

σ -constant (sigma constant)

Specifically the substituent constant for *meta*- and for *para*-substituents in benzene derivatives as defined by Hammett on the basis of the ionization constant of a substituted benzoic acid in water at 25 °C, i.e. $\log (K_a/K_a^0)$, where K_a is the ionization constant of a *m*- or *p*-substituted benzoic acid and K_a^0 that of benzoic acid itself.

The term is also used as a collective description for related electronic substituent constants based on other standard reaction series, of which, σ^+ , σ^- and σ^0 are typical; also constants which represent dissected electronic effects such as σ_I and σ_R . For this purpose it might be better always to spell out the term in full, i.e. as 'Hammett sigma constant', and restrict σ -constants to the scale of substituent constants which is based on benzoic acid. A large positive σ -value implies high electron-withdrawing power by inductive and/or resonance effect, relative to H; a large negative σ -value implies high electron-releasing power relative to H.

See also *Hammett equation*, *ρ -value*, *Taft equation*.

1994, 66, 1171