

Ritchie equation

The linear free-energy relation

$$\log_{10}k_{\text{N}} = \log_{10}k_0 + N_+$$

applied to the reactions between nucleophiles and certain large and relatively stable organic cations, e.g. arenediazonium, triarylmethyl and aryltropylium cations in various solvents. k_{N} is the rate constant for reaction of a given cation with a given nucleophilic system (i.e. given nucleophile in a given solvent). k_0 is the rate constant for the same cation with water in water, and N_+ is a parameter which is characteristic of the nucleophilic system and independent of the cation. A surprising feature of the equation is the absence of a coefficient of N_+ , characteristic of the substrate (*cf.* the s in the Swain–Scott equation), even though values of N_+ vary over 13 log units. The equation thus involves a gigantic breakdown of the reactivity–selectivity principle. The equation has been extended both in form and in range of application.

Source:

PAC, 1994, 66, 1077 (*Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)*) on page 1161