Isotope Effects in the Reaction of $\text{H}^+(\text{H}_2\text{O})_2/\text{D}^+(\text{D}_2\text{O})_2$ with Acetone/Dimethylsulfoxide

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We investigated isotope effects in the reactions of protonated water dimer ions $\text{H}^+(\text{H}_2\text{O})_2/\text{D}^+(\text{D}_2\text{O})_2$ with acetone and dimethylsulfoxide (DMSO) using a guided ion beam apparatus. The reaction cross section, σ_r , of $\text{H}^+(\text{H}_2\text{O})_2$ with acetone was found to be slightly larger than that of $\text{D}^+(\text{D}_2\text{O})_2$ at low collision energies, <0.5 eV, where the ratio of the σ_r , was less than 1.5. The σ_r of $\text{H}^+(\text{H}_2\text{O})_2$ with DMSO was approximately twice as large as that of $\text{D}^+(\text{D}_2\text{O})_2$ with DMSO. Major reaction products were Y^+X , where $\text{Y}=\text{H}$, D and $\text{X}=\text{acetone}$, DMSO . We examine two possible reaction processes, the proton transfer reaction *via* intermediate compounds and direct proton transfer.

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1. Introduction

Among hydrogen-bonded clusters, protonated water clusters, $\text{H}^+(\text{H}_2\text{O})_n$, are of particular concern. Ionic water clusters have been studied within the fields of solvation chemistry and atmospheric chemistry and in examinations of the nature of hydrogen-bonded systems.^{1)–6)} These studies have included analysis of both cluster structures and cluster reaction. Reaction rates are given by the product of the reaction cross sections, σ_r , and the collision velocities. We have investigated the reaction cross sections by using a guided ion beam (GIB) apparatus that realizes accurate measurement of σ_r at given collision energies.⁷⁾ We recently found anomalous enhancement of reaction cross section in the reaction of $\text{H}^+(\text{H}_2\text{O})_n$ with dimethylsulfoxide (DMSO) at $n=2$, while such enhancement was not observed with acetone.⁸⁾ Incidentally, both acetone and DMSO play important roles in the atmosphere; they are composed of the same number of atoms, 10, and have similar geometrical structures. The σ_r of $\text{H}^+(\text{H}_2\text{O})_2$ with DMSO was observed to be $\sim 1,000 \text{ \AA}^2$ at the collision energy of 0.1 eV, which was as twice large as that of $\text{H}^+(\text{H}_2\text{O})_4$. On the other hand, such phenomena were not observed with acetone. These observations were discussed in the term of proton transfer reaction.

Substituting D_2O for H_2O would be a useful way to further investigate our finding. The deuterium atom can work simply as a label when the H/D isotope effects are small. For example, an H/D exchange reaction was observed in the collision of $\text{H}^+(\text{H}_2\text{O})_n$ and

D_2O ,⁹⁾ and the mechanism of randomization of H and D atoms has been clarified. In the collision of $\text{H}_2\text{O}^+-\text{H}_2\text{O}$, the proton transfer was found to be the major channel for oxonium ion production rather than an atom pickup channel.¹⁰⁾ We can learn more about the reaction mechanisms of interest by studying isotope effects. We may be able to discern the reaction process by comparing the difference between the results with H_2O and D_2O . For instance, D_2O was enriched in the cluster phase during free jet expansions.¹¹⁾ This observation suggested that the formation of clusters in supersonic free jets is largely governed by unimolecular decomposition kinetics. Comparing the reaction cross sections of $\text{H}^+(\text{H}_2\text{O})_2$ and $\text{D}^+(\text{D}_2\text{O})_2$ would be, therefore, a powerful way to investigate the reaction scheme.

In this article, we report the reaction cross sections of $\text{H}^+(\text{H}_2\text{O})_2/\text{D}^+(\text{D}_2\text{O})_2$ with acetone/DMSO measured in a guided ion beam apparatus. We discuss here the reaction scheme and the observed isotope effects.

2. Experimental Setup and Analysis

A guided ion beam (GIB) apparatus⁷⁾ was used for the present study. This apparatus was composed of a corona discharge cluster-ion source, two octopole ion beam guides, a quadrupole mass filter, a Bessel box energy analyzer, a collision cell, and a quadrupole mass spectrometer. Water vapor was supplied into the cluster-ion source from a glass chamber in a bath kept at 15°C with nitrogen at a flow rate of 12 sccm (standard cubic centimeters per minute). The values of HWHM (Half Width at Half Maximum) of the translational energy distributions of the cluster ions were about 0.1 eV.

The σ_r was given by the following equation:

$$\sigma_r = \frac{k_B T}{Pl} \ln \frac{I(0)}{I(l)} \quad (1)$$

where $I(0)$ and $I(l)$ are the intensities of the parent

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cluster ion at the entrance and at the exit of the collision cell, respectively; l is the effective path length of the collision cell (0.1 m); T and P are the temperature (25°C) and the pressure of the reactant, X=acetone or DMSO, respectively; and k_B is Boltzmann's constant. The pressures P of X were measured by a spinning rotor gauge (MKS SRG-2). The internal energies of the parent cluster ions were estimated by RRK (Rice–Ramsperger–Kassel) theory⁷⁾ to be 1.2 eV.

3. Results

Observed reaction products were mainly H^+X/D^+X and H^+X_2/D^+X_2 at all examined collision energy and pressure levels. Figure 1 shows typical mass spectra at a collision energy, E_{col} , of 0.1 eV. The abundance of other reaction products such as $H^+X(H_2O)/D^+X(D_2O)$ was less than 10%, even at the lowest collision energy, and it was hard to tell the signals of these products from noise. The reason why H^+X_2/D^+X_2 were observed was probably that the mass of the parent clusters is small compared to those of reactant molecules, that is, when they collide, the product ions slowed down and have increased chance to collide once more even though the pressure of the reactants was very low. The total ion intensities and σ_r were confirmed to be independent of P in the range of 2×10^{-4} – 8×10^{-4} Pa for acetone and 6×10^{-5} – 3×10^{-4} Pa for DMSO, and the fluctuation of σ_r was within $\pm 20\%$. This assures accuracy of the measured reaction cross sections.

Figure 2 shows the reaction cross sections, σ_H and σ_D , of $H^+(H_2O)_2$ and $D^+(D_2O)_2$, respectively, with acetone as a function of collision energy in the center of the mass frame together with the collision cross section of

$H^+(H_2O)_2$, σ_{col} , and geometrical cross section, σ_g . The σ_{col} calculation method was described previously.⁸⁾ The σ_g was determined as $\pi(d_1 + d_2 + 2d_3)^2$, where d_1 and d_2 are the distances from the centers of masses of X and the water dimer, respectively, to the most distant atom, and d_3 is the van der Waals radii of a H atom. The σ_r of $H^+(H_2O)_2$ was found to be somewhat larger than that of $D^+(D_2O)_2$ at low collision energies, < 0.5 eV, in the reaction with acetone. The isotope effects were not discern-

Fig. 2. The reaction cross sections of $H^+(H_2O)_2/D^+(D_2O)_2$ with acetone as a function of the collision energy. Open and solid circles represent the cases of $H^+(H_2O)_2$ and $D^+(D_2O)_2$, respectively. The solid line shows the collision cross section, σ_{col} , at low collision energies, and the geometrical cross section, σ_g , at high collision energies.

Fig. 1. The mass spectra of $D^+(D_2O)_2$ reaction at a collision energy of 0.1 eV with (a) acetone at a pressure of 2.2×10^{-4} Pa and (b) DMSO at a pressure of 2.6×10^{-4} Pa.

Fig. 3. The reaction cross sections of $\text{H}^+(\text{H}_2\text{O})_2/\text{D}^+(\text{D}_2\text{O})_2$ with DMSO as a function of the collision energy. Open and solid circles represent the cases of $\text{H}^+(\text{H}_2\text{O})_2$ and $\text{D}^+(\text{D}_2\text{O})_2$, respectively. The solid line shows the collision cross section, σ_{col} , at low collision energies, and the geometrical cross section, σ_{g} , at high collision energies.

Fig. 4. Reaction cross section ratio, $\sigma_{\text{H}}/\sigma_{\text{D}}$, as a function of collision energy. Open and solid squares represent values for acetone and DMSO, respectively.

ible at higher collision energies. On the other hand, in the case of collision with DMSO, the σ_{r} of $\text{H}^+(\text{H}_2\text{O})_2$ was found to be much larger than that of $\text{D}^+(\text{D}_2\text{O})_2$ and σ_{col} at all examined collision energies, as shown in Fig. 3. The ratio of the reaction cross sections, $\sigma_{\text{H}}/\sigma_{\text{D}}$, is plotted in Fig. 4. The ratio, $\sigma_{\text{H}}/\sigma_{\text{D}}$, for DMSO appeared to be approximately 2 at all examined collision energies, whereas $\sigma_{\text{H}}/\sigma_{\text{D}}$ for acetone was less than 1.5.

4. Discussion

Observed reaction products can be generated *via* intermediate compounds in general. The cluster ion $\text{H}^+(\text{H}_2\text{O})_2/\text{D}^+(\text{D}_2\text{O})_2$ and reactant X can form an intermediate $[\text{H}^+(\text{H}_2\text{O})_2\text{X}]^*/[\text{D}^+(\text{D}_2\text{O})_2\text{X}]^*$, which has a much longer lifetime than the vibrational frequency as they collide with each other. Because of the high internal energy of the intermediate, evaporation of water mole-

Table 1. Proton Affinities^{a)}

	Mass (amu)	PA (eV)	
		Exp. ¹²⁾	Cal.
$\text{H}^+(\text{H}_2\text{O})_2$	37	—	8.64
Acetone	58	8.42	8.51
DMSO	78	9.17	9.34

^{a)} Proton affinities (PA) and dipole moments were calculated with B3LYP/cc-pVTZ (correlation-consistent polarization plus valence triple zeta). The proton affinities, defined as $\text{PA} = E(\text{H}^+\text{Y}) - E(\text{Y})$ and corrected with zero-point vibrational energies where E is the total energy and $\text{Y} = (\text{H}_2\text{O})_2$, DMSO, acetone and DMSO.

cules follows, where a water molecule preferably evaporates from the intermediate because the proton affinity of water is lower than that of X; that is, the bond energy of water to the rest of the intermediate is smaller (see Table 1). This reaction scheme is summarized as:

An H/D exchange reaction may occur in the intermediate when $\text{D}^+(\text{D}_2\text{O})_2$ collides with acetone/DMSO. The reaction products of acetone/DMSO and $\text{D}^+(\text{D}_2\text{O})_2$ after evaporation of two water molecules are expected to be $\text{C}_3\text{H}_n\text{D}_m\text{O}^+/\text{C}_2\text{H}_n\text{D}_m\text{SO}^+$ where n and m are 2–6 and 1–5, respectively. When the H/D exchange takes place, $n + m$ would equal 7 where $n \leq 5$ and $m \geq 2$, where corresponding masses are 61–64 with acetone and 81–84 with DMSO. As can be seen in Fig. 1, however, we observed only $\text{C}_3\text{H}_6\text{DO}^+/\text{C}_2\text{H}_6\text{DSO}^+$, where $n=6$ and $m=1$, with the mass values of 60.08/80.13. The mass spectra show that there was no H/D exchange process in the intermediate or the reaction scheme did not include the intermediate.

When we can assume the reaction path (i), proton transfer occurs in the intermediate cluster. The internal proton transfer process is expected to be barrierless, thus, little isotope effect is expected at this stage. We expect the isotope effect in the first step of the reaction to form the intermediate, which is proportional to the collision rate. In such case, a ‘spectator stripping’ or ‘pairwise interaction’ model can explain the isotope effect.¹⁰⁾ This model predicts a larger reaction cross section for heavier isotopes at a given collision energy in the center of the mass frame: the isotope effect should disappear when the reaction cross sections are plotted against the relative velocities. In the present case, the difference of the relative velocities of $\text{H}^+(\text{H}_2\text{O})_2$ and $\text{D}^+(\text{D}_2\text{O})_2$ is about 4%, which gives $\sigma_{\text{H}}/\sigma_{\text{D}} = 0.94–0.96$ for acetone and ~ 0.96 for DMSO at, e.g., 0.1–0.3 eV of collision energy. The experimental values of $\sigma_{\text{H}}/\sigma_{\text{D}}$ shown in Fig. 4 are larger than 1 with either acetone or DMSO at low collision energies. Obviously, the spectator stripping model does not apply to our observation. This fact suggests that the contribution from the intermediate was minor.

Because of the hyper-thermal energy conditions, the relevant interaction times are comparable to the molecular vibrational periods. If the reaction probability

depends strongly on the phase of the relevant vibrational motion, the higher vibrational frequency associated with the lighter isotope would result in a greater probability of the appropriate phase during the collision event. The vibrational frequencies of H₂O molecule are 30% to 40% higher than those of D₂O, for example, the symmetrical stretching frequencies of H₂O and D₂O are 3,657 and 2,671 cm⁻¹, respectively. The difference of the vibrational periods may explain the isotope effect observed with acetone where $\sigma_{\text{H}}/\sigma_{\text{D}}$ was less than 1.5 and the observed σ_{r} was about the same or less than the calculated σ_{col} . The vibrational frequencies difference alone is not sufficient to explain the difference of the results with acetone and DMSO and the anomalous enhancement of the σ_{r} of H⁺(H₂O)₂ with DMSO, however.

The other candidate for the reaction process is the direct proton transfer;

We calculated the energy barrier for proton transfer for further consideration of the current observation. First, geometries of (H₂O)₂, H⁺(H₂O)₂, X, H⁺X were optimized by the *ab initio* molecular orbital (MO) method using MP2/6-31 G**^{*}. Then, orientation of the molecules were optimized for (a) H⁺(H₂O)₂ + X, (b) (H₂O)₂ + H⁺ + X, (c) (H₂O)₂ + H⁺X, where H⁺ was placed at the middle point of two molecules for (b). The energies for (b) were determined to be the energy barrier for proton transfer. It was found that the energy barrier was about 5.4 and 2.6 eV for acetone and DMSO, respectively, when the distance between the centers of mass of the water dimer and acetone or DMSO was 18.3 Å that corresponds to reaction cross section of $\sim 1,050 \text{ \AA}^2$ observed in the reaction of H⁺(H₂O)₂ + DMSO at ~ 0.1 eV. The reaction potential barrier induced an H/D isotope effect. When the barrier is too high, neither H⁺ nor D⁺ can transfer. The lower energy barrier in the case of DMSO might increase the probability of a H⁺ transfer

while still preventing a D⁺ transfer. When we assume that the direct proton transfer occurs, the proton transfer reaction cross section of H⁺(H₂O)₂ with DMSO was found to be almost equal to the total reaction cross section, because the observed reaction products were mainly proton transfer products H⁺[(CH₃)₂SO] and H⁺[(CH₃)₂SO]₂.

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