

Temperature Dependences of the Rate Constants and Branching Ratios for the Reactions of $\text{OH}^-(\text{H}_2\text{O})_{0-4} + \text{CH}_3\text{Br}$

A. A. Viggiano,* Susan T. Arnold,† Robert A. Morris, A. F. Ahrens,‡ and P. M. Hierl§

Phillips Laboratory, Geophysics Directorate, Ionospheric Effects Division (GPID), 29 Randolph Road, Hanscom AFB, Massachusetts 01731-3010

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Various effects of solvation, isotopic substitution, and temperature on the reactions of $\text{OH}^-(\text{H}_2\text{O})_{n=0-4}$ with CH_3Br are reported. Increasing solvation is found to decrease reactivity dramatically as has been observed previously. For $n = 0$ the rate constant is large, and the temperature dependence is small, $T^{-0.58}$; Br^- is the only product. For $n = 1$ the rate constant is about a factor of 1.5 smaller than that for the $n = 0$ reaction, and the temperature dependence is $T^{-1.6}$. This reaction produces about 90% Br^- and 10% $\text{Br}^-(\text{H}_2\text{O})$, with this ratio roughly independent of temperature. The rate constant for the $n = 2$ reaction is almost 2 orders of magnitude lower than that for $n = 1$. The $n = 2$ reaction is complicated in that the low-temperature behavior depends on the identity of the buffer gas. In a He buffer at all temperatures, only Br^- and $\text{Br}^-(\text{H}_2\text{O})$ products are observed, while in a H_2 buffer another product, $\text{OH}(\text{H}_2\text{O})_2\text{CH}_3\text{Br}^-$, is observed at low temperatures in addition to the above products. The temperature dependence of this reaction is flat in a He buffer over the entire experimental temperature range and in a H_2 buffer in the range 300 K and above. The temperature dependence in a H_2 buffer is about T^{-4} for temperatures below 300 K. The $n = 3$ reaction is about a factor of 10 slower than the $n = 2$ reaction at 163 K and proceeds entirely by association. For $n = 4$ an upper limit for the rate constant of $k \leq 2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ is found at 163 K. For the reaction of $\text{OH}^-(\text{H}_2\text{O})$ with CH_3Br eight isotopic variants were studied: $\text{OH}^-(\text{H}_2\text{O})$ with 0–3 deuterium atoms and both CH_3Br and CD_3Br . No isotopic effect was found between CD_3Br and CH_3Br . For $\text{OH}^-(\text{H}_2\text{O})$ isotopic substitution, the reactivity order was $\text{H}_2\text{DO}_2^- \geq \text{HD}_2\text{O}_2^- > \text{H}_3\text{O}_2^- \geq \text{D}_3\text{O}_2^-$. The ions group into two categories: those incorporating both hydrogen and deuterium and those with only hydrogen or deuterium. The former group was found to react about 10% more rapidly than the latter group.

Introduction

Gas phase nucleophilic substitution reactions, $\text{S}_{\text{N}}2$, have been the subject of a large number of studies in the past several years. A good review of previous work is presented in Wang et al.¹ and will not be repeated here. Several aspects of gas phase $\text{S}_{\text{N}}2$ reactions have been studied in our laboratory, including temperature dependences, internal energy dependences, competition with other reactive channels, isotope effects, and solvation effects.

A number of studies have focused on the $\text{S}_{\text{N}}2$ reaction of OH^- with CH_3Br .^{2–5} The reaction of methyl bromide with the unsolvated OH^- ion is fast, approaching the collision rate. However, solvation substantially decreases the reactivity of this system. The effects of solvation on this reaction have been studied by Bohme and colleagues^{6,7} at 300 K in a flowing afterglow and by Hierl et al.⁸ in a beam apparatus over the translational energy range between 0.1 and 5 eV. At 300 K, the first water molecule reduces the reactivity to about 60% of that for the unsolvated ion and the second water molecule further reduces the reactivity to only 0.2% of the unsolvated ion value. In addition to studying the effects of solvation on this system, Hierl et al. observed that increasing kinetic energy decreases the cross section for both the unsolvated and the singly solvated OH^- ion. Bohme and Raksit have also measured the reactions

of both $\text{OH}^-(\text{H}_2\text{O})_n$ and $\text{OD}^-(\text{D}_2\text{O})_n$ with CH_3Br .⁷ However, their error limits for these reactions are too large for any conclusions to be drawn about an isotope effect.

We have recently added a supersonic expansion cluster ion source to our selected ion flow tube to study better the effects of solvation on reactivity.⁹ In this paper we report on various effects of solvation, isotopic substitution, and temperature on the reactions of $\text{OH}^-(\text{H}_2\text{O})_{n=0-4}$ with CH_3Br . We have studied the temperature dependence of the rate constant and the branching fraction for $n = 0-2$. For the $n = 2$ cluster reaction, we observed an association channel in addition to the $\text{S}_{\text{N}}2$ channels which produce Br^- and $\text{Br}^-(\text{H}_2\text{O})$. For the $n = 1$ cluster reaction, we studied deuterium substitution in both $\text{OH}^-(\text{H}_2\text{O})$ (fully and partially substituted) and CH_3Br (fully substituted) as a function of temperature. For the larger cluster ions, $n = 3$ and 4, measurements were made at 163 K only. The former ion reacts only by association, and the latter ion was found to be totally unreactive. Finally, we have examined the temperature dependence of the $\text{OH}^-(\text{H}_2\text{O})_{n=1-2}$ reactions in both He and H_2 buffers, and we found a substantial difference in the $n = 2$ reaction, indicating the buffer gas plays a role in this reaction.

Experimental Section

The experiments were performed in a variable temperature selected ion flow tube. Most of the apparatus is standard,^{10,11} and only details pertinent to the present experiments will be discussed. Two different sources were used to produce the $\text{OH}^-(\text{H}_2\text{O})_n$ cluster ions in this study. For all of the cluster data taken in a He buffer and for all of the OH^- data, a standard

* Author to whom correspondence should be addressed.

† Air Force Geophysics Scholar. Permanent address: 2133 Rayburn, House Office Building, Washington, DC 20515.

‡ Permanent address: Topeka High School, Topeka, KS 66604.

§ Permanent address: Department of Chemistry, University of Kansas, Lawrence, KS 66045-0046.

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electron impact ion source was used with pure water as the source gas.

For the experiments done in a H_2 buffer, the $\text{OH}^-(\text{H}_2\text{O})_n$ ions were produced using a new supersonic expansion ion source, which is described in detail elsewhere.⁹ Briefly, ions were formed by expanding a mixture of H_2O and Ar, held at about 4 atm, through a 25 μm orifice and then ionizing the gas just downstream of the expansion with an electron filament (ThO_2/Ir). To form larger clusters, the source was heated to 60–70 °C to increase the percentage of H_2O vapor in the expansion. The ions were sampled by a blunt skimmer and passed into a quadrupole mass filter. Although the cluster sizes reported here are relatively small, the source is capable of producing clusters as large as the mass spectrometer can detect (~ 680 amu).

The mass-selected cluster ions were then injected into a buffer gas flow. The $\text{OH}^-(\text{H}_2\text{O})_{n=1-4}$ clusters made using the supersonic expansion source were injected into a H_2 buffer, while the reactions of $\text{OH}^-(\text{H}_2\text{O})_{n=0-2}$ clusters made by electron impact were studied in a He buffer for comparison. The ions are quickly thermalized in thousands of collisions with the buffer gas before encountering any reactant gas. Typical operating pressures are 0.2 Torr for the H_2 buffer experiments and 0.4 Torr for the He buffer experiments. To study the reactions of $\text{OH}^-(\text{H}_2\text{O})_{n=1}$, we injected that particular cluster ion into the flow tube and obtained signals of $>90\%$ purity. To study the larger clusters, we typically injected the $n + 1$ cluster ion because one solvent molecule would dissociate upon injection. This worked reasonably well; nearly 80% of the signal was the ion of interest, while $\sim 10\%$ of the signal was present as $n + 1$ and $\sim 10\%$ was present as $n - 1$. To the best of our knowledge, no breakup of the clusters occurred during sampling. This was tested by varying the sampling voltages and observing no change in the ratio of the ion signals. This is consistent with all of our previous work on water clusters. The decay plots were linear, and no evidence of excited states was observed.

The presence of more than one primary ion has no effect on the rate constants. A problem would occur only if one primary ion produces another primary ion. That is not the case for the present experiments. The presence of more than one primary ion does complicate the branching ratio determinations. One must subtract the known amount of product for the small clusters to derive the branching fraction for the larger ones. This works well in most cases but would lead to large errors in the smaller products. Because we can make a $>90\%$ pure beam for $n = 1$, we believe the $n = 1$ results to be essentially unaffected, the additional error being on the order of a percentage point, i.e. 10% of 10%. This is supported by the data in the He and H_2 buffers being in excellent agreement.

For the isotopically labeled $\text{OH}^-(\text{H}_2\text{O})$ experiments, a mixture of H_2O and D_2O was added to the supersonic expansion source, and all masses from 35 to 38 amu were simultaneously injected into the flow tube by using low resolution in the upstream quadrupole. A H_2 buffer gas was used for these experiments. Rate constants for the four isotopic variants, H_3O_2^- , H_2DO_2^- , HD_2O_2^- , and D_3O_2^- , were measured simultaneously, thereby reducing all systematic errors to very low levels such that the relative rate constants could be measured to within a few percent.

The CH_3Br and CD_3Br reactant gases were added without purification. At low temperatures the reactant inlet was heated to prevent freezing in the inlet line; this technique has been described previously.¹² We measured relative rate constants for the CH_3Br and CD_3Br reactants by rapidly switching between the two gases; CH_3Br rate constants were measured, followed by CD_3Br rate constants, and finally CH_3Br rate constants again. We believe relative rate constants could be measured to within

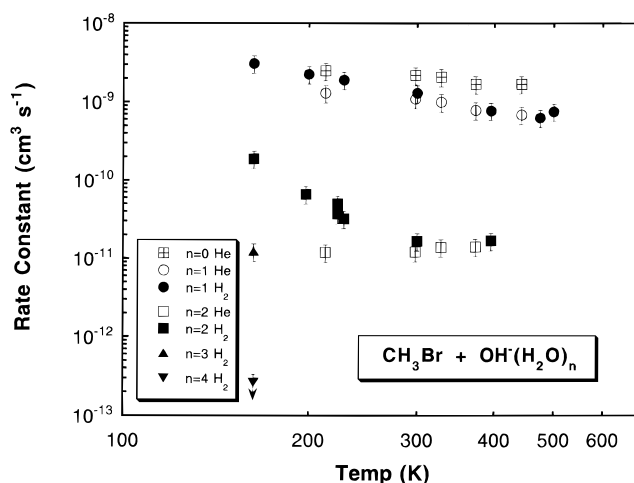


Figure 1. Rate constants for the reactions of $\text{OH}^-(\text{H}_2\text{O})_n$ with CH_3Br as a function of temperature. Open points refer to data taken in a He buffer and solid points to data taken in H_2 . Squares with crosses, circles, squares, triangles, and inverted triangles refer to $n = 0, 1, 2, 3$, and 4, respectively. Twenty-five percent error limits on each point are shown.

TABLE 1: Comparison of Rate Constants for the Reaction of $\text{OH}^-(\text{H}_2\text{O})_n$ with CH_3Br

<i>n</i>	rate constants ($\text{cm}^3 \text{s}^{-1}$)			
	163 K	300 K	collision rate constant (300 K)	previous results (300 K)
0		2.2×10^{-9}	2.79×10^{-9}	1.0×10^{-9} (ref 6) 9.9×10^{-10} (ref 2) 1.9×10^{-9} (ref 3) 2.2×10^{-9} (ref 5)
1	3.1×10^{-9}	1.2×10^{-9}	2.09×10^{-9}	6.3×10^{-10} (ref 6) 1.7×10^{-9} (ref 5)
2	1.9×10^{-10}	1.7×10^{-10}	1.81×10^{-9}	2×10^{-12} (ref 6)
3	1.2×10^{-11}		1.66×10^{-9}	$< 2 \times 10^{-13}$ (ref 6)
4	$< 2.7 \times 10^{-13}$		1.56×10^{-9}	

5% this way. The only uncertainties come from the slope of the ion decay plot and the gas correction factors needed to measure the flow rates of the two gases. The flow rates were measured using an MKS flow controller. We used the vibrational frequencies from Herzberg¹³ to calculate the heat capacity, which was then used to calculate the gas correction factors.¹⁴ The gas correction factors are 0.60 and 0.52 for CH_3Br and CD_3Br , respectively.

Uncertainty in the absolute rate constants is estimated as 25%, and the uncertainty in the relative rate constants is 15%¹⁰ except as noted above for the isotope effect measurements for the $n = 1$ cluster. The branching fractions were calculated without a mass discrimination correction. The correction is minimized by taking data under low-resolution conditions. Because the mass balance was good, the errors are expected to be only 5–10 percentage units. For $n = 2$ a small (~ 5 –10%) additional uncertainty may be associated with the branching ratio determinations because of the subtraction necessary to take into account the smaller clusters present in the flow tube.

Results

Rate constants for the reactions of $\text{OH}^-(\text{H}_2\text{O})_n$, $n = 0$ –4, with CH_3Br are shown as a function of temperature in Figure 1. The rate constants for 300 and 163 K are listed in Table 1 along with previous 300 K results. The data taken using the supersonic expansion source and a H_2 buffer are shown as solid symbols. The data taken with the high-pressure source and a He buffer are shown as open points. The most pronounced trend in the data is that reactivity decreases dramatically with

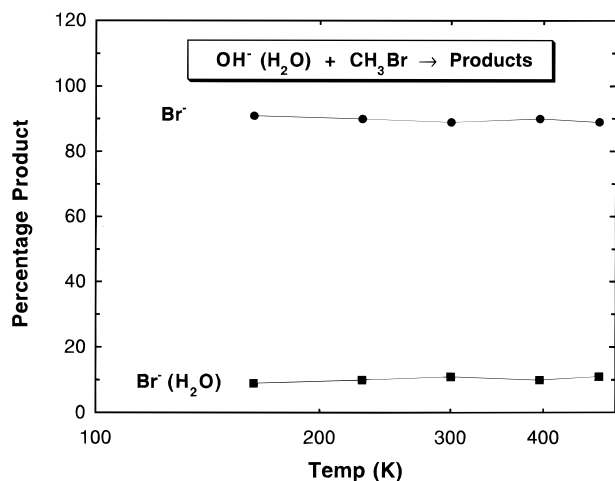
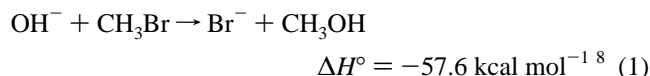


Figure 2. Branching fractions for the reaction of $\text{OH}^-(\text{H}_2\text{O})$ with CH_3Br as a function of temperature expressed as percentages. Only data taken in a H_2 buffer are shown.

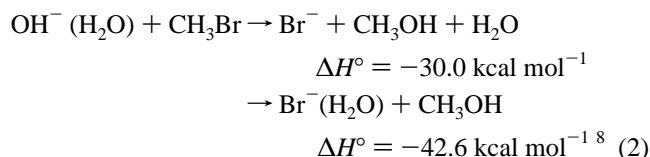
increasing cluster size. The rate constants drop by a factor of 10^4 in going from $n = 0$ to $n = 4$. The small rate constant measured for $n = 4$ ensures that an HBr impurity has not affected the data for the smaller clusters. We have found that HBr reacts with all of the ions in this study at the collision rate¹⁵ so that the $n = 4$ rate constant determines the maximum HBr concentration as approximately 1 part in 10^4 . The large dependence on solvation has been seen previously at room temperature.^{6,7}

The rate constants for OH^- approach, but are not equal to, the collision rate constant, and the data show a slight negative temperature dependence, $T^{-0.58}$. The reaction efficiency at low temperature is 75%, and it decreases to 65% at high temperature. The only product observed in the present study is Br^-



although proton transfer has been observed at higher energies in a beam study.⁸

The rate constants for $\text{OH}^-(\text{H}_2\text{O})$ reacting with CH_3Br are slightly smaller than those for unsolvated OH^- . The negative temperature dependence for this reaction is $T^{-1.6}$. No difference is observed between the data taken in H_2 and He buffers within experimental error. This reaction forms two $\text{S}_{\text{N}}2$ products, namely Br^- and $\text{Br}^-(\text{H}_2\text{O})$



In the beam study, both CH_2Br^- and OH^- were also observed as products at translational energies above their thermodynamic thresholds of 1.5 and 1.2 eV, respectively.⁸ The branching fractions for reaction 2 are shown in Figure 2 as a function of temperature. The unsolvated Br^- product accounts for ~90% of the reactivity. Within our experimental uncertainty, the branching fraction does not depend on temperature.

While the addition of one H_2O molecule to the OH^- ion changes the kinetics only slightly, the addition of a second H_2O changes the reactivity substantially. The rate constants for $\text{OH}^-(\text{H}_2\text{O})_2$ reacting with CH_3Br are nearly a factor of 100 smaller than those for the $\text{OH}^-(\text{H}_2\text{O})$ reaction. The $\text{OH}^-(\text{H}_2\text{O})_2$

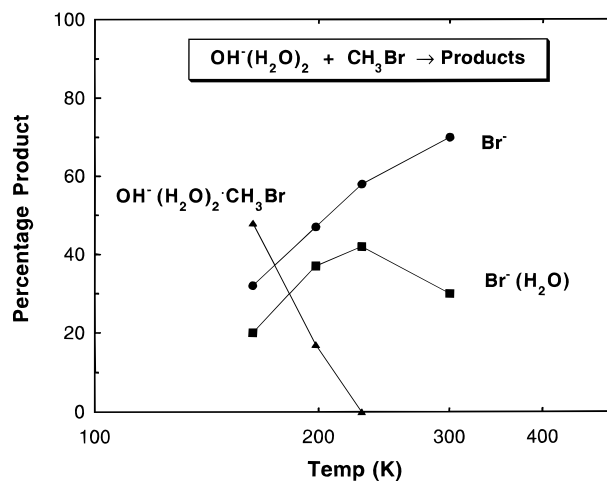
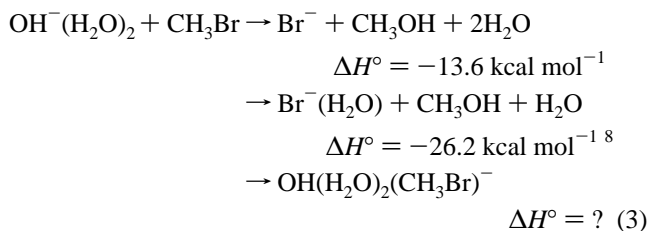


Figure 3. Branching fractions for the reaction of $\text{OH}^-(\text{H}_2\text{O})_2$ with CH_3Br as a function of temperature expressed as percentages. Only data taken in a H_2 buffer are shown.

reaction could not be studied above 400 K since this reactant ion thermally decomposes in the flow tube above this temperature. The problem of thermal decomposition is confined to a narrow temperature range. Depending on the temperature, thermal decomposition of water clusters becomes a problem over a 10–30 K wide temperature range.^{9,12}

In contrast to the $n = 1$ reaction, the $n = 2$ reaction shows a significant difference between the data taken in He and H_2 buffers at temperatures below 300 K. The data taken in a He buffer show little temperature dependence with perhaps a slight increase (~15%) as the temperature increases. At 300 K and above, the H_2 data agree well with the He data. However, below 300 K, the rate constants for the disappearance of $\text{OH}^-(\text{H}_2\text{O})_2$ taken in a H_2 buffer show a sharp increase with decreasing temperature; these low-temperature H_2 data show a T^{-4} dependence. The disagreement between the H_2 and He buffer data for $n = 2$ is explained by the presence of an association channel which is observed with the H_2 buffer but not with the He buffer. We have observed considerably larger association rate constants in a H_2 buffer previously.^{16,17} The possibility of a chaperone mechanism cannot be ruled out.

The reaction of $\text{OH}^-(\text{H}_2\text{O})_2$ with CH_3Br has three pathways:



No $\text{Br}^-(\text{H}_2\text{O})_2$ product was seen, in accord with the results of Bohme and Raksit.⁷ It is possible that some $\text{Br}^-(\text{H}_2\text{O})_2$ forms in the reaction but thermally dissociates in the flow tube since the bond strength for the second water in $\text{Br}^-(\text{H}_2\text{O})_2$ is only 12.3 kcal mol⁻¹. The second water in $\text{OH}^-(\text{H}_2\text{O})_2$ is bound by 16.4 kcal mol⁻¹, and this ion thermally dissociates in our apparatus at 500 K. The branching fractions for the three channels are shown in Figure 3 for the data taken in a H_2 buffer. One clearly sees the onset of an association channel at low temperatures. This association channel has not been observed previously.⁷ The Br^- channel increases monotonically with increasing temperature. The $\text{Br}^-(\text{H}_2\text{O})$ channel has a maximum between 200 and 300 K. Substantially more $\text{Br}^-(\text{H}_2\text{O})$ is found for the $n = 2$ reaction than for the $n = 1$ reaction.

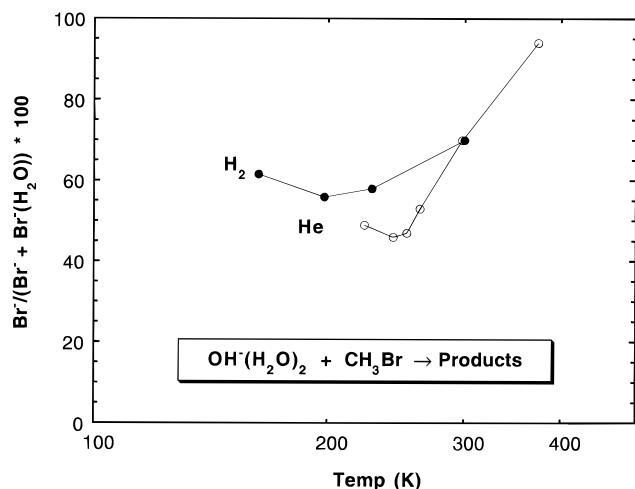


Figure 4. Br^- fraction divided by the sum of the Br^- plus $\text{Br}^-(\text{H}_2\text{O})$ fractions for the reaction of $\text{OH}^-(\text{H}_2\text{O})_2$ with CH_3Br as a function of temperature. Solid circles and open circles represent data taken in H_2 and He buffers, respectively.

Figure 4 illustrates the percentage of the Br^- signal divided by the sum of the Br^- plus $\text{Br}^-(\text{H}_2\text{O})$ signals for both the He- and H_2 -buffered experiments. This is simply the Br^- branching fraction for the He buffer case. For the H_2 buffer, this is the Br^- branching fraction ignoring the association channel. The room temperature data points agree extremely well. The fraction of Br^- increases with increasing temperature above 250 K. Below 250 K there may be a slight increase in the percentage of Br^- , although this is at the limit of our uncertainty. It does appear that the Br^- channel levels out at low temperature. This is in contrast to the $n = 1$ reaction, for which a flat dependence is observed over the entire temperature range. The H_2 buffer data show a slightly higher fraction of Br^- at low temperature than observed in the He case. This may result either from a small systematic error or from the presence of the association channel which competes with one or the other of these channels. In any case the difference is rather small, especially considering that the data were taken 10 years apart, i.e., relative error would be expected to be greater than usual.

We were able to examine the $n = 3$ and 4 reactions at only the lowest temperature of the study, 163 K. Above this temperature the ions could not be produced in abundance due to thermal decomposition of the ions in the flow tube and/or weak primary ion signals. Below 163 K, the CH_3Br would freeze in the inlet lines. The reaction of $n = 3$ with CH_3Br is just over 10 times slower than the $n = 2$ reaction and proceeds by association. We cannot rule out a small ($<10\%$) $\text{S}_{\text{N}}2$ channel forming $\text{Br}^-(\text{H}_2\text{O})_{n=0,1}$ because this would have been masked by the products from the $\text{OH}^-(\text{H}_2\text{O})_2$ reaction which occurred in the flow tube at the same time. The reaction of $\text{OH}^-(\text{H}_2\text{O})_4$ is at least a factor of 40 slower than the reaction with $\text{OH}^-(\text{H}_2\text{O})_3$. We report this rate as an upper limit due to the possibility of impurities in the CH_3Br causing the reactivity.

For the reaction of $\text{OH}^-(\text{H}_2\text{O})$ with CH_3Br we studied eight isotopic variants: $\text{OH}^-(\text{H}_2\text{O})$ with zero to three deuterium atoms reacting with both CH_3Br and CD_3Br . The results are listed in Table 2. The results are reported as relative rate constants with the rate constant for the fastest reaction set equal to 1. For each temperature and for both CH_3Br and CD_3Br , the reaction with H_2DO_2^- , which could be $\text{OH}^-(\text{HOD})$ or $\text{OD}^-(\text{H}_2\text{O})$, was found to have the largest rate constant. We found little variability with condition and therefore also report the average isotope effect for all conditions. We found no difference between CH_3Br and CD_3Br , the average ratio of rate constants

TABLE 2: Isotopic Study of the $\text{OH}^-(\text{H}_2\text{O}) + \text{CH}_3\text{Br}$ Reaction^a

temp (K)	neutral	rel rate constant				$k(\text{H}_2\text{DO}_2^-)$ (cm^3s^{-1})
		H_3O_2^-	H_2DO_2^-	HD_2O_2^-	D_3O_2^-	
200	CH_3Br	0.92	1.00	0.98	0.91	2.45 (−9)
	CD_3Br	0.94	1.00	0.99	0.95	2.38 (−9)
300	CH_3Br	0.90	1.00	0.97	0.89	1.44 (−9)
	CD_3Br	0.88	1.00	0.96	0.84	1.54 (−9)
500	CH_3Br	0.91	1.00	0.98	0.91	8.30 (−10)
	CD_3Br	0.93	1.00	1.00	0.92	7.99 (−10)
av ^b		0.91	1.00	0.98	0.90	

^a The rate constants for a given isotopic variant of $\text{OH}^-(\text{H}_2\text{O})$ are reported relative to the rate constant for H_2DO_2^- listed in the last column. ^b Average over all conditions.

for these neutrals being 1.00 ± 0.03 . It was not possible to accurately determine the product distribution for the various isotopes.

Deuterium substitution in H_3O_2^- showed a larger variation. In all cases the reactivity order was $\text{H}_2\text{DO}_2^- \geq \text{HD}_2\text{O}_2^- > \text{H}_3\text{O}_2^- \geq \text{D}_3\text{O}_2^-$, except for the 200 K data for CD_3Br where the order for the last two was reversed but only by 1%. The ions group into two categories: those incorporating both hydrogen and deuterium and those with only hydrogen or deuterium. The former group reacts about 10% more rapidly than the latter group. The variation in the relative rate constants within the two groups appears real in that it is reproducible for each temperature and isotopic form of CH_3Br studied. However, the variation is within our estimated error, $\pm 3\%$, for all ions except for D_3O_2^- ($\pm 6\%$). The larger uncertainty stems from lower signal levels for D_3O_2^- . We believe the average effect of isotopic substitution in the ions to be accurate to $\pm 2\text{--}3\%$ for all ions.

Discussion

Bohme and colleagues^{6,7} have previously measured the rate constants for $n = 0\text{--}3$ at room temperature. For $n = 0$ and 1, they reported rate constants that are roughly half those measured in the present study. This is just outside the combined uncertainty in the measurements. For $n = 2$, Bohme and Mackay⁶ reported a rate constant that is nearly a factor of 10 smaller than what was found in the present study, and for $n = 3$ they found an immeasurably small rate. Other room temperature studies^{3,4} are in good agreement with the present data. Bohme's measurements were made in a flowing afterglow, a technique similar to that used here except that the ions are formed within the flow tube and are not mass selected. We are confident in our rate constants to within our stated accuracy because we measure all parameters needed for a rate constant for each measurement. Also, the good agreement between the He and H_2 data, which were taken 10 years apart, lends support to the present data, as does the good agreement with the only other SIFT study for $n = 0$ and 1.⁵ The much smaller rate constant for $n = 2$ measured by Bohme may be caused by some unknown chemistry in the flowing afterglow, in which the H_2O source gas is present, possibly a reverse reaction involving the cluster product. The present experiments avoid this potential problem since the flow tube is dry; that is, the H_2O is confined to the source chamber. Bohme and Raksit⁷ found that about 10% of the $n = 1$ reaction forms $\text{Br}^-(\text{H}_2\text{O})$, in good agreement with the present measurements.

Hierl et al.⁸ studied the reactions of $n = 0\text{--}1$ in an ion beam–collision cell experiment from ~ 0.1 to 5 eV collision energy.

While their results do not overlap the thermal experiments, their low-energy extrapolations are in general agreement with the present results. For $n = 0$ they observed a cross section (converted to a rate constant) extrapolated to room temperature in good agreement with the present measurement. At higher energies they also observed an endothermic proton transfer. For $n = 1$, they observed equivalent rate constants slightly higher than the present results. The extrapolated branching fraction into $\text{Br}^-(\text{H}_2\text{O})$ is in good agreement with the present results, although the branching fraction was observed to decrease with increasing energy. This indicates that at temperatures higher than those used in the present study the branching fraction into $\text{Br}^-(\text{H}_2\text{O})$ would probably decrease. This is consistent with the branching fraction data for $n = 2$, which show a flat regime at low temperatures and an increasing fraction of Br^- at higher temperatures.

The isotope effects reported in the present study can be compared to the isotope effects reported for the reactions of $\text{F}^-(\text{H}_2\text{O})$ with CH_3X ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). In those reactions, O'Hair et al.²⁰ found that the isotope effect increases with decreasing rate constant. The rate constants for CH_3Br and CH_3I are most similar in magnitude to the present rate constants. For those reactions of $\text{F}^-(\text{H}_2\text{O})$, they found the rate constant ratios for $\text{CH}_3\text{X}/\text{CD}_3\text{X}$ to be 0.92 and 0.93 for $\text{X} = \text{Br}$ and I , respectively. The corresponding values for $\text{F}^-(\text{D}_2\text{O})$ are similar. These small isotope effects may be compared with the zero isotope effect measured in the present work on $\text{OH}^-(\text{H}_2\text{O})$. While this comparison is between different ions, disagreement of this order ($\sim 8\%$) is found for results from our two laboratories on the isotope effect in the reaction of Cl^- with CH_3Br .^{18,19}

For D_2O substitution in the reactant ion, O'Hair et al.²⁰ found $\text{F}^-(\text{H}_2\text{O})/\text{F}^-(\text{D}_2\text{O})$ rate constant ratios of 0.83 and 0.89 for $\text{CH}_3\text{-Br}$ and CH_3I , respectively. Similar numbers apply for D_2O substitution in the reactions with CD_3Br and CD_3I . These are on the same order as the difference found in the present study between the mixed isotope and purely labeled H_3O_2^- ions. The 10% difference between the pure and mixed H_3O_2^- isotopes is surprising considering the fact that the reactions are fast, approaching the collision rate at low temperature. Although this difference is very surprising, it is also very reproducible. The measurements were all made simultaneously, so essentially all systematic errors should have been eliminated. The pure results being the same seems to rule out thermodynamics as the source of the effect based on the work of O'Hair et al. One possible explanation is a symmetry effect similar to those observed by Gellene and co-workers.²¹ They have found a symmetry restriction based on the Pauli principle, which enhances formation of nonsymmetric ion association complexes. An independent measurement of this effect would be valuable in determining if the effect observed here is real.

The small negative temperature dependence of the rate constant reported here for the nucleophilic displacement reaction between OH^- and CH_3Br has been seen in previous studies for comparable $\text{S}_\text{N}2$ reactions such as the reactions of F^- with the methyl halides²² and OH^- with CH_3Cl .²³ Two factors are thought to contribute to this behavior. First, the rate constant for the collision of an ion with a polar molecule is a gradually decreasing function of temperature. Second, theoretical considerations predict²⁴⁻³¹ that the reaction efficiency (i.e., fraction of collisions resulting in product formation) will be a decreasing function of temperature for exothermic nucleophilic displacement at an sp^3 carbon atom. These predictions, based upon the double-well potential model first proposed by Brauman,^{3,6} assume that the reaction efficiency at a given temperature is the consequence of the competition between two pathways for

the unimolecular decay of the reactant adduct ($\text{OH}^-\cdot\text{CH}_3\text{Br}$, in this case): dissociation back to reactants or transformation to the product adduct ($\text{Br}^-\cdot\text{CH}_3\text{OH}$). Since dissociation back to reactants involves a looser transition state and hence a higher density of states than does the forward transformation, the rate constant for the backward reaction increases more rapidly with temperature than does that for the forward reaction. Consequently, a decreasing fraction of the collision adducts will surmount the central barrier and result in product formation with increasing temperature. This effect has been modeled quantitatively.³²

The two principal consequences of reactant solvation, namely the reduction of the rate constant and its altered temperature dependence, are also consistent with the predictions of the double-well model. These effects are discussed in turn.

Solvation of the ionic reactant without comparable solvation of the ionic product reduces the reaction exothermicity and stabilizes the reactants more than it does the transition state corresponding to the central barrier in the reaction coordinate (i.e., the energy difference ΔE_0^\ddagger between this transition state and the reactants becomes less negative). At a given temperature, this decrease in the magnitude of $-\Delta E_0^\ddagger$ will increase the fraction of reaction adducts that dissociate backward to regenerate the reactants at the expense of those which surmount the central barrier and are transformed into product adducts. This suggests a decreasing reaction efficiency with increasing reactant solvation, as is observed here. We have previously reported similar behavior for the reactions of $\text{OH}^-(\text{H}_2\text{O})_{0-2}$ with CH_3Cl .²³ As in the present study, the CH_3Cl rate constants decrease with increasing reactant solvation, the decrease being even larger than that found here. We attribute this latter observation to the fact that the reaction of OH^- with CH_3Cl is less exothermic (and hence more sensitive to reactant stabilization) than is the reaction with CH_3Br .

The same model explains the gross features of the temperature dependences of the $\text{S}_\text{N}2$ rate constants with increasing reactant solvation. At first, reactant solvation makes E_0 less negative, which causes the temperature dependence of the reaction efficiency (and hence of the overall reaction rate constant) to become more negative. This is what is observed in the present case in going from $n = 0$ (where $k \propto T^{-0.58}$) to $n = 1$ (where $k \propto T^{-1.6}$). With further reactant solvation, E_0 passes through zero and then becomes positive, causing the temperature dependence of the reaction efficiency to become flat and then positive. The onset of this behavior is demonstrated by the leveling out of the $n = 2$ temperature dependence. The strong negative temperature dependence for the $n = 2$ reaction in H_2 buffer below 250 K is typical for association reactions, and it mainly reflects the temperature dependence of the collision complex lifetime;³³ thus, it is irrelevant to the present discussion of the temperature dependence of the $\text{S}_\text{N}2$ reaction channel.

Similar behavior has been observed in the nucleophilic displacement reactions of $\text{OD}^-(\text{D}_2\text{O})_{0-2}$ with CH_3Cl .²³ For $n = 1$, the temperature dependence of the rate constant for the reaction with CH_3Cl is substantially larger than that reported here for the reaction with CH_3Br . Again, we attribute this to the CH_3Cl reaction being less exothermic (and thus having a less negative value of ΔE_0^\ddagger) than the corresponding CH_3Br reaction. Comparisons for $n = 2$ are more difficult, since we have observed different temperature dependences for the $\text{CH}_3\text{-Br}$ reaction in He and H_2 buffers. The rate constants for the reaction of $\text{OD}^-(\text{D}_2\text{O})_2$ with CH_3Cl data in the range of 300 K and above also have a flat temperature dependence. An upturn at low temperatures is observed, similar to that seen in the H_2 buffer for CH_3Br , possibly indicating an influence of the buffer

that is just starting to become important at the lowest temperatures studied. Due to the lower dipole moment of CH_3Cl compared to CH_3Br , it is expected that CH_3Cl would bond less strongly to a particular ion and therefore have a lower association rate.³⁴

If this explanation of the temperature dependences observed for the $\text{S}_\text{N}2$ reactions of $\text{OH}^-(\text{H}_2\text{O})_n$ ($n = 0-2$) is correct, a low-pressure study (where collisions with the buffer are absent) of the $n = 3$ reaction would be expected to show a positive temperature dependence.

In solution, the solvent is ubiquitous and thus all ionic species experience varying degrees of solvation. The ionic charge, however, is strongly localized in the ionic reactant and the ionic product, and both will be strongly stabilized by solvation; the transition state, on the other hand, has a delocalized charge and will therefore be much less strongly stabilized by solvation. Consequently, one would expect $\text{S}_\text{N}2$ reactions in solution to have large, positive values of ΔE_0^\ddagger and thus to have large, positive temperature dependences. Positive temperature dependences are commonly found in solution.³⁵

The difference between the He and H_2 buffer data for reaction 3 is connected to the onset of the association channel. On close examination the large rate constants observed in the hydrogen buffer are found at temperatures where the association channel is negligible. This shows that the bimolecular rate constants at low temperatures in the hydrogen buffer are affected by collisions with the buffer gas. In other words, the complex lives long enough to undergo collisions with the buffer gas, which in turn increases the rate constant. The onset of the association channel at just slightly lower temperatures guarantees that the complex lifetime is at least on the order of the collision time scale with the buffer gas, $\sim 10^{-7}$ s.

The influence of the buffer gas on an $\text{S}_\text{N}2$ reaction has been observed by Giles and Grimsrud³⁶ in the reaction of Cl^- with CH_3Br . In that reaction, increasing pressure increases the rate constant, and this is consistent with our data. H_2 is more efficient at transferring energy than is He. Therefore, the effects of increasing pressure would be seen in a H_2 buffer^{16,17,37} before they would be observed in He, and the effect would be to increase the rate constant. The increase in the H_2 data relative to the He data does not necessarily mean that no collisions of the complex with He take place but rather that the He collisions are less efficient in transferring energy from the complex. He is known to be a very inefficient third body.^{16,17,37}

The amount of hydration in the products can also be compared to our previous study of $\text{OH}^-(\text{H}_2\text{O})_{0-2}$ with CH_3Cl .²³ In that study, we found that 15% of the product was hydrated in the $n = 1$ reaction and 40% for the $n = 2$ reaction. Both of these values are similar to the corresponding results in the present study.

The predisposition toward forming unsolvated species has been observed previously. Hierl et al.²³ have explained this by invoking a mechanism that involves a concerted transfer of the solvent during the Walden inversion. This is quite unfavorable both energetically and entropically.

Conclusions

Combining the present study with past work on the reactions of $\text{OH}^-(\text{H}_2\text{O})_n$ with CH_3Br makes this reaction one of the most complete data sets in ion molecule kinetics. Previously, this set of reactions was studied as a function of n from $n = 0$ to $n = 3$, as a function of isotope for $n = 0$, and as a function of kinetic energy for $n = 0-1$. To this we add temperature dependences for rate constants and branching fractions for $n = 0-2$ and kinetics information for $n = 3-4$ at 163 K. We have

observed a dependence on the buffer gas for the $n = 2$ reaction. For $n = 1$ we measured temperature dependences for eight isotopic variants and found particularly unusual behavior for deuterium substitution in the ion. A thorough theoretical investigation of this very comprehensive data set would be a good test of the current theoretical understanding of gas phase $\text{S}_\text{N}2$ reactions.

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References and Notes

- (1) Wang, H.; Zhu, L.; Hase, W. L. *J. Phys. Chem.* **1994**, *98*, 1608.
- (2) Tanaka, K.; Mackay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643.
- (3) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.
- (4) Ingemann, S.; Nibbering, N. M. M. *Can. J. Chem.* **1984**, *62*, 2273.
- (5) DePuy, C. H.; Gronert, S.; Mullin, A.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1990**, *112*, 8650.
- (6) Bohme, D. K.; Mackay, G. I. *J. Am. Chem. Soc.* **1981**, *103*, 978.
- (7) Bohme, D. K.; Raksit, A. B. *J. Am. Chem. Soc.* **1984**, *106*, 3447.
- (8) Hierl, P. M.; Paulson, J. F.; Henchman, M. J. *J. Phys. Chem.* **1995**, *99*, 15655.
- (9) Arnold, S. T.; Morris, R. A.; Viggiano, A. A. *J. Chem. Phys.* **1995**, *103*, 9242.
- (10) Viggiano, A. A.; Morris, R. A.; Dale, F.; Paulson, J. F.; Giles, K.; Smith, D.; Su, T. *J. Chem. Phys.* **1990**, *93*, 1149.
- (11) Viggiano, A. A.; Morris, R. A.; Van Doren, J. M.; Paulson, J. F. *J. Chem. Phys.* **1992**, *96*, 275.
- (12) Viggiano, A. A.; Dale, F.; Paulson, J. F. *J. Chem. Phys.* **1988**, *88*, 2469.
- (13) Herzberg, G. *Molecular Spectra and Molecular Structure: II. Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand: New York, 1945.
- (14) MKS Flow Controller Manual.
- (15) Arnold, S. T.; Viggiano, A. A. *J. Chem. Phys.*, submitted for publication.
- (16) Viggiano, A. A.; Dale, F.; Paulson, J. F. *J. Geophys. Res.* **1985**, *90*, 7977.
- (17) Viggiano, A. A. *J. Chem. Phys.* **1984**, *81*, 2639.
- (18) Viggiano, A. A.; Paschkewitz, J. S.; Morris, R. A.; Paulson, J. F.; Gonzalez-Lafont, A.; Truhlar, D. G. *J. Am. Chem. Soc.* **1991**, *113*, 9404.
- (19) Gronert, S.; DePuy, C.; Bierbaum, V. *J. Am. Chem. Soc.* **1991**, *113*, 4009.
- (20) O'Hair, R. A. J.; Davico, G. E.; Hacaloglu, J.; Dang, T. T.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1994**, *116*, 3609.
- (21) Griffith, K. S.; Gellene, G. I. In *Isotope Effects in Gas Phase Chemistry*; Kaye, J. A., Ed.; American Chemical Society: Washington, DC, 1992.
- (22) Su, T.; Morris, R. A.; Viggiano, A. A.; Paulson, J. F. *J. Phys. Chem.* **1990**, *94*, 8426.
- (23) Hierl, P. M.; Ahrens, A. F.; Henchman, M.; Viggiano, A. A.; Paulson, J. F.; Clary, D. C. *J. Am. Chem. Soc.* **1986**, *108*, 3142.
- (24) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891.
- (25) Olmstead, W. P. *Sn2*, Thesis Stanford University, 1977.
- (26) Brauman, J. I. In *Kinetics of Ion-Molecule Reactions*; Ausloos, P., Ed.; Plenum: New York, 1979.
- (27) Sen Sharma, D. K.; Kebarle, P. *J. Am. Chem. Soc.* **1982**, *104*, 19.
- (28) Magnera, T. F.; Kebarle, P. In *Ionic Processes in the Gas Phase*; Almoester Ferreira, M. A., Ed.; Reidel Publishing: Boston, 1984.
- (29) Caldwell, G.; Magnera, T. F.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 959.
- (30) Grimsrud, E. P.; Chowdhury, S.; Kebarle, P. *J. Chem. Phys.* **1985**, *83*, 1059.
- (31) Sharma, R. B.; Sen Sharma, D. K.; Hiroaka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 3747.
- (32) Meyer, S. A. *Sn2*, University of Kansas, 1987.
- (33) Viggiano, A. A. *J. Chem. Phys.* **1986**, *84*, 244.
- (34) Bates, D. R. *Chem. Phys. Lett.* **1984**, *112*, 41.
- (35) Bathgate, R. H.; Moelwyn-Hughes, E. A. *J. Chem. Soc.* **1959**, 2642.
- (36) Giles, K.; Grimsrud, E. P. *J. Phys. Chem.* **1992**, *96*, 6680.
- (37) Ferguson, E. E. *J. Phys. Chem.* **1986**, *90*, 731.