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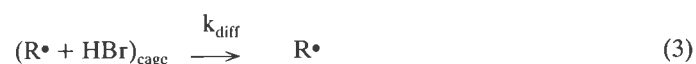
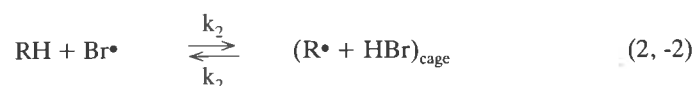
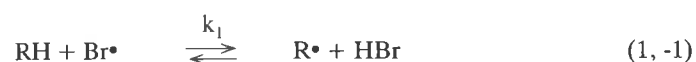
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Free radical bromination internal and external return

The importance of reversible hydrogen atom transfer (external return), (-1), has been established as a kinetically significant process since the early studies of the mechanism of free radical bromination [1]. Only recently [2-4], however, has the reversible reaction been recognized as a significant cage process, (2), which takes place during solution phase brominations. It has been shown that the rate of internal return (-1) is competitive with diffusion (3) and that this competition is viscosity dependent [5].



The viscosity dependence of the kinetic deuterium isotope effect for benzylic bromination at a constant temperature has been determined. As the relative viscosity decreases the deuterium isotope effect increases. Since the viscosity decreases as the temperature increases the magnitude of the TDKIE was determined at constant viscosity. The mechanistic interpretation of the TDKIE for these brominations is therefore subject to modification.

It has been reported that the temperature dependence of the Hammett linear free energy relationship obtained from the com-

petitive bromination of a series of substituted toluenes increases in magnitude as the temperature increases [6]. This observation has been rationalized as being due to entropic control of the free energy of activation. This conclusion was arrived at, however, without considering viscosity dependent internal cage return. When the temperature is held constant and the viscosity is changed, the Hammett ρ value does increase in magnitude (i.e., becomes more negative). However, when a plot of ρ vs. temperature is constructed from values of ρ determined in solvents, which at those temperatures had constant viscosities, the slope of the plot describes normal enthalpic control ; i.e., as the magnitude of ρ became smaller.

The effect of internal and external return on the interpretation of the results of kinetic studies of reversible homolytic reactions will be discussed.

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