The gas phase reactivity of hydroxyl radical in the atmosphere. Hydrogen atom transfer versus proton coupled electron transfer processes.

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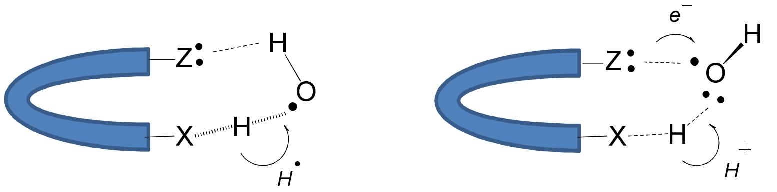
Hydroxyl radical is the main oxidant in atmosphere and reacts, in a great part, by abstracting hydrogen atoms from organic species. It is generally accepted that the hydrogen abstraction by hydroxyl radical proceeds by the concerted breaking and forming of the covalent bond as it is indicated in equation 1.

$$\text{X-H} + \text{OH} \rightarrow \text{X} + \text{H}_2\text{O} \tag{1}$$

In this case, the OH radical approaches the X-H bond with its unpaired electron and form the H-OH bond whereas the X-H bond is broken. This process is named hydrogen atom transfer (*hat*) and it is schematized in Figure 1a. It is known that the associated energy barrier is related to the bond dissociation energy of the X-H bond, which depends on the triplet repulsion energy for the X•/OH• pair at the transition structure.[1] Depending on the nature of X (for instance, having a terminal atom Z with a lone pair of electrons) the hydroxyl radical can approach in a different manner to the X-H reactant and react in a different way, undergoing a proton coupled electron transfer (*pcet*) mechanism. This process is schematized in Figure 1b, where an electron is transferred from the lone pair of the Z terminal atom to the oxygen atom of the OH radical, and, simultaneously, the hydrogen atom bonded to X is transferred as a proton to the OH moiety.[2,3]



a) Hydrogen atom transfer b) Proton coupled electron transfer

The relevance of the *hat* and *pcet* processes will be studied by considering the oxidation of atmospheric acids by hydroxyl radical, analyzing also the effect of water vapor on the reactivity of these species.[4]

References

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