EFFECT OF HIGHER ORDER SOLVATION AND TEMPERATURE ON S\textsubscript{N}2 AND E2 REACTIVITY (POSTPRINT)

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Effect of Higher Order Solvation and Temperature on $S_N2$ and $E2$ Reactivity

Nicole Eyet\(^1\), Joshua J. Melko, Shaun G. Ard, and Albert A. Viggiano

The reactivity of microsolvated fluoride ions, $F(CH_3OH)_{2-}$, with methyl, ethyl, n-propyl, and t-butyl bromide is evaluated over a broad range of temperatures. Significant decreases in reactivity are observed as either solvation or temperature increases. Increasing solvation increases sensitivity to the reaction barrier as revealed by a larger temperature dependence. These reactions are dominated by an $SN_2$ mechanism for the methyl bromide reaction, while the $SN_2$ and $E2$ mechanisms compete for the reactions with ethyl and n-propyl bromide reactions. The elimination mechanism, with some association, dominates the t-butyl bromide reactions. In all cases the unsolvated bromide ion is the primary ionic product. Branching ratios are discussed in both qualitative and quantitative terms for all reactions at 300 K.

Flow tube, Time-of-flight, Kinetics, Ion-Molecule Reaction

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14. ABSTRACT
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Abstract

The reactivity of microsolvated fluoride ions, $F^-(CH_3OH)_{n-2}$, with methyl, ethyl, $n$-propyl, and $t$-butyl bromides is evaluated over a broad range of temperatures. Significant decreases in reactivity are observed as either solvation or temperature increases. Increasing solvation increases sensitivity to the reaction barrier as revealed by a larger temperature dependence. These reactions are dominated by an $S_N2$ mechanism for the methyl bromide reaction, while the $S_N2$ and $E2$ mechanisms compete for the reactions with ethyl and $n$-propyl bromide reactions. The elimination mechanism, with some association, dominates the $t$-butyl bromide reactions. In all cases the unsolvated bromide ion is the primary ionic product. Branching ratios are discussed in both qualitative and quantitative terms for all reactions at 300K.

1. Introduction

The fundamental differences between gas-phase and solution-phase reactions raise interesting questions about the transition between the gas phase and solution [1]. These differences include extreme variation in both reaction rate constants and mechanisms. The addition of a small number of solvent molecules to gas-phase ions provides insight into this transition. Recent investigations of microsolvated ions have addressed the impact of solvation on a series of alkyl bromide reactants. Methyl, ethyl, $n$-propyl, and $t$-butyl halides, which has been investigated as a function of solvent [15,18,19]. The sterically bulky neutral reactant inhibits the $S_N2$ pathway and the reaction proceeds through the $E2$ pathway. The mechanism was affected only when extremely weakly bound solvents were used for microsolvating. In all cases, solvation of the nucleophile reduces the reaction rate, often dramatically [16,17]. This decrease has been shown to be a result of an increase in the rate limiting barrier height due to solvation [20–22].

Theoretical work has suggested that increasing the solvation of the reactant ion for a reaction that has competing pathways will stabilize the $S_N2$ transition state more than the elimination transition state, making the $S_N2$ pathway lower in energy [23]. It has been suggested that even two strongly bound solvent molecules may be enough to promote this change in mechanism.

In this work, we evaluate the effects of temperature and solvation on a series of alkyl bromide reactants. Methyl, ethyl, $n$-propyl, and $t$-butyl bromide are allowed to react with $F^-(CH_3OH)_{n-2}$. These neutral reagents allow for $S_N2$, E2, and the competition of the two mechanisms to be investigated. Reaction rate constants and product ion branching ratios are determined for each reactant and at temperatures ranging from ~150 K to 450 K.

2. Experimental

Measurements reported here were performed using the selected ion flow tube (SIFT) apparatus at the Air Force Research Laboratory, Space Vehicles Directorate, Kirtland AFB, NM 87117-5776, United States.

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Fluoride ions were produced from electron impact on nitrogen trifluoride. Solvated ions, $F^-(\text{CH}_3\text{OH})_{\text{n},2}$, were produced by adding methanol to the source region of the instrument. Efforts were made to gently inject a specific species and minimize fragmentation. When instrument conditions did not allow, an ion with an “extra” solvent molecule was injected with sufficient force to remove the most weakly bound solvent molecule. In either case, several reactant ions were present in the reaction flow tube at times; these ions have the ability to produce the same products, significantly complicating the determination of branching ratios but not rate constants. A heated neutral injector is used to introduce neutral reactants at low temperatures. Stainless steel tubing (1/8 in.) silver soldered to a thicker (1/4 in.) stainless tube is electrically isolated from the flow tube at opposite sides of the alkyl group [15]. In this geometry, the bulky neutral product lies between the newly formed ionic product and the smaller neutral products and thus hinders, but doesn’t necessarily prevent, the formation of solvated products. In cases in which more than one solvated product may form, the more strongly bound product is found in higher quantity; for example $\text{Br}^- (\text{HF})$ is more strongly bound than $\text{Br}^- (\text{CH}_3\text{OH})$.

Trends within the observed branching ratios are also evident. Reaction of $F^-(\text{CH}_3\text{OH})$ with methyl bromide at 300 K produces 80% $\text{Br}^-$ and 20% $\text{Br}^- (\text{CH}_3\text{OH})$. More of the solvated product is found for $F^-(\text{CH}_3\text{OH})_{\text{n},2}$ reacting with this alkyl halide where 60% $\text{Br}^-$ and 40% $\text{Br}^- (\text{CH}_3\text{OH})$ are formed. The ability of the buffer gas to alter the nascent distribution through thermal dissociation of the association product was not investigated. The geometry of the doubly solvated ion has been calculated previously [29]. In this structure, the methanol hydrogen bond of each alcohol interacts with the fluoride ion and are ~180° away from each other. The symmetry of this structure suggests that there should be approximately twice as many opportunities for reactions to produce a solvated product ion, consistent with what is observed. This is in line with the previously measured microsolvated $\text{Sn}_2$ reactions [12,16] where the solvation of the leaving group increases as the solvation of the reactant ion increases.

A similar trend is observed for $F^-(\text{CH}_3\text{OH})$ with $t$-butyl bromide. Branching ratios measured here are consistent with the previously measured branching ratios [19] of $\text{Br}^- 85\%$, $\text{Br}^- (\text{HF}) 15\%$, and trace amounts of $\text{Br}^- (\text{CH}_3\text{OH})$. Branching ratios of $F^-(\text{CH}_3\text{OH})_{\text{n},2}$ with $t$-butyl bromide show $\text{Br}^-$ to be a major product and both $\text{HF}$ and $\text{Br}^- (\text{CH}_3\text{OH})$ are minor products. Reactions of $F^-(\text{CH}_3\text{OH})$ and $F^-(\text{CH}_3\text{OH})_{\text{n},2}$ with ethyl and $n$-propyl bromide follow similar patterns. Not surprisingly, solvation of the product ion is more likely to occur with doubly solvated reactants. Furthermore, as the size of the alkyl group increases from 1 to 4 carbons, the amount of HF-solvated products increases from none, to trace, to minor products... at 300 K.

The mechanisms for the competing $\text{Sn}_2$ and $\text{E}_2$ mechanisms of the alkyl halide reactions are illustrated in Fig. 1. As there is no alpha carbon to make a double bond, reactions with methyl halides...
HF-solvated products are observed for the reactions with methyl and ethyl bromide. However, measurable (>10%) amounts of solvated reactants, no HF solvated ionic products are observed with the existence of the competing elimination mechanism. For singly solvated reactant ions, it was previously shown that the non-solvated reactant ions, it was previously shown that the competition between these two mechanisms changed as a result of increasing solvation, we would expect an alteration of these trends. However, the reaction rate constant dependence of both pathways with increasing solvation, but preferentially stabilizing the SN2 transition state at a lower energy activation energy of both pathways with increasing solvation, but increasing microsolvation would promote the substitution pathway.

The results presented here represent the first investigation of how microsolvation affects this competition. The direct observation of elimination products, e.g. products containing HF, proves the existence of the competing elimination mechanism. For singly solvated reactants, no HF solvated ionic products are observed with methyl and ethyl bromide. However, measurable (>10%) amounts of HF-solvated products are observed for the reactions with n-propyl and t-butyl bromide. For doubly solvated reactant ions, trace amounts of HF-solvated products are observed for the reaction with ethyl bromide; minor amounts of HF-solvated products are observed for the n-propyl and t-butyl bromide reactions. These results describe a system in which the transition from SN2 to E2 mechanism occurs gradually as the neutral reagent’s alkyl group gets more hindered, consistent with evidence for this progression originally postulated by DePuy et al. [33]. For reactions with non-solvated reactant ions, it was previously shown that the reaction efficiency was either constant or increased slightly when comparing reactions with methyl and ethyl bromide. The efficiency then decreased when studying the reaction with n-propyl bromide. This has been attributed to the general decline in SN2 efficiency. An increase in the efficiency when comparing these rate constants to the rate constant determined for t-butyl bromide reactions is explained as an increase in the prevalence of the elimination pathway. Here, the bare fluoride ion reaction efficiencies approach unity for the reactions with methyl, ethyl and n-propyl bromide. A slight decrease in efficiency, due to the less exothermic reaction pathway, is observed for the reaction with t-butyl bromide. If the competition between these two mechanisms changed as a result of solvation, we would expect an alteration of these trends. However, both the singly solvated and the doubly solvated fluoride ion follow the previously observed trend.

For all the reactions above room temperature (>300 K) with a given neutral reagent, rate constants for the reactions with bare fluoride ions are the largest, and rate constants for reactions with doubly solvated fluoride are the smallest. This is consistent with previously studied methanol solvated reactions [19,27]. At other temperatures in the range of 150–400 K the reactions generally follow the same trend (Fig. 2). However, the reaction rate constant measured for F− (CH3OH)2 + C4H9Br was larger than the reaction rate constant measured for F− (CH3OH)2 + C2H5Br at both 200 and 250 K. Interestingly, the decrease in efficiency with increasing solvation was also somewhat muted for the reactions with C3H7Br, though the reasons behind these observations are unknown.

### Table 1

<table>
<thead>
<tr>
<th>Reaction</th>
<th>k (10−10 cm² molec⁻¹ s⁻¹) at 300 K</th>
<th>Reaction efficiency (k/kσ0)</th>
<th>Ionic product</th>
<th>BR at 300 K</th>
<th>ΔHrxn SN2 (kJ mol⁻¹)</th>
<th>ΔHrxn E2 (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F− + CH3Br</td>
<td>28.2</td>
<td>1.06</td>
<td>Br⁻</td>
<td>1.0</td>
<td>−164</td>
<td>−</td>
</tr>
<tr>
<td>F− (CH3OH) + CH3Br</td>
<td>1.48</td>
<td>0.08</td>
<td>Br⁻</td>
<td>0.8</td>
<td>−288</td>
<td>−</td>
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<tr>
<td>F− (CH3OH)2 + CH3Br</td>
<td>0.018</td>
<td>0.001</td>
<td>Br⁻</td>
<td>0.6</td>
<td>−210</td>
<td>−</td>
</tr>
<tr>
<td>F− + C2H5Br</td>
<td>28.3⁺</td>
<td>0.89⁺</td>
<td>Br⁻</td>
<td>1.0</td>
<td>−179</td>
<td>−119</td>
</tr>
<tr>
<td>F− (CH3OH) + C2H5Br</td>
<td>5.87</td>
<td>0.28</td>
<td>Br⁻</td>
<td>0.85</td>
<td>−303</td>
<td>−243</td>
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<tr>
<td>F− (CH3OH)2 + C2H5Br</td>
<td>2.46</td>
<td>0.14</td>
<td>Br⁻</td>
<td>Major</td>
<td>−218</td>
<td>−160</td>
</tr>
<tr>
<td>F− + C3H7Br</td>
<td>28.4</td>
<td>0.89</td>
<td>Br⁻</td>
<td>1.0</td>
<td>−167</td>
<td>−134</td>
</tr>
<tr>
<td>F− (CH3OH) + C3H7Br</td>
<td>2.4</td>
<td>0.11</td>
<td>Br⁻</td>
<td>Major</td>
<td>−291</td>
<td>−258</td>
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<tr>
<td>F− (CH3OH)2 + C3H7Br</td>
<td>0.02</td>
<td>0.001</td>
<td>Br⁻</td>
<td>Major</td>
<td>−206</td>
<td>−173</td>
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<tr>
<td>F− + C4H9Br</td>
<td>16.9</td>
<td>0.51</td>
<td>Br⁻</td>
<td>1.0</td>
<td>−</td>
<td>−123</td>
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<tr>
<td>F− (CH3OH) + C4H9Br</td>
<td>6.17</td>
<td>0.28</td>
<td>Br⁻</td>
<td>Major</td>
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<td>−186</td>
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<tr>
<td>F− (CH3OH)2 + C4H9Br</td>
<td>0.367</td>
<td>0.02</td>
<td>Br⁻</td>
<td>Major</td>
<td>−162</td>
<td>−101</td>
</tr>
</tbody>
</table>

* Rate constant at 250 K.
* These values are consistent with previously measured values of 85% Br⁻, 12% Br⁻ (HF), and 3% Br⁻ (CH3OH) [18].
The temperature dependence of the unsolvated fluoride ion was the least pronounced for each of the neutral reactants. This is consistent with the rate constants approaching the collision controlled limit (50–100% efficient at 300 K). The temperature dependences of these reactions were $T^{-0.7}$, $T^{-0.6}$, $T^{-0.4}$, and $T^{-0.2}$ for reactions with methyl, ethyl, $n$-propyl, and $t$-butyl bromide respectively. This trend suggests the barrier heights decrease slightly with increasing neutral reactant size. Interestingly, the least efficient reaction had the smallest temperature dependence, consistent with a change in mechanism.

Reactions of the singly solvated fluoride ions were more sensitive to temperature than their unsolvated counterparts, in part because they are less efficient. Collisional efficiencies of only 8–28% were found at 300 K. The temperature dependences of these reactions were $T^{-1}$, $T^{-2}$, $T^{-3}$, $T^{-4}$, for reactions with methyl, ethyl, $n$-propyl, and $t$-butyl bromide respectively. The temperature coefficient follows the same trend as the efficiency, e.g. more efficient reactions have less steep temperature dependences. This is expected behavior, as higher barriers lead to both slower rates and often larger temperature dependences.

Doubly solvated fluoride ions have a more complicated temperature dependence and may be influenced by other factors. At 300 K, efficiencies vary as 0.1%, 14%, 0.1% and 2% for the reactions with methyl bromide, ethyl bromide, $n$-propyl bromide, and $t$-butyl bromide, respectively. In all cases, the efficiency decreases with the number of solvent molecules implying that the rate limiting barrier gets closer to the energy of the reactants, limiting reactivity. $F^-(CH_3OH)_2$ reacts with CH$_3$Br at rates that approach our detection limit over the temperature range studied. The temperature dependence showed a very small positive dependence but that may be a function of the reactivity being at the detection limit or may imply a near zero barrier. More pronounced temperature dependences are observed for the reaction with ethyl bromide ($T^{-12}$) and for the reaction with $n$-propyl bromide ($T^{-10}$). Reactions with $t$-butyl bromide have a steep temperature dependence below ~300 K. Above these temperatures, the reaction rate constant becomes approximately constant at an order of magnitude above our detection limit. These temperature dependences are exceedingly large. Even though the observed products are predicted, these large dependences may hint at hidden mechanisms. Previously in our laboratory temperature dependences have shown that mechanisms involving association, ligand switching, and thermal dissociation/reaction (with He) were occurring [9,14]. In the previous example, the hidden mechanism became apparent because the standard mechanism was endothermic, e.g. production of Br$^-$ from the reaction of Cl$^-(D_2O)$ with CH$_3$Br. In the present study, all the observed channels are exothermic. The presence of an association product suggests similar issues may be present here, although the complication of multiple reactant ions makes confirmation difficult.

The large temperature dependence also hints that hidden reactions may be occurring at low temperature. For instance association may occur at levels significantly above the trace detected. This stabilized complex $F^-(CH_3OH)_2(RBr)$ can then be activated by helium similar to the example given in the previous paragraph. The barrier to go to Br$^-$ containing products would be smaller than the dissociation to reactants. The leveling out of the dependence at high temperature for the $t$-butyl bromide reaction implies that the effect of such chemistry no longer occurs.

4. Conclusion

We have studied the temperature dependences of a series of reactions of $F^-(CH_3OH)_n$ ($n=0–2$) with alkylbromides. As has been observed previously in other systems, solvation and temperature decrease rate constants for these reactions. The temperature
dependences go from small to moderate to large as n goes from 0–2. These reactions primarily occur via an S$_n$2 mechanism for the methyl bromide reaction, while the S$_2$2 and E2 mechanisms compete for the ethyl and n-propyl bromide reactions. The t-butyl bromide reactions proceed predominantly through an elimination mechanism, with some association occurring. For all reactions, the unsolvated ions dominate the products, but both Br$^-$ (HF) and Br$^-$ (CH$_2$OH)$_2$ were observed; solvated product ions become more likely as the reactant ion becomes more solvated. For n = 2, the elimination product is seen as Br$^-$ (HF) for all reactions where it is possible, and more so in sterically hindered species as the S$_2$2 pathway gets more difficult. Finally, the strong temperature dependences of the doubly solvated anion may hint at other reaction pathways.

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