Medium effects on a C-H bond fission reaction. Solvent and salt effects on the solvolysis of arylsulfonylmethyl perchlorates.
Menninga, Lubbertus

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1976

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Menninga, L. (1976). Medium effects on a C-H bond fission reaction. Solvent and salt effects on the solvolysis of arylsulfonylmethyl perchlorates. s.n.

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
In this thesis, medium effects on the general base-catalyzed solvolysis of two arylsulfonylmethyl perchlorates (1 and 2) are described and analyzed in some detail. For the aqueous media, special attention is given to possible effects due to changes in the diffusonally averaged water structure.

The solvolysis of 1 and 2 is subject to general base-catalysis, involving rate determining proton transfer to a Brønsted base (B). The transition state for proton transfer occurs early on the reaction coordinate, involving little charge separation.

\[
\text{ArSO}_2\text{CH}_2\text{OCIO}_3 + B \rightarrow \text{ArSO}_2\text{CH}^-\text{O}^-\text{ClO}_3^- + B^- \rightarrow \text{ArSO}_2\text{H} + \text{ClO}_3^- + \text{HCOOH}
\]

1, Ar = p-NO\textsubscript{2}C\textsubscript{6}H\textsubscript{4}  
2, Ar = p-CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4}

Chapter I presents a short review on the structural properties of water and aqueous solutions including water-structure effects on chemical phenomena. Furthermore, some emphasis is placed on questions related to basicity and ion solvation in aqueous solutions.

The solvolysis of 1 and 2 in several pure solvents is described in chapter II. It appears that alcohols and some dipolar aprotic solvents exhibit a greater basicity than water towards 1 and 2, despite their low Brønsted basicity. The most important factor determining the solvolysis rate seems to be the inherent basicity or the hydrogen bonding ability of the solvent molecules. No correlation exists between the rates of solvolysis and
the Brønsted basicity or the polarity of the solvent. Consideration of the results described in chapter II leads to the conclusion that the transition state for the solvolysis of 1 and 2 may be characterized by (i) a partial negative charge (possibly delocalized), which shows no or very small hydrogen bonding interactions with the solvent, and (ii) a partial positive charge, residing mainly on the partially transferred proton, and which strongly interacts with the solvent. Our results demonstrate clearly the greater kinetic basicity of several non-aqueous solvents as compared with water.

Dramatic changes in the activation parameters for the solvolysis of 1 and 2 in water upon addition of dioxane, alcohols, or acetonitrile have been observed (chapter III). Minima in $\Delta H^*$ and $\Delta S^*$ occur for solvent compositions at which maximum water structure has been claimed. The change in the inherent basicity of a water molecule upon addition of organic solvents seems to be the main factor influencing the energetics of the solvolysis of 1 and 2. Hydrogen bond formation between the solvent (S) and water causes a charge-induction on the water-oxygen atom ($\Delta^-$), leading to a higher kinetic basicity of water.

\[
\begin{align*}
S & \quad \rightarrow \quad H - O \\
\Delta^+ & \quad \rightarrow \quad \Delta^+ \\
\Delta_s w & \quad \rightarrow \quad \Delta_{sw}
\end{align*}
\]

In addition, an increase in the degree of water structure, which means a greater extent of hydrogen bonding between the water molecules, leads also to an enhancement of the water basicity.

\[
\begin{align*}
\Delta^+ & \quad \rightarrow \quad O \quad \rightarrow \quad H - O \\
\Delta^+ & \quad \rightarrow \quad \Delta_{ww}
\end{align*}
\]
In order to dissect initial state and transition state effects, we have measured the solubility of a model compound in several aqueous organic solvent mixtures. These results clearly indicate that changes in the water structure affect the energetics of the initial state.

The salt effects on the solvolysis of 1 and 2 may be interpreted along similar lines (chapter IV). We observed that the effect of a relevant series of electrolytes on the rate of hydrolysis is dependent on the type of charge and charge density of the ions. A rationalization for the salt effects is advanced, in which it is suggested that electrostatic interaction between ions and the transition state, operating via polarized water molecules, is the dominating factor in determining the kinetic basicity of water. Thus, anion-water interaction causes an increased water basicity, leading to a stabilization of the transition state. Cations will decrease the kinetic water basicity. Support for this explanation has been found in the salt effects in dioxane-water mixtures and in ethanol.

Salt-induced changes of the water structure most likely affect the initial state of the reaction. Unfortunately, this effect is to a great extent obscured in the activation parameters by the above mentioned electrostatic interactions.

Throughout this study, the $\text{OH}^-$ contribution to the solvolysis of 1 and 2 in the different media is neglected. Justification for this neglect is found in the value of $k_{\text{OH}^-}$ for the hydrolysis of 2, as measured by the stopped flow technique (appendix).