

PREDICTING THE EFFECTS OF SOLVENT MIXTURES ON THE KEMP REACTIONS

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Reaction rates and selectivity can vary dramatically with choice of solvent.^[1] Hence, understanding and being able to predict the effects that solvents have on reactivity is important as it allows for easier solvent choice and gives the ability to select the 'best' solvent for a given purpose. These solvent effects are typically explained using empirical descriptions of polarity, or measures of the interactions of the solvent, though not all effects can be rationalised.^[1] Rather less studied are the effects of solvent mixtures, which increases the number of potential solvent choices exponentially.

We have been exploring the solvent-solute interactions that affect the reactivity of the Kemp reactions (Scheme 1)^[2,3] using an electrostatic solvent competition model based on supramolecular interactions.^[4] The hydrogen-bond donating (α) and accepting ability (β) of the solvents are used to understand and predict the rate constants for the reactions shown below in mixtures of chloroform and alcohols (ethanol and trifluoroethanol).

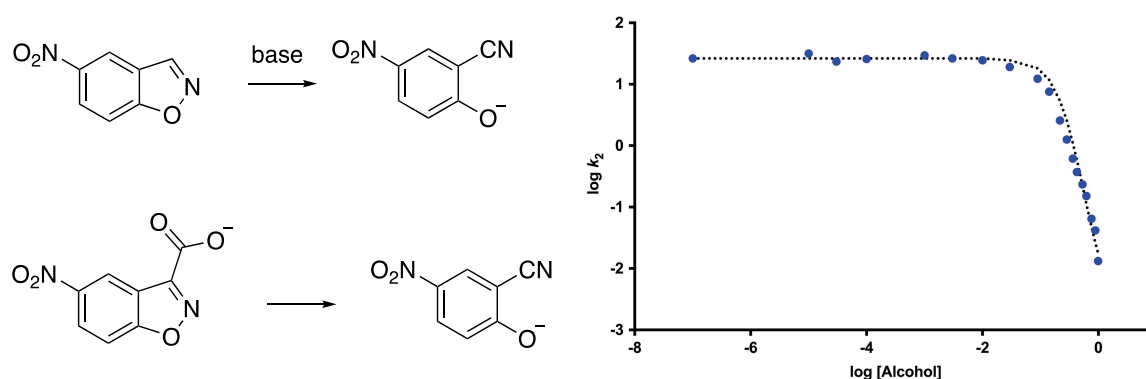


Figure 1. The Kemp elimination of 5-nitro-1,2-benzisoxazole (top-left) and the Kemp decarboxylation of 5-nitro-1,2-benzisoxazole-3-carboxylate (bottom-left), which have been examined in organic solvent mixtures and the dependence of the bimolecular rate constant on the proportion of chloroform and ethanol (right) in the elimination reaction mixture.

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