

### **$\sigma$ -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,  $\sigma^+$ ,  $\sigma^-$  and  $\sigma^0$  are typical; also constants which represent dissected electronic effects such as  $\sigma_I$  and  $\sigma_R$ . For this purpose it might be better always to spell out the term in full, i.e. as 'Hammett sigma constant', and restrict  $\sigma$ -constants to the scale of substituent constants which is based on benzoic acid. A large positive  $\sigma$ -value implies high electron-withdrawing power by inductive and/or resonance effect, relative to H; a large negative  $\sigma$ -value implies high electron-releasing power relative to H.

See also *Hammett equation*,  *$\rho$ -value*, *Taft equation*.

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