INVESTIGATING THE POLARITY EFFECTS ON THE REACTION RATE FOR THE METHYLATION OF TRIBUTYLAmine WITH DIMETHYL CARBONATE

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ABSTRACT

Polar solvents are well known to increase the rate of $S_N2$ reactions. This effect was explored for the methylation of tributylamine with dimethyl carbonate by varying concentrations of reagents and solvents. The Kier Polarity Index (PI) (Kier, L. B., and L. H. Hall. 1981. Derivation and significance of valence molecular connectivity. Journal of Pharmaceutical Science 70: 583-589 and Kier, L. B. 1981. Quantitation of solvent polarity based on molecular structure. Journal of Pharmaceutical Science 70: 930-933.) with methanol as a solvent produced a plot of ln k vs. PI that was linear. This index was chosen for its simplicity in calculations for both individual reagents and mixtures. The methanol model successfully predicted rate constants for reaction mixtures using alcohol solvents, but it did not work well for reaction mixtures using water or aprotic solvents like acetonitrile. This is not surprising because Abraham et al. (Abraham, M. H. 1969. Solvent effects on the free energies of the reactants and transition states in the Menschutkin reaction of trimethylamine with alkyl halides. Chemical Communications 1307-1308.) report organic solvents affect the stability of the transition state and water affects the stability of the reactants. Several groups (e.g. Haberfield, P., A. Nudelman, A. Bloom, R. Romm, and H. Ginsberg. 1971. Enthalpies of transfer of transition states in the Menshutkin reaction from a polar protic to a dipolar aprotic solvent. Journal of Organic Chemistry 36: 1792-1795.) report differing rates for protic and aprotic solvents. Future work will explore other polarity indices in an effort to expand the range of solvents where rates can be successfully predicted.