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σ-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. $\log_{10}\left(\frac{K_a}{K_a^0}\right)$), 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

Source:

PAC, 1994, *66*, 1077 *(Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994))* on page 1171

