Rate Constants for Reactions in Viscous Media: Correlation between the Viscosity of the Solvent and the Rate Constant of the Diffusion-Controlled Reactions

Olea, Andres F.

Thomas, J. K.

The kinetics of the quenching of excited pyrene by several molecules in a variety of hydrocarbon solvents and in a diol are reported. The rate constants for reaction of the excited pyrene are, for the most part, diffusion-controlled and considerably faster than those calculated by use of the Smoluchowski and Stokes?Einstein equations. Measurements of the diffusion constants of the reactants and direct use of the Smoluchowski equation does predict rate constants that are in agreement with those measured. Application of the Stokes?Einstein equation shows that this equation does not calculate the correct diffusion constant for the reactants in the media studied. A free volume theory with transition-state concepts suggests that the diffusion constants of reactants in the liquids used vary as the increase of the square root of the bulk viscosity. This is in very good agreement with the experimental findings. A discussion of what the data mean for diffusion-controlled reactions involving ele