Kinetic Salt Effect

The kinetic salt effect is the effect of salts preset in solution on the rate of a reaction.

Introduction

In biological systems, salts influence how well proteins and DNA function. Salts are formed by ionic bonds, between a metal and an electromagnetic atom(s). Some examples of salts include NaCl, KCl, and Na2SO4. Salt molecules are able to disassociate, forming cations and anions. An increase in the charge (- or +) of a transition state or an activated complex results in an increase in solvation (creating more order in the system), and causes a decrease in the change of entropy (ΔS). In contrast, a decrease in the charge of the transition state causes an increase in ΔS.

\[
\text{I}^- + \text{C}^+ \rightleftharpoons \text{E}^o \rightarrow \text{Product} \tag{1}
\]

The kinetic salt effect describes the way salts stabilize reactants. For example, in the above reaction, each reactant has a charge. The negatively-charged reactant is stabilized by the positive charges from the salt, and the positively-charged reactant is stabilized by the negative charges from the salt. As a result, the rate at which the reactants come together decreases, thus decreasing the rate at which E forms. Because a charged intermediate is also stabilized in the solution, the half life of the intermediate at equilibrium increases, shifting the reaction toward product formation. Because the rate of the product formation is higher due to increased amounts of the intermediate present on the solution, first order kinetics is used to derive the rate constant equation:

\[
\log K_{TS} = \log K_{TS^o} + 2Z_AZ_B\sqrt{I} \tag{2}
\]

where

- Z is the charge on the cation and ion from the salt. Z_AZ_B is a product value.
- I is the ionic strength. I is also dependent on the solubility of the salt in the reaction mixture. Ionic strength is directly proportional to the solubility of the salt. Changing the ionic strength manipulates the solvation of the reactants and intermediates, thus changing ΔS, and affecting the reaction rate.
- \(\log K_{TS^o}\) is the rate constant without the salt in the reaction mixture.
- A is also a constant for the solvent the solution is in. The A value for water is 0.509 at 298 K.
The relationship between $Z_A Z_B$, $I$, and the rate of the reaction is presented in tabular form below:

<table>
<thead>
<tr>
<th>$Z_A Z_B$</th>
<th>Rate of Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>Increases (salt present in the reaction mixture)</td>
</tr>
<tr>
<td>-</td>
<td>Decreases (the ionic strength increases)</td>
</tr>
</tbody>
</table>

Note: $I=0$ at very dilute salt concentrations or if the salt is inert.

References

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