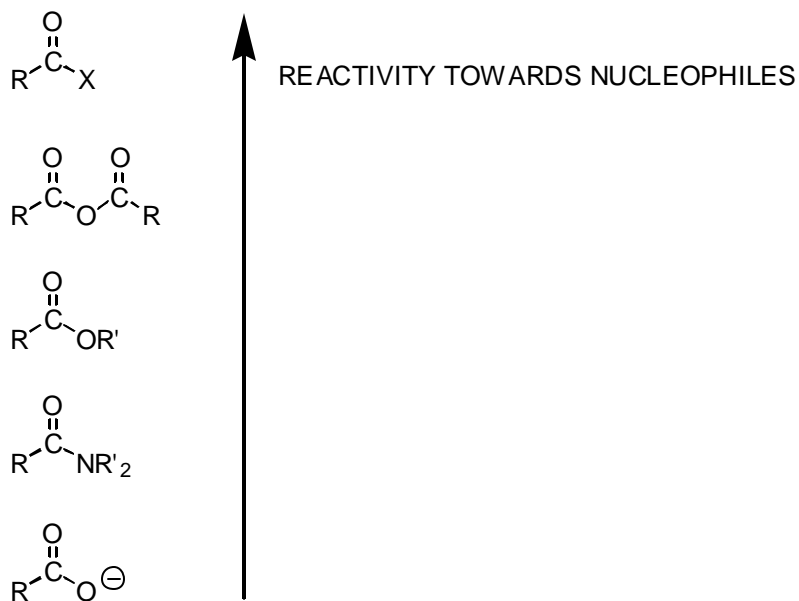
- C. Esters – the oxygen atom's lone pair conjugates with the carbonyl group, causing a significant reduction of the positive charge at the carbonyl carbon.



- D. Amides – since nitrogen is a better electron donor than oxygen, the conjugation effect is more pronounced in amides. The second resonance structure has such a significant contribution that the C – N bond acquires a considerable double bond character, reflected in the RESTRICTED rotation of this bond. Also, the partial positive charge at the carbonyl carbon is smallest.



The amount of charge on the carbonyl carbon is directly related to its susceptibility to a nucleophilic attack, i.e. to the reactivity of the corresponding derivative in reactions with nucleophiles. Due to the above discussed varying degree of resonance stabilization, the following order of reactivity of acid derivatives is observed:



2. **Electronic Structure of Nitriles** – they are analogs of alkynes. The carbon and nitrogen of the $\text{C} = \text{N}$ bond are both sp -hybridized. One s - and two p -bonds are formed. The lone pair of nitrogen resides on an sp -orbital. Due to the particular hybridization mode, sp , the angle at the nitrile carbon is about 180° .