

Markownikoff rule

‘In the addition of hydrogen halides to unsymmetrically constituted [unsaturated] hydrocarbons, the halogen atom becomes attached to the carbon bearing the lesser number of hydrogen atoms.’ Originally formulated by Markownikoff (Markovnikov) to generalize the orientation in additions of hydrogen halides to simple alkenes, this rule has been extended to polar *addition reactions* as follows. ‘In the *heterolytic* addition of a polar molecule to an alkene or alkyne, the more electronegative (nucleophilic) atom (or part) of the polar molecule becomes attached to the carbon atom bearing the smaller number of hydrogen atoms.’

This is an indirect statement of the common mechanistic observation, that the more electropositive (electrophilic) atom (or part) of the polar molecule becomes attached to the end of the multiple bond that would result in the more stable *carbenium ion* (whether or not a carbenium ion is actually formed as a *reaction intermediate* in the addition reaction). Addition in the opposite sense is commonly called ‘anti-Markovnikov addition’.

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