Effect of Ion Hydration in the Gas-Phase Proton-Transfer Reaction of OH^- with HBr

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We have examined the role of solvation on intrinsic ion reactivity by measuring rate constants for the reactions of $OH^-(H_2O)_n$, $0 \le n \le 11$, with HBr at 100 K. The reactions all proceed by proton transfer with accompanying solvent transfer. For $0 \le n \le 7$, the reactions proceed at the collisional rate, while rate constants for the larger cluster reactions decrease slowly with cluster size. The reaction for $n = 11$ is only one-third efficient. Product ion distributions were measured for the clusters $0 \le n \le 7$. For clusters containing two or more solvent molecules, the reactions with HBr all yield three product ions of the form $Br^-(H_2O)_m$ which differ only in the degree of solvation of the core ion. The average number of solvent molecules lost during the reaction, represented by $\langle n - m \rangle$, increases with increasing cluster size; the value of $\langle n - m \rangle$ for $n = 7$ is 3.4. The significant decrease in reaction efficiency at larger cluster sizes is discussed in terms of reaction energetics and possible structural changes within the primary cluster ion series.

Introduction

The influence of solvation on intrinsic ion reactivity has been explored through the study of gas-phase cluster ions; this work has been reviewed by Bohme[1] and more recently by Castleman and colleagues.[2,3] In general, solvation effects are examined by studying the reactivity of ion−molecule clusters as a function of stepwise solvation, from the unsolvated ion to larger clusters where the degree of solvation approximates that found in solution. Initially, kinetic studies of hydrated anionic clusters of the form $X^-(H_2O)_n$ were limited to relatively small cluster sizes, containing only three to four solvent molecules. Recently, however, such studies have been extended to larger cluster sizes. Castleman *et al.*[4,5] have examined solvation effects in reactions of cluster ions containing up to 50 solvent molecules, and we have studied reactions of hydrated halides with as many as 16 water molecules[6] and also reactions of hydrated electron clusters containing up to 35 water molecules.[7]

In this paper, we report on the role of ion solvation in the gas-phase proton transfer reaction of $OH^-(H_2O)_n$ with HBr. The measurements were made using a variable temperature selected ion flow tube (SIFT) equipped with a supersonic expansion ion source. To explore how stepwise solvation influences intrinsic ion reactivity, reaction rate constants were measured for the clusters $0 \le n \le 11$. In addition, product ion distributions were measured for the clusters $0 \le n \le 7$ to examine the degree to which the solvent molecules participate in the reaction.

Experimental Section

The SIFT apparatus has been described previously in detail,[8,9] and only details pertinent to the present study will be discussed. The $OH^-(H_2O)_n$ clusters were produced using a supersonic expansion ion source which also has been described elsewhere.[7,10] The temperature of the flow tube was maintained at 100 K in order to prevent thermal dissociation of the primary and product ions. Although no thermal decomposition of the ions is expected at this temperature, some collisional dissociation of the primary ions occurs as a result of being injected into the flow tube. The percentage of primary ions that dissociate upon injection increases with increasing cluster size due in part to the increasing internal energy of the cluster. To reduce collisional dissociation of the primary ions, a hydrogen buffer gas (0.17 Torr) was used rather than the standard helium buffer.[11] Under these conditions, one prominent primary ion remained in the flow tube when small clusters were injected, while injection of larger clusters resulted in two or three significant primary ions remaining in the flow tube.

The HBr reactant gas was added to the flow tube through a heated finger inlet to prevent freezing; this technique has been described previously.[12] Rate constants were determined by the standard technique of recording the pseudo-first-order attenuation of the primary ion count rate as a function of reactant neutral flow rate. Estimated uncertainties in the reported rate constants are ±25%, and the relative uncertainty is ±15%.[8]

Product ion determination was straightforward and done in the standard fashion for small cluster sizes. However, for the larger clusters, where more than one primary ion was present during the reaction, the product distribution could only be determined by subtracting out the known product distribution(s) of the smaller cluster(s). Product channels which comprise at least 5% of the total product ions were able to be derived in this manner. It was not possible to obtain accurate product branching ratios for cluster sizes larger than $n = 7$ due to mass coincidence problems and the difficulty of extracting size-dependent data when several primary ions were present. Estimated uncertainties in the product branching ratios are ±10%.

Results

Rate constants for the reactions of $OH^-(H_2O)_n$ with HBr at 100 K are shown in Figure 1 as a function of cluster size and are listed in Table 1 for $0 \le n \le 11$. Collision rate constants, calculated using the parametrized trajectory calculations of Su and Chesnavich,[13,14] are represented as the solid curve in Figure 1. For $OH^-(H_2O)_n$ clusters with $n \le 7$, the reactions with HBr proceed at the gas-phase collision limit, the measured efficiency being between 0.94 and 1.08, well within the error limits of being collisional. With further solvation, the efficiency of the reaction gradually decreases until it is only one-third the collisional rate at $n = 11$.

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TABLE 1: Rate Constants, Reaction Efficiencies, and Product Branching Ratios for the Reactions of $OH^-(H_2O)_n$ with HBr[a]

$OH^-(H_2O)_n$ reactant for $n =$	k_2 (10^{-9} cm^3 s^{-1})	reaction efficiency	$Br^-(H_2O)_m$ products for $m =$	branching ratio	$\langle n - m\rangle$	$\sim\langle\Delta H^0\rangle$ (kJ mol^{-1}) av m
0	2.80	1.02	0	1.00	0.0	−282
1	1.93	0.92	0	0.91	0.9	−192
			1	0.09		
2	1.77	0.97	0	0.56	1.5	−145
			1	0.39		
			2	0.05		
3	1.65	0.98	0	0.25	2.1	−105
			1	0.58		
			2	0.17		
4	1.59	1.01	1	0.30	2.3	−88
			2	0.65		
			3	0.05		
5	1.60	1.05	1	0.10	2.6	−60
			2	0.40		
			3	0.50		
6	1.61	1.09	3	0.70	2.7	−46
			4	0.25		
			5	0.05		
7	1.36	0.94	3	0.35	3.3	−24
			4	0.55		
			5	0.10		
8	1.21	0.86				
9	1.07	0.78				
10	0.73	0.53				
11	0.43	0.32				

[a] The average number of water solvents lost during the reaction is represented by $\langle n - m\rangle$. $\langle\Delta H\rangle$'s were calculated for $n \leq 7$ using eqs 1−3, assuming products with $\langle m\rangle$ solvent molecules. The enthalpy change for the most exothermic channel is obtained by subtracting the product of $\langle n - m\rangle$ times ~40−50 kJ mol^{-1} from the ΔH given for the average m.

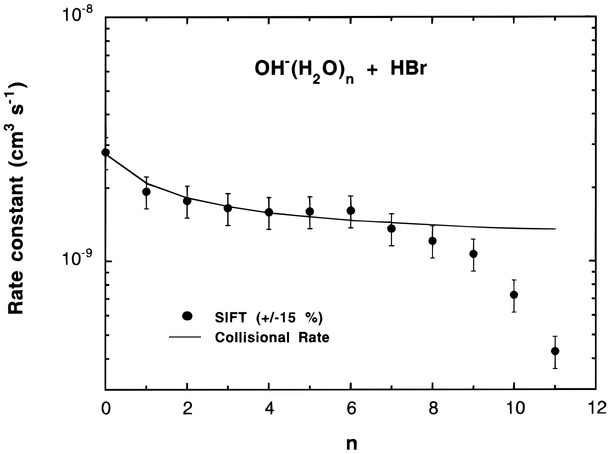

Figure 1. Rate constants for the reactions of $OH^-(H_2O)_n$ with HBr at 100 K, shown as a function of cluster size for $0 \leq n \leq 11$. The solid line represents the collision rate constants.[13,14] Error bars reflect relative error only.

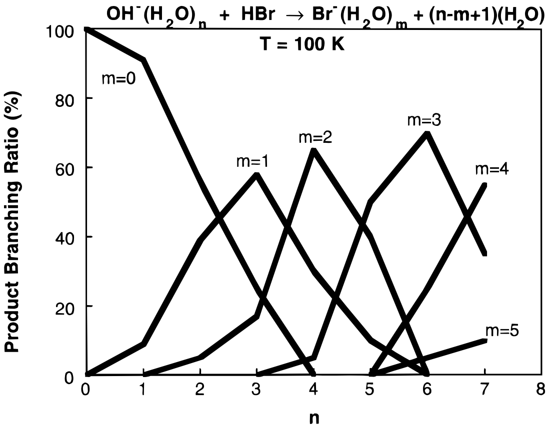

Figure 2. Product distributions for the reactions of $OH^-(H_2O)_n$, $n \leq 7$, with HBr at 100 K. The average number of water solvent molecules associated with the proton transfer product ion, Br^-, increases with increasing $OH^-(H_2O)_n$ cluster size.

Product ion distributions for the reactions of HBr with $OH^-(H_2O)_n$, $n \leq 7$, are shown in Figure 2, and the branching ratios are listed in Table 1. The smallest cluster $OH^-(H_2O)$ reacts with HBr to form predominately the unsolvated proton transfer product, Br^-, and only a small fraction of solvated product ion. Presumably, this is due to the large exothermicity of the reaction which "boils off" most of the water molecules. Reactions of HBr with the larger clusters ($n \geq 2$) all yield three product ions of the form $Br^-(H_2O)_m$ which differ only in the degree of solvation of the core ion. As shown in Figure 2, the solvation number of the products, m, increases with increasing solvation of the reactant ion. Furthermore, the average number of solvent molecules lost during the reaction, represented by $\langle n - m\rangle$ in Table 1, increases with increasing cluster size. Additional clusters comprising less than 5% of the products may have been missed due to the presence of more than one primary ion.

Discussion

Rate constants have previously been measured for a number of solvated proton-transfer reactions between small negative cluster ions and inorganic and organic acids; this work has been reviewed by Bohme.[1,2] In general, proton-transfer reactions with unsolvated or partially solvated ions proceed at the collision rate when the reaction is exothermic. However, when the reaction is nearly thermoneutral or endothermic, the reaction efficiency drops dramatically.

For the reactions of HBr with $OH^-(H_2O)_n$ for $n > 7$, we note a strong correlation between reactivity and reaction exothermicity of the most probable product. The energetics of the cluster reaction are determined by the difference in the gas-phase acidities of H_2O and HBr and by the differences in the relative solvation energies of $OH^-(H_2O)_n$ and $Br^-(H_2O)_n$. The reaction between HBr and the unclustered OH^- ion is exothermic by 282 kJ mol^{-1},[16] and the exothermicity gradually decreases with increasing $OH^-(H_2O)_n$ cluster size because of the relative stabilities of the reactant and product ions. By representing the overall reaction in terms of individual steps, one can estimate reaction exothermicities for the average product channel, $Br^-(H_2O)_{\langle m \rangle}$, observed and for the most exothermic product channel possible:

$$OH^-(H_2O)_n \rightarrow OH^- + n(H_2O) \quad (1)$$

$$OH^- + HBr \rightarrow Br^- + H_2O \quad (2)$$

$$Br^- + n(H_2O) \rightarrow Br^-(H_2O)_m + (n - m)H_2O \quad (3)$$

where $\Delta H^0{}_2 = -282$ kJ mol^{-1}, and reaction enthalpies for eqs 1 and 3 are estimated using the stepwise reaction enthalpies for $\{OH^-(H_2O)_i + H_2O\}$ and $\{Br^-(H_2O)_i + H_2O\}$.

$$\Delta H^0{}_1 = -\sum_{i=0}^{n-1} \Delta H^\circ_{i,\,i+1}\{OH^-(H_2O)_i + H_2O \rightarrow OH^-(H_2O)_{i+1}\} \quad (4)$$

$$\Delta H^0{}_3 = \sum_{i=0}^{m-1} \Delta H^\circ_{i,\,i+1}\{Br^-(H_2O)_i + H_2O \rightarrow Br^-(H_2O)_{i+1}\} \quad (5)$$

The stepwise enthalpies used to calculate ΔH_1 are taken from Castleman *et al.*,[15] and the stabilization energies recently determined by photoelectron spectroscopy for $Br^-(H_2O)_n$ are used to compute ΔH_3.[16] The cluster ion reaction enthalpies for the average product channel, calculated using eqs 1−3 for $n \leq 7$, are shown in Table 1. The most exothermic channel is obtained by subtracting the product of $\langle n - m \rangle$ times ~40−50 kJ mol^{-1} from the ΔH given in Table 1. This all assumes that the neutral water molecules leave as monomers. Our data do not address the possibility of neutral water cluster formation when more than one water molecule is “boiled off”.

The exothermicity of the most probable channel decreases from −282 to −24 kJ mol^{-1} over the range of cluster sizes $0 \leq n \leq 7$. Interestingly, the reaction efficiency begins to decrease at the same cluster size where the exothermicity of the average channel approaches zero. However, it is important to note that, even though the reaction exothermicity of the most probable product gradually decreases with increasing cluster size, the reaction still has a very exothermic channel available at all the cluster sizes examined in this study. Thus, it is not clear that the significant decrease in reaction efficiency is strictly due to energetics.

In this laboratory, we have recently shown that significant reactivity decreases within a cluster series can also be an indication of structural changes within the primary cluster ion.[6] In our recent study of Cl_2 reacting with cluster ions of the form $X^-(H_2O)_n$, where X is a halogen, we observed significant decreases in reactivity at $n = 4$ and $n = 6$ for F^- and Cl^-, respectively, while we observed no decrease in reactivity for hydrated clusters of Br^- and I^-. By assuming that fully solvated “internal” cluster ions react at a much slower rate than the corresponding partially solvated “surface” ions, the significant change in reaction efficiency was related to the closing of an initial solvation shell. The data suggested a changeover from external to internal ion solvation in $F^-(H_2O)_n$ and $Cl^-(H_2O)_n$ clusters but not in the solvated clusters of larger halides. For $F^-(H_2O)_n$ and $Cl^-(H_2O)_n$ clusters, the transition points suggested by the kinetic data were in agreement with the results of *ab initio* calculations on the cluster ions.[17−22]

With regard to $OH^-(H_2O)_n$ clusters, *ab initio* calculations by Combariza and Kestner[18] predict that interior solvation of the subion develops between $n = 4$ and 6, which is in good agreement with a previous reactivity study of $OH^-(H_2O)_n$ clusters. In reactions with CO_2 and $OH^-(H_2O)_n$, Castleman *et al.*[5] observed that the reaction efficiency decreases at relatively small sizes, becoming slower than collisional at $n = 5$. In the present study, we observe a significant decrease in reactivity beginning around $n = 8$, which at first glance might rule out a switch to internal solvation as the cause of the decrease in reaction efficiency. However, unlike CO_2, HBr has a relatively large permanent dipole, which should make it easier to interact with a partially shielded OH^-; i.e., the polar HBr may be able to burrow through a small number of water molecules to find the ionic core while the nonpolar CO_2 could not.

Detailed calculations of this process would be extremely difficult and are beyond the scope of the present experiments. The exact nature of the decrease in the rate constant with cluster size therefore awaits further work.

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