Temperature Dependences of the Rate Constants and Branching Ratios for the Reactions of $F^-(H_2O)_{0-5}$ with CH_3Br

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The effects of solvation, isotopic substitution, and temperature on the reactions of $F^-(H_2O)_{n=0-5}$ with CH_3Br have been studied. The reaction of $n = 0$ produces Br^- as the exclusive ionic product and has a rate which is fast, approaching the collision rate, with a slight negative temperature dependence of $T^{-0.9\pm0.1}$. The reaction of $n = 1$ is a factor of 3 slower with a slightly larger negative temperature dependence, $T^{-1.1\pm0.05}$. The main ionic product is Br^-, with smaller amounts of $Br^-(H_2O)$ also formed. Substituting D_2O for H_2O causes the $n = 1$ rate constant to increase slightly. The $n = 2$ reaction has a much slower rate and produces three ionic products: Br^-, $Br^-(H_2O)$, and $F^-(H_2O)_2(CH_3Br)$. The $n = 3$ reaction is immeasurably slow. The rate constants for the $n = 4$ and 5 reactions are greater than those for the $n = 3$ reaction. The ionic products of these reactions are $F^-(H_2O)_3$ and $F^-(H_2O)_4$, respectively.

Introduction

A considerable amount of work has focused on gas phase bimolecular nucleophilic displacement reactions (S_N2). Previously, we have used a variable temperature-selected ion flow tube (SIFT) to study the effect of hydration level and temperature on the rate constants and products of the S_N2 reactions $OD^-(D_2O)_n + CH_3Cl$, $OH^-(H_2O)_n + CH_3Br$, and $Cl^-(D_2O)_n + CH_3Br$.[1−3] Our results corroborate other experimental[4−9] and theoretical studies[10−14] by showing that nucleophilic displacement reactions have rates which decrease with increasing hydration and preferentially lead to unhydrated products. In addition, we have found that in the absence of a fast S_N2 reaction channel other mechanisms such as association and ligand switching can become important.[2,3] Here we extend our previous work by studying the reactions of $F^-(H_2O)_{0-5}$ with CH_3Br.

Experimental Section

Experiments were performed in a variable temperature SIFT. The apparatus has been described in detail elsewhere,[15−17] and only information pertinent to the present experiments will be discussed. A mixture of H_2O and Ar, held at 4 atm, was expanded through a 25 μm orifice and then ionized with an electron filament (ThO_2/Ir). $F^-(H_2O)_n$ ions were produced by adding CF_4 to the expansion just downstream of the ionization region. The resulting ions were sampled with a blunt skimmer and passed through a quadrupole mass filter. The selected ions were injected into the flow tube though a Venturi inlet. Water was not added to the flow tube, so a portion of the hydrates inevitably dissociated. The kinetics of a given hydrate could only be characterized accurately when the dissociation time scale was greater than the flow tube residence time (10 ms). This restriction set the upper temperature limit for the $n \geq 3$ reaction studies.

Reactions of $F^-(H_2O)_{n=1}$ were studied by adjusting the upstream quadrupole mass filter to pass only $F^-(H_2O)$. At room temperature this technique produced approximately 90% $F^-(H_2O)$, with the remainder being F^- resulting from dissociation. To study the $n = 2$ and 3 reactions, we injected the $n + 1$ cluster ion at a high enough energy to dissociate one water molecule. For the $n = 4$ and 5 reactions, we injected a broad distribution of clusters by adjusting the upstream quadrupole to pass $F^-(D_2O)_{n>4}$ ions. The flow tube temperature was then set to a value which caused the majority of the clusters to thermally decompose into one or two clusters in the upstream region of the flow tube.[3]

The CH_3Br was added without purification. At low temperatures, the reactant inlet was heated to prevent freezing in the inlet line; this technique has been described previously.[18] The CH_3Br had low levels of reactive impurities as found in our previous study of $OH^-(H_2O)_n$ reacting with CH_3Br.[2] In particular, we found that the maximum HBr concentration was approximately 1 part in 10^4.

The reported rate constants are the mean of three or more measurements. Uncertainty in the absolute rate constants is estimated as 25%, and the uncertainty in the relative rate constants is 15%.[15] The branching fractions were calculated without a mass discrimination correction. The correction is minimized by taking data under low-resolution conditions.

Results

Figure 1 shows the rate constants measured for $F^-(H_2O)_{0-5} + CH_3Br$ as a function of temperature. Table 1 contains the rate constants obtained at temperatures near 185 and 300 K. The $n = 0$ reaction was studied at temperatures ranging from 180 to 500 K. The observed rate constants are large, approaching the collision limit.[19,20] A power law expression of $(3.1 \times 10^{-7})T^{-0.9\pm0.1}$ cm^3 s^{-1} was fitted to the data. The only observed ionic product was Br^-:

$$F^- + CH_3Br \rightarrow Br^- + CH_3F \qquad \Delta H^0 = -173 \text{ kJ mol}^{-1} \tag{1}$$

The thermochemical data for reaction 1 and all subsequently listed reactions have been taken from Lias et al.[21] and Kessee and Castleman.[22] The results for reaction 1 are in excellent

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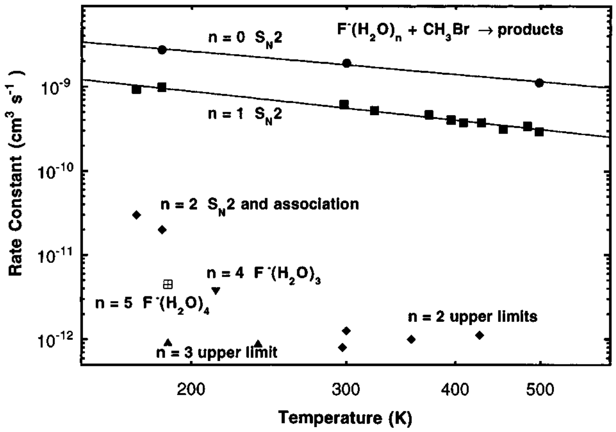

Figure 1. Rate constants for the reactions of $F^-(H_2O)_n$ plus CH_3Br as a function of temperature. Circles, squares, diamonds, triangles, inverted triangles, and boxed plusses represent $n = 0-5$, respectively.

TABLE 1: Rate Constants Measured for $F^-(H_2O)_n$ + CH_3Br at Temperatures Near 185 and 300 K

n	*k* ($cm^3\ s^{-1}$) 185 K	*k* ($cm^3\ s^{-1}$) 300 K
0	2.7×10^{-9}	1.9×10^{-9}
1	9.9×10^{-10}	6.2×10^{-10}
2	2.0×10^{-11}	1.3×10^{-12}
3	$<1.0 \times 10^{-12}$	
4	$(3.7 \times 10^{-12})^a$	
5	4.5×10^{-12}	

[a] Value obtained at 210 K.

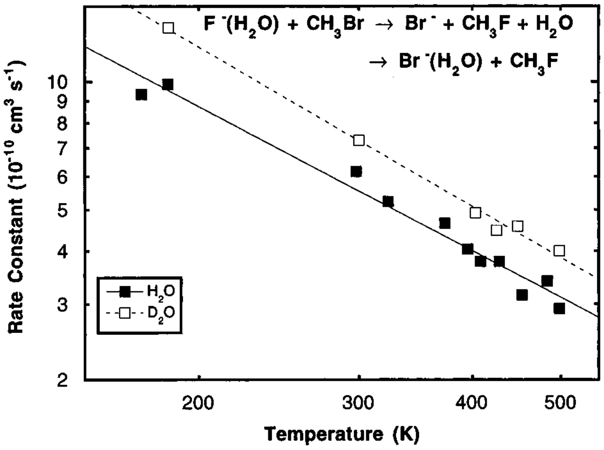

Figure 2. Rate constants for the reactions of $F^-(H_2O)$ and $F^-(D_2O)$ plus CH_3Br as a function of temperature. Filled squares and open squares represent $F^-(H_2O)$ and $F^-(D_2O)$, respectively.

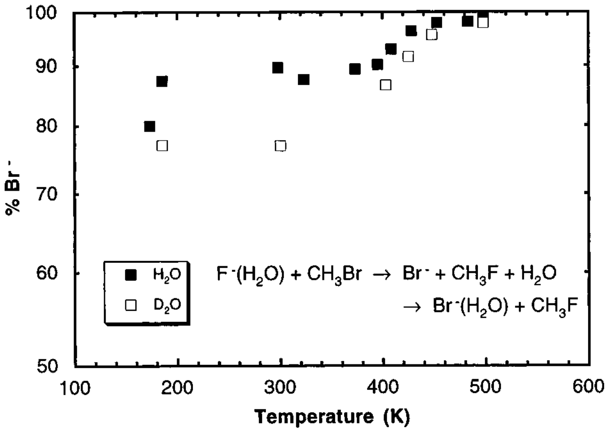

Figure 3. Branching ratio for the reactions of $F^-(H_2O)$ and $F^-(D_2O)$ plus CH_3Br as a function of temperature. Filled squares and open squares represent $F^-(H_2O)$ and $F^-(D_2O)$, respectively.

agreement with a previous SIFT measurement from our laboratory[23] and with the results of O'Hair et al.,[9] the only other reported SIFT measurement at room temperature. Several other groups have obtained results that are consistently 30−60% lower than these values using other techniques.[7,24−26] No explanation for the discrepancy is obvious.

The $n = 1$ rate constant was studied at temperatures ranging from 173 to 500 K. A comparison with the $n = 0$ data shows that the addition of one water molecule decreases the reaction rate by about a factor of 3. A power law expression of $(3.5 \times 10^{-7})T^{-1.1\pm0.05}$ $cm^3\ s^{-1}$ was fitted to the data. Thus, the temperature dependence is slightly more negative than found for $n = 0$. We studied the $n = 1$ reaction for both H_2O and D_2O. The rate constants for both these species are shown in Figure 2. Although the $F^-(D_2O)$ reaction is about 25% faster than the $F^-(H_2O)$ reaction, a similar temperature dependence is observed. Two ionic products are observed: Br^- and $Br^-(H_2O)$ (or $Br^-(D_2O)$),

$$F^-(H_2O) + CH_3Br \rightarrow Br^- + CH_3F + H_2O \qquad \Delta H^0 = -76\ \text{kJ mol}^{-1}$$

$$\rightarrow Br^-(H_2O) + CH_3F \qquad \Delta H^0 = -128\ \text{kJ mol}^{-1} \quad (2)$$

The temperature dependence of the branching ratio is shown in Figure 3. At all temperatures the predominant product is Br^-. The percentage of Br^- increases from about 80% at low temperature to essentially 100% at 500 K. Slightly more Br^- is found for $F^-(D_2O)$ than for $F^-(H_2O)$. A previous study by Bohme and Raksit[7] reported the $n = 1$ rate to be almost a factor of 10 smaller than the $n = 0$ rate, a much greater reduction than found here. However, the Bohme and Raksit[7] measurements were performed in a flowing afterglow apparatus that had several F^- hydrates present simultaneously. Presumably, the $n = 1$ and 2 clusters were in equilibrium and the $n = 1$ rate was influenced by the presence of the extremely slow $n = 2$ reaction. More recently, O'Hair et al.[9] found values about 20% lower than our results but well within the combined error limits. They also observed Br^- to be the major product and a similar isotope effect.

The $n = 2$ reaction was studied at temperatures ranging from 173 to 426 K. At temperatures greater than room temperature the reaction was so slow that only an upper limit of 1×10^{-12} $cm^3\ s^{-1}$ could be determined for the rate constant. This value is consistent with the upper limit of 5×10^{-13} $cm^3\ s^{-1}$ reported by Bohme and Raksit.[7] At low temperatures the rate constants are large enough for measurement but still a factor of 40 smaller than the $n = 1$ rate. Three products channels were observed,

$$F^-(H_2O)_2 + CH_3Br \rightarrow Br^- + CH_3F + 2H_2O \qquad \Delta H^0 = -6\ \text{kJ mol}^{-1}$$

$$\rightarrow Br^-(H_2O) + CH_3F + H_2O \qquad \Delta H^0 = -59\ \text{kJ mol}^{-1}$$

$$\rightarrow F^-(H_2O)_2CH_3Br \qquad \Delta H^0 = ? \quad (3)$$

The branching into the three channels was 68% into Br^-, 4% into $Br^-(H_2O)$, and 28% into $F^-(H_2O)_2(CH_3Br)$. These results pertain to an average of data obtained at 173 and 185 K and a pressure of 0.38 Torr. While production of $CH_3F + Br^-(H_2O)_2$ is the most exothermic channel, it was not observed to occur.

The $n = 3$ reaction was studied at 240 and 190 K. At both temperatures, the reaction is so slow that products could not be observed and only an upper limit of 1×10^{-12} cm^3 s^{-1} could be placed on the rate constant A literature comparison is not possible since there have been no previous measurements of the rate constants for $n = 3$ and higher. The $n = 4$ and 5 reactions are faster than the $n = 3$ reaction. The $n = 4$ reaction was studied at 213 K and $n = 5$ reaction was studied at 190 K. Both reactions have rate constants of approximately 4×10^{-12} cm^3 s^{-1}. The only observed ionic products were $F^-(H_2O)_{n-1}$. We have observed similar behavior in the reactions of $Cl^-(H_2O)_n$ with CH_3Br.[3] Based on those results, we postulate the following mechanism: The first step is ligand switching,

$$F^-(H_2O)_n + CH_3Br \rightarrow F^-(H_2O)_{n-1}(CH_3Br) + H_2O \quad (4)$$

which is followed by thermal decomposition,

$$F^-(H_2O)_{n-1}(CH_3Br) + He \rightarrow F^-(H_2O)_{n-1} + (CH_3Br) + He \quad (5)$$

The rate determining step is likely to be the ligand-switching step, which would be slightly endothermic thereby resulting in the small rate constant. The thermal decomposition step is fast enough to keep the concentration of $F^-(H_2O)_{n-1}(CH_3Br)$ at undetectable levels.

Discussion

The dynamics of gas phase S_N2 reactions have previously been explained in terms of a double-well potential energy surface.[4,25,27] This model maintains that an S_N2 reaction of $X^-(H_2O)_n + CH_3Y$ proceeds by forming a collision complex, $(H_2O)_nX^-(CH_3Y)$, which then passes through a Walden inversion transition state to form an exit−channel complex, $(XCH_3)Y^-(H_2O)_n$. The exit−channel complex then dissociates to form the products $CH_3X + Y^-(H_2O)_n$. Hydration stabilizes the reactants more than it does the transition state because the charge in the transition state is less localized. As a result, the addition of each water molecule leads to a higher central barrier and hence a decreased reaction rate. This qualitative model has been supported by subsequent experimental[1−9] and theoretical studies;[10−14] however, it is now known that transfer of water molecules to the leaving ion is inefficient, and thus highly hydrated product ions are not observed.[1−3,9]

Our results for the $F^-(H_2O)_n + CH_3Br$ reaction are also consistent with the qualitative model. In the case of $F^-(H_2O)_n + CH_3Br$, the addition of one water molecule to the bare fluoride ion decreases the reaction rate by a factor of 3. The addition of the second water decreases the rate by greater than a factor of 40, and the third water molecule makes the rate immeasurably slow. This decrease in S_N2 reactivity is similar to that observed for $OH^-(H_2O)_n + CH_3Br$.

For the $n = 0-3$ reactions we find Br^- to be the major ion product, with the amount of $Br^-(H_2O)$ formed always less than 25% and decreasing with increasing temperature. Once again, this result is similar to that found for $OH^-(H_2O)_n + CH_3Br$ with the exception that the fraction of $Br^-(H_2O)$ production was independent of temperature for the OH^- case. The reason for this difference is uncertain.

Increasing hydration level from $n = 0$ to $n = 1$ increases the magnitude of the negative temperature dependence. A similar result has been observed for the cases of $OH^-(H_2O)_n + CH_3Br$ and $OD^-(D_2O)_n + CH_3Cl$.[1,2] This effect is likely to be the result of the increased central barrier height: Magnera and Kerbarle[28] have performed a RRKM simulation on the S_N2 reaction of Cl^- + n-butyl chloride for a variety of central barrier heights. They found that when the central barrier height (as referenced from the potential energy of the free reactants) is less than −17 kJ mol^{-1}, the temperature dependence becomes more negative as the central barrier height is increased. The central barrier height for the $F^- + CH_3Br$ reaction has been calculated to be −67 kJ mol^{-1}. While the barrier height for the $F^-(H_2O) + CH_3Br$ reaction is not known, it is likely to be greater than that of the $F^- + CH_3Br$ reaction and within the range necessary the lead to a slight increase in the negative temperature dependence. The calculations of Magnera and Kerbarle show that for barrier heights greater than −17 kJ mol^{-1} the temperature dependence becomes more positive as the barrier height is increased. At this stage the nucleophilic displacement reaction would be very slow, perhaps too slow for accurate measurement. However, we have observed a slight positive temperature dependence in the reaction of $OH^-(H_2O)_2$ with CH_3Br, at temperatures of 300 K and higher.[2]

When the nucleophilic displacement reaction channel becomes inefficient, association or endothermic ligand switching reaction channels can become important. For $n = 2$ we observe a significant amount of association to form $F^-(H_2O)_2CH_3Br$, while for $n = 4$ and 5 we observe ligand switching. We have previously observed association for the $OH^-(H_2O)_n + CH_3Br$ reaction at $n = 2$ and 3, and ligand switching for the $Cl^-(D_2O)_n + CH_3Br$ reaction at $n \geq 1$. It is somewhat surprising that F^- hydrates ligand switch with CH_3Br while OH^- hydrates do not. One possible explanation is that ligand switching is more endothermic for the OH^- case because the hydration energies of OH^- are greater than those of F^- and/or because the methyl bromide complexation energy of OH^- is less than that of F^-. Small energy differences, on the order of 5 kJ mol^{-1}, would be sufficient to cause ligand switching to be observed for F^- and not for OH^-. The existing experimental[22,29] and theoretical data,[30−34] while indicating that the relevant energies for F^- and OH^- are similar, are not sufficiently accurate to test this explanation.

Conclusions

We have now used the SIFT technique to study the effect of hydration and temperature on three S_N2 reactions: $F^-(H_2O)_n + CH_3Br$, $Cl^-(D_2O)_n + CH_3Br$, and $OH^-(H_2O)_n + CH_3Br$. These results along with those from other laboratories can be explained in terms of a potential energy surface with a transition state that is not as efficiently stabilized by hydration as the reactants, resulting in reaction rates which decrease with increasing hydration levels. In the absence of an efficient S_N2 reaction channel, other mechanisms become important such as association and endothermic ligand switching.

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