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Effects of Hydration on Reactions of O⁻(H₂O)ₙ (n = 0-2). 2. Reactions with H₂ and D₂

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The rate constants for the reactions of O⁻(H₂O)ₙ (n = 0-2) with H₂ and D₂ have been measured as a function of temperature. In addition, the dependences of the rate constants on average center-of-mass kinetic energy ($\langle KE_{cm} \rangle$) and the branching ratios for n = 0 have been measured at several temperatures. For n = 0, the reactions with H₂ and D₂ are 48% and 50% efficient, respectively, and depend only weakly on temperature and $\langle KE_{cm} \rangle$. Both associative detachment and a channel that produces OH⁻ are observed. The minor (<15%) OH⁻ channel becomes more important at higher temperatures and $\langle KE_{cm} \rangle$. One H₂O ligand reduces the rate constants on the order of a factor of 50. The reaction pathways for n = 1 are approximately 90% associative detachment and 10% production of OH⁻(H₂O). The rate constants for n = 1 are found to increase with increasing temperature. The second H₂O ligand reduces the rates to below our detectable limit. No dependence on rotational energy was found in either the rate constant or the branching ratio for n = 0.

Introduction

Associative detachment reactions of negative ions

$$A^- + B \rightarrow AB + e \qquad (1)$$

have been studied extensively over many years.[1-3] The studies have involved measurements of temperature dependences and energy dependences of the rate constants, competition with other channels, product electron kinetic energy distributions, and product vibrational population distributions. The reactions have also been investigated extensively theoretically.[4] Recent attention has focused on calculating the vibrational product distributions to support the elegant experimental work on this subject.

One study at 300 K probed the associative detachment reactions of hydrated ions.[5] In that study, hydration was found to reduce the rate constants. In the present work, the rate constants for the reactions of O⁻(H₂O)ₙ with H₂ and D₂ were measured as a function of temperature for n = 0-2 and as a function of average center-of-mass kinetic energy ($\langle KE_{cm} \rangle$) for n = 0. For n = 0, the reaction has a minor channel that produces OH⁻. We have studied the temperature and $\langle KE_{cm} \rangle$ dependences of the branching ratio between these two channels. This is the first investigation of solvated ion associative detachment reactions as a function of temperature. These studies are part of a larger study of the reactivity of O⁻(H₂O)ₙ. The reactions of O⁻(H₂O)ₙ with O₂, CO₂, CO, NO, SO₂, CH₄, N₂O, and H₂O have been reported previously.[6]

Experimental Section

The measurements were performed in the Geophysics Laboratory fast-flow system that incorporates both a mass-selected ion source and a high-pressure ion source. The reactions of unsolvated O⁻ were investigated by using the selected ion source. $\langle KE_{cm} \rangle$ was varied at several temperatures by means of a drift tube. These measurements are conventional.[7,8] The reactions of the hydrated species were investigated by using the high-pressure ion source.[6,9,10] Since the experimental details have been previously reported, no further details will be presented here.

Higher $\langle KE_{cm} \rangle$ values were obtained for the D₂ reactions due to the higher mass of D₂ compared with H₂. For the same electric field applied to the drift tube, a larger energy is obtained for heavier reactant neutrals. This is a result of converting the laboratory-frame ion energy obtained from the Wannier formula[11] into a center-of-mass energy.

Results

Figure 1 shows the rate constants for the reactions of O⁻(H₂O)ₙ (n = 0-1) with both H₂ and D₂, plotted as a function of $\langle KE_{cm} \rangle$.

The open symbols refer to the H₂ reactions, and the solid symbols represent the results for the D₂ reactions. The data for n = 0 are given as $\langle KE_{cm} \rangle$ dependences measured at three different temperatures, represented by squares, triangles, and inverted triangles for temperatures of 176, 296, and 490 K, respectively.

Rate constants for the n = 1 reactions were measured as a function of temperature only. The results, obtained at 251, 343, and 473 K, were converted to $\langle KE_{cm} \rangle$ dependences and plotted as diamonds in Figure 1. The rate constants are estimated to be accurate within ±25%, and the precision is ±15%.[8] No reaction was observed for n = 2, i.e., k < 10⁻¹² cm³ s⁻¹, and therefore the results are not plotted.

The rate constants for n = 0 were found to decrease slightly with increasing temperature and energy. Note, however, that the decrease with increasing temperature is within our experimental error. For n = 1, both reactions show rate constants that increase with increasing temperature. The increase is about 50% over the temperature range studied, 251-473 K.

For the unclustered O⁻ reactant ion, two channels are open:

$$O^- + H_2 \rightarrow H_2O + e \qquad (2a)$$

$$O^- + H_2 \rightarrow OH^- + H \qquad (2b)$$
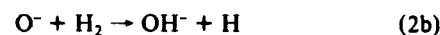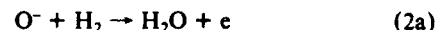
These channels are exothermic by 344 and 27 kJ mol⁻¹, respectively.[12,13] The fraction of each reaction producing OH⁻ (or OD⁻) is shown in Figure 2. Both reactions are dominated by the associative detachment channel. In the H₂ reaction, the fraction of OH⁻ produced increases from 4.8% at 0.022 eV to 13.0% at 0.18 eV. The comparable numbers for D₂ are 2.4% at 0.022 eV and 14.2% at 0.269 eV. Since the associative detachment channel produces no detectable product, the branching fraction was

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‡On contract to GL from Wentworth Institute of Technology, Boston, MA. Present address: Department of Chemistry, Eastern Illinois University, Charleston, IL.
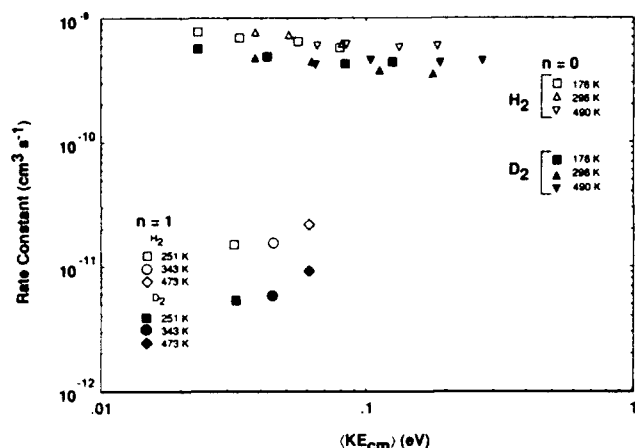
Figure 1. Rate constants for the reactions of $O^-(H_2O)_n$ with H_2 and D_2 as a function of $\langle KE_{cm} \rangle$. Open and solid symbols refer to reactions with H_2 and D_2, respectively. Squares, triangles, and inverted triangles refer to the $n = 0$ reaction at temperatures of 176, 296, and 490 K, respectively. The data for the $n = 1$ reaction represent pure temperature dependences converted to $\langle KE_{cm} \rangle$. For $n = 1$, squares, circles, and diamonds represent temperatures of 251, 343, and 473 K, respectively. $\langle KE_{cm} \rangle$ is given by the Wannier formula[11] as $\langle KE_{cm} \rangle = [(m_i + m_b)m_n/2(m_i + m_n)]v_d^2 + \frac{3}{2}kT$, where m_i, m_b, and m_n are the masses of the reactant ion, buffer gas, and reactant neutral, respectively, v_d is the ion drift velocity, and T is the temperature.
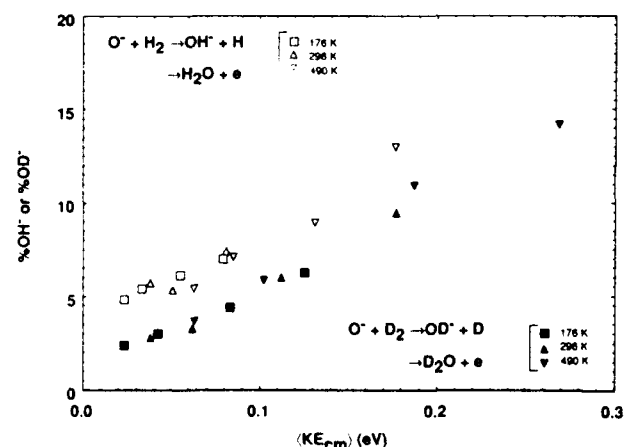

Figure 2. Percentage of the O^- reactions with H_2 and D_2 that produce OH^- or OD^- as a function of $\langle KE_{cm} \rangle$. Open and solid symbols refer to reaction with H_2 and D_2, respectively. Squares, triangles, and inverted triangles refer to temperatures of 176, 296, and 490 K, respectively.

calculated by comparing the decrease in the O^- signal to the increase in the OH^- (or OD^-) signal. The masses of the reactant and product ions are similar. Therefore little mass discrimination is expected, and accurate branching ratios can be measured. We estimate an absolute accuracy of ±1 percentage point and a relative accuracy of ±0.3 percentage point in the branching fractions, the latter being based on the scatter in the data.

For $n = 1$, there are also two exothermic channels

$$O^-(H_2O) + H_2 \rightarrow 2H_2O + e \qquad (3a)$$

$$O^-(H_2O) + H_2 \rightarrow OH^-(H_2O) + H \qquad (3b)$$
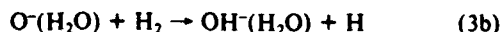
These channels are exothermic by 267 and 26 kJ mol⁻¹, respectively.[12-14] These reaction enthalpies were obtained by using a value of the $O^-(H_2O)$ cluster bond strength of 105 kJ mol⁻¹ calculated at the MP2/6-311++G(2d,2p)//MP2/6-31+G* level. This value of the cluster bond strength must be considered as preliminary and is actually a lower limit. The true exothermicity is therefore less than or equal to 26 kJ mol⁻¹.

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Determining the product distribution into channels 3a and 3b proved difficult due to the influence of extraneous ions in the flow tube at similar mass numbers. At 343 K for the D_2 reaction, we could determine that reaction 3b contributed approximately 10% of the total reaction. The branching ratio at 343 K depended on the H_2O concentration in the flow tube above a minimum level of 3×10^{11} cm⁻³. At lower H_2O concentrations, the branching ratio remained constant. This resulted from the fact that the reaction of $OD^-(H_2O)$ with H_2O is rapid. Attempts to study the branching ratio at other temperatures were unsuccessful. No branching ratios for the reaction of $O^-(H_2O)$ with H_2 could be measured due to the interference from Cl^- and $OH^-(H_2O)$ (both of which have masses of 35 amu) present in the tube in the absence of H_2. Reactions of $O^-(D_2O)$ could not be studied due to small amounts of H_2O impurities present in the helium buffer.

Both the rate constants and branching ratios for the $n = 0$ reactions agree well with previous room-temperature determinations.[15] To our knowledge, no previous measurements of the temperature dependences of these reactions have been reported. The reactions have been studied as a function of energy in both drift tubes[15,16] and beam systems.[17-19] These previous measurements led to rate constants that are independent of energy at low energies and also indicated the increasing importance of the OH^- (or OD^-) channel as energy is increased.

The collisional rate constants[20] for O^- reacting with H_2 and D_2 are 1.57×10^{-9} and 1.17×10^{-9} cm³ s⁻¹, respectively. The measured rate constants at room temperature and below represent 48% and 50% of the collisional rate constants for H_2 and D_2, respectively.

Discussion

The data show several interesting trends. The reaction efficiencies for $n = 0$ are considerably lower than 100% and show little temperature dependence. Frequently, ion–molecule reactions that proceed at less than the collisional limit show appreciable negative temperature dependences.

Another trend is that solvation effectively quenches the reactivity. Comparing the results for $n = 0$ and $n = 1$, we find that the reactivity decreases by factors of approximately 50 and 90 for H_2 and D_2, respectively, upon solvation of O^- by one H_2O molecule. Addition of a second H_2O molecule reduces the rate constants to below our detection limit. Additionally, positive temperature dependences are observed for the $n = 1$ reactions. Few exothermic ion–molecule reactions are known to have positive temperature dependences.[3]

These reactions are examples of associative detachment reactions of the insertion type, i.e., reactions in which generation of the neutral product requires the insertion of one of the reactants into a bond of the other. It has been postulated that these reactions take place in a two-step mechanism.[1] The first step of the mechanism is a chemical reaction in which the products do not separate, i.e.

$$O^- + H_2 \rightarrow (OH^- \cdots H)^* \qquad (4)$$
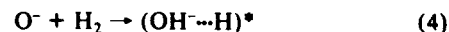
The complex produced in the first reaction can either dissociate back into reactants or undergo rearrangement followed by autodetachment

$$(OH^- \cdots H)^* \rightarrow H_2O + e \qquad (5)$$
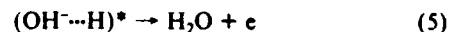
A requirement for the overall reaction to occur is that the first step (reaction 4) be exothermic. This mechanism has been shown to explain a number of associative detachment reactions of the insertion type.[1,21]

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For $n = 0$ in the reactions under consideration here, the first step not only is exothermic but also may lead to a minor product channel. The question remains as to why the reaction is 48% efficient and shows little temperature or $\langle KE_{cm} \rangle$ dependence, especially at low energy. Mauer and Schultz[17] have presented schematic potential energy curves for this reaction. They feature one attractive curve (for each O^- state) and two repulsive curves. For trajectories that follow the attractive curve, reaction presumably proceeds on every collision. An efficiency of 33% would then be expected for the overall reaction. This is less than the measured efficiency. It is therefore likely that the repulsive curves contribute to the reactivity. In reality, all ion–molecule potential curves have an attractive nature at long interparticle distances due to the ion-induced dipole interaction. Presumably, this interaction is large enough in at least one of the repulsive curves that a curve crossing can take place before the curve or curves become strongly repulsive.[17]

The observation of little temperature or energy dependence is consistent with this picture. Since $\sim 50\%$ of the collisions react and one-third of the trajectories begin on the attractive curve, the attractive curve is responsible for approximately two-thirds of the reactivity. This fraction of the reactivity is likely to be energy independent. An energy dependence due to the repulsive curves might then be masked by the large fraction that is energy independent.

The temperature and energy dependences of the branching fraction are also consistent with the two-step mechanism. The branching fraction is controlled by the competition between dissociation and autodetachment from the complex formed in reaction 4. Autodetachment requires some rearrangement and therefore involves a tight complex. The dissociation channel would involve a loose complex. Phase space theory would then predict that the process involving a loose complex is favored at higher temperatures or energies.[22] As the temperature or energy is raised, the complex would dissociate more readily before rearrangement (autodetachment) and favor the OH^- channel, consistent with the present observations.

More difficult to explain is why one solvent molecule reduces the reaction efficiency by such a large factor when there still remain two exothermic channels. One might predict some reduction of the efficiency due to steric effects, but the observed decrease is larger than we naively expected. Approximately only half of the approaches of H_2 to O^- would be expected to be blocked effectively by one H_2O ligand molecule.

Another possibility is that, once the first step of the two-step insertion mechanism occurs, considerable rearrangement is required for the H to move from the unsolvated end of the O atom to the other side. This is shown schematically as

$$(H\text{-}HO\text{-}H_2O)^{-*} \rightarrow (HO\text{-}H\text{-}H_2O)^{-*} \qquad (6)$$

While this may explain why the associative detachment channel is slow, it does not explain why the channel that forms $OH^-(H_2O)$ is also slow, since this channel requires only that the H atom dissociate from the complex. This channel is approximately equally exothermic with the unsolvated reaction because the strengths of the O^- and OH^- bonds to H_2O are similar. Therefore it appears either that the atom-transfer step, i.e., the formation of $(H\text{-}HO\text{-}H_2O)^{-*}$, is slow or that a different mechanism applies. This latter possibility seems unlikely, since we observe both the $OH^-(H_2O)$ product channel (approximately 10% at 343 K) and the associative detachment channel.

A detailed analysis of the cause of the low value of the rate constant for $n = 1$ is beyond the scope of this paper. A simple possibility remains. Frequently, ion–molecule reactions proceed without barriers. This is in contrast to reactions between neutrals, for which barriers are frequently seen. The explanation for this is that ion–molecule reactive surfaces are always attractive and that the kinetic energy gained during the course of a collision can

be used to break the bonds necessary for the reactions to occur. The maximum amount of energy available for this is the strength of the ion–neutral bond. It is also well-known that adding ligands reduces the bond strengths of subsequently added molecules.[23] Perhaps what is happening in the reactions studied here is that the H_2O ligand reduces the interaction energy between O^- and H_2, decreasing the probability for breaking the H_2 bond. Not only might this make the barrier to the bond breaking closer to the energy of the reactants but it might also give rise to a barrier above the zero of energy, as implied by the present positive temperature dependence. This is one of the few examples of an exothermic ion–molecule reaction with a positive temperature dependence.[3]

Considering that the first hydration decreases the rate constant so substantially, it is not surprising that the second hydration makes the reaction unobservable. The mechanism for the decrease caused by the first hydration would also probably apply to the second. In addition, a more severe steric constraint probably applies to the second hydration.

There has been one previous study of associative detachment reactions as a function of hydration. This involved the reactions of H atoms with $Cl^-(H_2O)_n$ ($n = 0-2$), $OH^-(H_2O)_n$ ($n = 0, 2, 3$), and $O_2^-(H_2O)_n$ ($n = 0-2$).[5] In all three of these series, adding H_2O molecules decreased the reactivity as well. In the last two cases the reactivity decrease was less than a factor of 10, and in the first case it was greater than a factor of 10. No definitive explanation of the decreases was given, but factors similar to those given here may be involved.

Recently, we have developed a technique for deriving rotational temperature dependences of rate constants for reactions between monatomic ions and neutrals with high-lying vibrational modes.[8,24,25] The technique involves measuring rate constants (or branching ratios) as a function of $\langle KE_{cm} \rangle$ at several temperatures. The rotational temperature dependence is given as the dependence of the rate constant (or branching ratio) on temperature at a particular $\langle KE_{cm} \rangle$. This is the type of data shown in Figures 1 and 2. Within experimental error, no temperature dependence is seen in either the rate constants or branching ratios at a particular $\langle KE_{cm} \rangle$ for the reactions of O^- with H_2 and D_2. This indicates that the rotational energies of H_2 and D_2 have little effect on the rate constants and branching ratios over the temperature range 176–490 K.

Previously, we have observed that frequently rate constants do not depend strongly on the rotational temperature of the reactant neutral.[8,24-27] Since the present reactions are near unit efficiency, we would not expect rotations to have a large effect on the rate constants; i.e., no form of energy is expected to have a large effect.

Predictions of the rotational temperature dependence of the branching ratio require detailed calculations. For the reaction of O^+ with HD, Dateo and Clary[28] have predicted and Sunderlin and Armentrout[29] have observed a dependence of the OH^+/OD^+ branching ratio on rotational energy of HD. We plan to look for a similar effect on the reaction of O^- with HD.

In conclusion, we have measured rate constants and branching ratios for the reactions of O^- with H_2 and D_2 as a function of $\langle KE_{cm} \rangle$ at several temperatures. The rate constants were found to decrease slightly with increasing temperature and $\langle KE_{cm} \rangle$. The main channel proceeds by associative detachment. The minor channel producing OH^- (or OD^-) becomes increasingly important at higher temperatures and energies. Addition of one water molecule to O^- decreases the reactivity by nearly 2 orders of

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magnitude. The main channel remains associative detachment. A minor (10%) channel produces $OH^-(H_2O)$. The temperature dependence of the rate constant for reaction of the singly solvated ion is positive. A second water solvent molecule decreases the reactivity to below our detection limit. The reactivity decrease appears too large to be caused by steric factors. A possible cause for the reduced reactivity is a reduced interaction energy of H_2 with $O^-(H_2O)$ compared with that of H_2 with O^-. No dependence on rotational energy was found for either the rate constants or the branching ratios for $n = 0$.

Note added in proof: Beam experiments, conducted at considerably higher energies than those of the present experiments, have been reported previously.[30]

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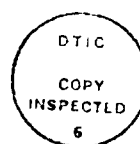
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