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Stern–Volmer kinetic relationships

This term applies broadly to variations of quantum yields of photophysical processes (e.g. fluorescence or phosphorescence) or photochemical reactions (usually reaction quantum yield) with the concentration of a given reagent which may be a substrate or a quencher. In the simplest case, a plot of $\frac{\Phi^0}{\Phi}$ (or $\frac{M^0}{M}$ for emission) vs. concentration of quencher, [Q], is linear obeying the equation:

$$\frac{\Phi^0}{\Phi} \text{ or } \frac{M^0}{M} = 1 + K_{\mathrm{sv}}\,[\mathrm{Q}]$$

In equation (1) K_{sv} is referred to as the Stern–Volmer constant. Equation (1) applies when a quencher inhibits either a photochemical reaction or a photophysical process by a single reaction. Φ^0 and M^0 are the quantum yield and emission intensity radiant exitance, respectively, in the absence of the quencher Q, while Φ and M are the same quantities in the presence of the different concentrations of Q. In the case of dynamic quenching the constant K_{sv} is the product of the true quenching constant k_{q} and the excited state lifetime, τ^0, in the absence of quencher. k_{q} is the bimolecular reaction rate constant for the elementary reaction of the excited state with the particular quencher Q. Equation (1) can therefore be replaced by the expression (2):

$$\frac{\Phi^0}{\Phi} \text{ or } \frac{M^0}{M} = 1 + k_{\mathrm{q}}\,\tau^0\,[\mathrm{Q}]$$

When an excited state undergoes a bimolecular reaction with rate constant k_{r} to form a product, a double-reciprocal relationship is observed according to the equation:

$$\frac{1}{\Phi_{\mathrm{p}}} = \left(1 + \frac{1}{k_{\mathrm{r}}\,\tau^0\,[\mathrm{S}]}\right)\frac{1}{A\cdot B}$$

where Φ_{p} is the quantum efficiency of product formation, A the efficiency of forming the reactive excited state, B the fraction of reactions of the excited state with substrate S which leads to product, and [S] is the concentration of reactive ground-state substrate. The intercept/slope ratio gives $k_{\mathrm{r}}\,\tau^0$. If [S] = [Q], and if a photophysical process is monitored, plots of equations (2) and (3) should provide independent determinations of the product-forming rate constant k_{r}. When the lifetime of an excited state is observed as a function of the concentration of S or Q, a linear relationship should be observed according to the equation:

$$\frac{\tau^0}{\tau} = 1 + k_{\mathrm{q}}\,\tau^0\;[\mathrm{Q}]$$

where τ^0 is the lifetime of the excited state in the absence of the quencher Q.

See also: self-quenching

Source:
PAC, 1996, *68*, 2223 *(Glossary of terms used in photochemistry (IUPAC Recommendations 1996))* on page 2277