Solvent Effects

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Microhydration Effects on the Intermediates of the S_N2 Reaction of Iodide Anion with Methyl Iodide**

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Reactions of halide anions with methyl halides $X^-+CH_3Y\rightarrow XCH_3+Y^-$ are bimolecular nucleophilic substitution (S_N2) reactions that have been well investigated in the last few decades.[1] Figure 1 shows the typical potential energy surfaces (PES) proposed for symmetric $X^-+CH_3X\rightarrow XCH_3+X^-$ S_N2 reactions along the reaction coordinate. In the gas phase, the PES has two minima, which correspond to the stable $X^-(CH_3X)$ complexes.[2] The PES is substantially distorted by solvation. As the negative charge is delocalized over the $(X\cdots CH_3\cdots X)^-$ moiety at the transition state, the stabilization energy gained by solvation is smaller for the transition state than that for the X^-+CH_3X reactants or the $X^-(CH_3X)$ complexes. In solution, a large potential barrier exists between the reactants and products. The rate constants of these reactions in protic solvents were reported to be a few orders of magnitude smaller than those in aprotic solvents; this trend was explained by the formation of solvation shells of protic molecules around the halide anions.[1,3] Morokuma has previously reported a theoretical study on the PES of the $Cl^-+CH_3Cl\rightarrow ClCH_3+Cl^-$ S_N2 reaction with a few H_2O molecules. The attachment of H_2O molecules to the $Cl^-(CH_3Cl)$ reactive system produces metastable isomers, which affect the reaction mechanism.[4] Johnson and coworkers have extensively investigated the structures and reactions of halide anion complexes in the gas phase using photodissociation spectroscopy.[5] Herein, we report the results of IR photodissociation (IRPD) spectroscopy on $I^-(CH_3I)(H_2O)_n$ ($n=1$–3) clusters. An analysis of the IRPD spectra, along with the aid of theoretical calculations, provides valuable information about the stable structures of these complexes. From these stable structures we obtain information about the deformation of the PES along the $I^-+CH_3I\rightarrow ICH_3+I^-$ S_N2 reaction coordinate caused by microhydration. The rate constant of this reaction has been measured in water, methanol, ethanol, and acetone; the rate constant in water was found to be four orders of magnitude smaller than that in acetone.[3,6] The binding energy between I^- anion and H_2O is 43 kJ mol^{-1}, a value that is comparable to that of the I^- anion with CH_3I (35 kJ mol^{-1}).[7] Other important previous studies related to this subject are discussed in the Supporting Information.

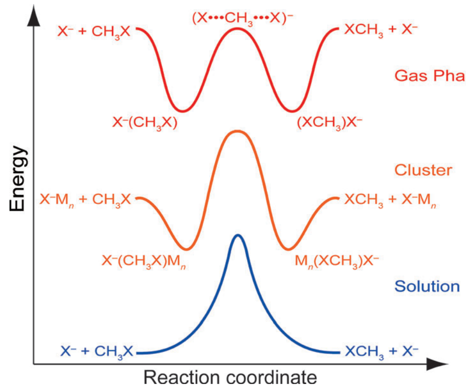

Figure 1. Potential energy surfaces of $X^-+CH_3X\rightarrow XCH_3+X^-$ S_N2 reactions in the gas phase, in clusters, and in solution.

Figure 2 shows the measured IRPD and calculated IR spectra of the $I^-(CH_3I)(H_2O)_{1-3}$ clusters in the C−H and O−H stretching regions. The strong bands in the 3200–3700 cm^{-1} region are due to the O−H stretching vibrations of the H_2O constituents. We have performed anharmonic analysis with a large basis set (MP2/aug-cc-pVDZ-PP for I atoms, and aug-cc-pVDZ for C, H, and O atoms) to obtain the vibrational frequencies in Figure 2; the level of electronic structure calculations and basis sets used in this study are carefully determined from the ability to reproduce the IR spectrum of $I^-(H_2O)$ in the gas phase (see the Supporting Information). The observed IR spectra are well reproduced by the calculated ones, as indicated by the dotted lines in Figure 2. The measured IRPD spectra can be attributed to two isomers for each cluster. Figure 3 shows the structure of the $I^-(CH_3I)(H_2O)_{1-3}$ complexes, as determined by a comparison of their computed anharmonic frequencies with the IRPD spectra. For the $n=1$ ion, the 3369 and 3696 cm^{-1} bands are assigned to the hydrogen-bonded and free O−H stretching vibrations of isomer **1A**, which is the most stable form for $n=1$. The

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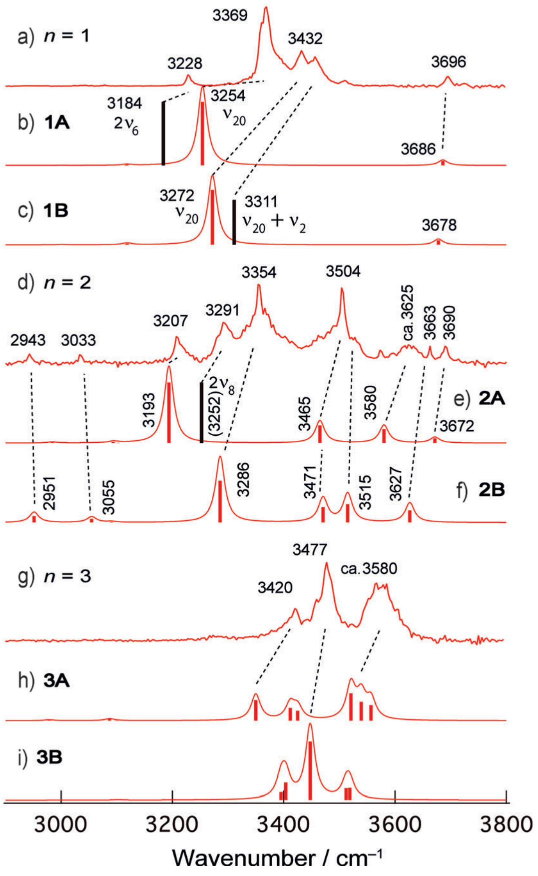

Figure 2. The IRPD (a, d, and g) and calculated (b, c, e, f, h, i) IR spectra of $I^-(CH_3I)(H_2O)_n$ ($n=1$–3) clusters in the C–H and O–H stretching region. Black bars show the position of overtone or combination vibrations. No scaling factor is used for the calculated anharmonic frequencies.

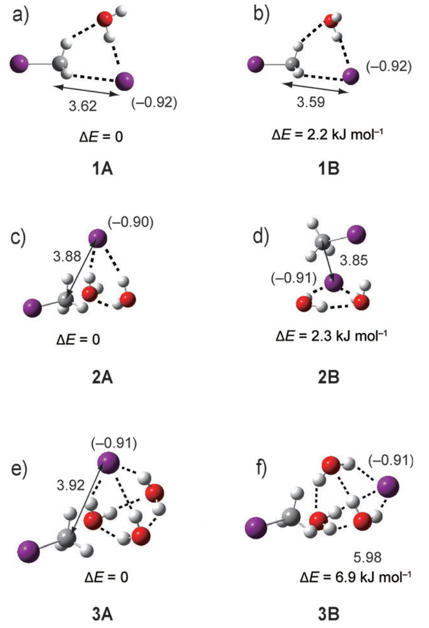

Figure 3. The structures of $I^-(CH_3I)(H_2O)_1$ (a, b), $I^-(CH_3I)(H_2O)_2$ (c, d), and $I^-(CH_3I)(H_2O)_3$ (e, f) determined in this study. The numbers shown correspond to the C–I⁻ distance in Å. The numbers in parentheses are the charge on the I atoms. ΔE denotes the Gibbs energy at 298.15 K relative to that of the most stable structures.

weak band at 3228 cm^{-1} is the first overtone of the bending vibration of H_2O in **1A**, the frequency of which is estimated to be 3184 cm^{-1}, as a result of the anharmonic analysis. As shown in the Supporting Information, an Ar-tagging experiment of $n=1$ suggests that the doublet structure around 3432 cm^{-1} is due to an isomer other than **1A**. This doublet structure is assigned to isomer **1B**; anharmonic analysis of **1B** predicts an H-bonded O–H stretch (ν_{20}) and its combination band with an intermolecular torsional motion ($\nu_{20}+\nu_2$) at 3272 and 3311 cm^{-1}, respectively. In the IRPD spectrum of the $n=2$ complex, there are more than four bands, which indicates the coexistence of isomers. As shown in Figure 2, all the bands in the IRPD spectrum of the $n=2$ cluster can be attributed to either isomer **2A** or **2B**. In the case of $n=3$, the 3420 and 3580 cm^{-1} components of the IRPD spectrum are ascribed to isomer **3A**, which is the most stable isomer. However, the 3477 cm^{-1} band of the observed spectrum seems too strong to be assigned solely to isomer **3A**. This band can be assigned to isomer **3B**, which has a sharp, strong band at 3448 cm^{-1}.

One noticeable feature in the IRPD spectra is that the C–H stretching bands appear only for the $n=2$ complex at 2943 and 3033 cm^{-1}. This is due to the relative arrangement between the I^- anion and CH_3I, which is characteristic of the $n=2$ complex. For better visualization of the relationship between the configuration and the IR absorption intensity of the C–H stretches, the position of the I^- anion with respect to the CH_3I component in the $I^-(CH_3I)(H_2O)_n$ isomers is displayed in Figure 4b, along with the structure of the non-hydrated $I^-(CH_3I)$ complex (Figure 4a). In Figure 4b the isomers are placed so that the CH_3I component is located at the same position in the three dimensional space. All of the H_2O molecules are omitted, and the position of the I^- anion relative to the CH_3I component is shown with spherical markers. The color of the markers indicates the IR intensity of the C–H stretching vibrations of the isomers; the IR intensity of each isomer is obtained by the summation of the IR intensity for all three C–H stretching vibrations. The $n=0$ ion has the I^- anion in the C_3 axis and a very weak IR intensity for the C–H stretching vibrations. In isomers **1A** and **1B**, the I^- anion is close to the C_3 axis, and thus similar to the non-hydrated $I^-(CH_3I)$ ion. For the $n=2$ complex, the I^- anion is located around the extended line of the C–H bond in isomer **2B**, which results in an enhanced IR intensity of the C–H stretching vibrations for **2B**. The calculated result is consistent with the experimental one, namely that the $n=2$ complex shows noticeable C–H bands in the IRPD spectrum. Isomer **2A** has the I^- anion slightly off from the extended line of the C–H bond, and so has a weaker IR intensity than that of **2B**. In isomer **3A**, the position of the I^- anion is similar to that in **2A**. For isomer **3B**, the I^- anion is located close to the C_3 axis, but the distance between the C atom and the I^- anion is very long (5.98 Å) because of the hydration shell formed between the I^- anion and the CH_3I moiety. The IR intensities of the C–H stretching vibrations of **3A** and **3B** are very weak. The red curve in Figure 4b shows the trend of the position of the I^- anion as the number of H_2O molecules increases. Solvation

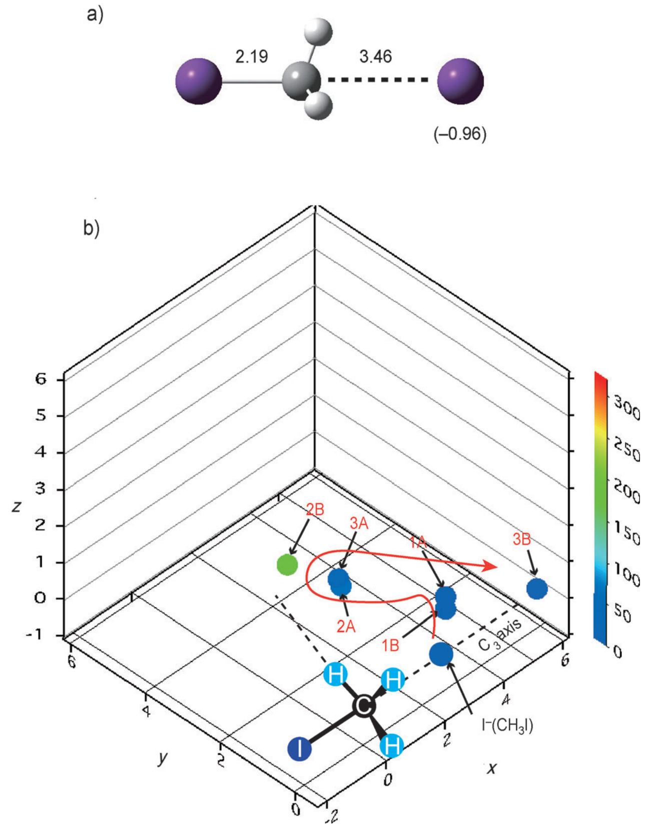

Figure 4. a) Optimized structure of the $I^-(CH_3I)$ ion. b) Positions of the I^- anion with respect to the CH_3I component (given in Å) in the structures of the $I^-(CH_3I)(H_2O)_n$ ($n=0$–3) complexes (see Figure 3). Spherical markers show the position of the I^- anion (given in Å). The color of the markers represents the IR intensity of the C–H stretching vibrations (given in km mol^{-1}).

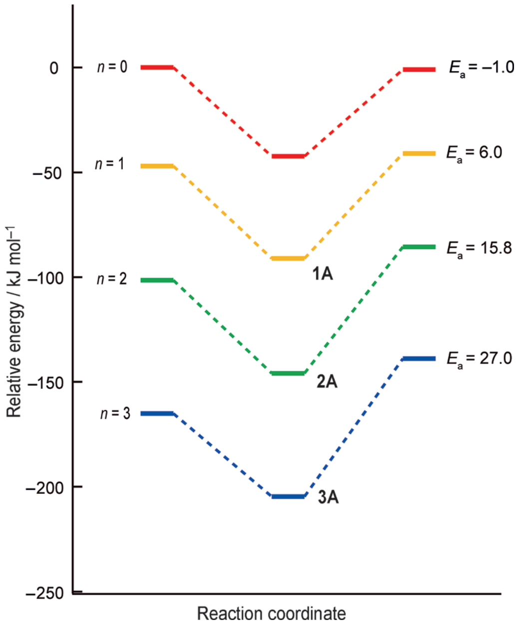

Figure 5. The energy levels of the $I^-(H_2O)_n$+CH_3I reactants, $I^-(CH_3I)(H_2O)_n$ ion complexes, and $(I\cdots CH_3\cdots I)^-(H_2O)_n$ transition states calculated at the MP2/aug-cc-pVDZ-PP (for I atoms)/aug-cc-pVDZ (for C, H, O atoms) level of theory. E_a is the barrier height (kJ mol^{-1}), which is obtained by subtracting the energy of the $[I^-(H_2O)_n$+$CH_3I]$ reactants from that of the $(I\cdots CH_3\cdots I)^-(H_2O)_n$ transition states.

with just two or three H_2O molecules moves the I^- anion away from the CH_3I moiety, a fact that effectively suppresses the S_N2 reaction.

The energetics of the $I^-(H_2O)_n$ and $I^-(CH_3I)(H_2O)_n$ complexes also predict a considerable inhibition of the $I^-+CH_3I \rightarrow ICH_3+I^-$ S_N2 reaction by microhydration. Figure 5 shows the energy levels of the $I^-(H_2O)_n$+CH_3I reactants, $I^-(CH_3I)(H_2O)_n$ complexes, and the transition state of the reaction with $n=0$–3. For the energy levels of $I^-(CH_3I)(H_2O)_n$, we adopt the total energy of the most stable isomers (**1A**, **2A**, and **3A**). The structures of the transition states are shown in the Supporting Information. For the $n=0$ ion, the energy of the I^-+CH_3I reactants is higher than that of the $(I\cdots CH_3\cdots I)^-$ transition state by 1.0 kJ mol^{-1}; there exists no potential barrier for the $n=0$ system from the reactant level. Solvation with one H_2O molecule stabilizes the I^- anion by 47.0 kJ mol^{-1}, whereas the energy of the transition state is lowered by 40.0 kJ mol^{-1}. As a result, the energy of the $(I\cdots CH_3\cdots I)^-(H_2O)_1$ transition state becomes higher than that of the $I^-(H_2O)_1$+CH_3I reactants by 6.0 kJ mol^{-1}. In the case of the $n=2$ system, the energy of the $(I\cdots CH_3\cdots I)^-(H_2O)_2$ transition state is higher than that of the $I^-(H_2O)_2$+CH_3I reactants by 15.8 kJ mol^{-1}. For the $n=3$ system, the barrier height is predicted to be 27.0 kJ mol^{-1}, which is larger than that of the $n=2$ system. These results suggest that solvation with just one H_2O molecule will substantially inhibit the $I^-+CH_3I \rightarrow ICH_3+I^-$ reaction, owing to the increase in the barrier height. The rate constant has not been reported for the $I^-+CH_3I \rightarrow ICH_3+I^-$ reaction as a function of the number of solvent H_2O molecules in the gas phase, but a sharp decrease in the reaction rate constant with a few H_2O molecules was reported for several $X^-(H_2O)_n$+CH_3Y systems.[8] The $I^-(CH_3I)(H_2O)_n$ complexes are trapped in deep potential minima between the $I^-(H_2O)_n$+CH_3I reactants and the $(I\cdots CH_3\cdots I)^-(H_2O)_n$ transition states. The depth of the potential wells from the transition state becomes deeper as the number of H_2O molecules increases (41.3 and 69.3 kJ mol^{-1} for $n=0$ and 3), but it becomes shallower from the $I^-(H_2O)_n$+CH_3I reactants (42.3 and 39.7 kJ mol^{-1} for $n=0$ and 3). This modulation of the PES by hydration results in the disappearance of the deep potential minima of $I^-(CH_3I)(H_2O)_n$ and the appearance of a large potential barrier between the reactants and products in solution, as shown in Figure 1.

Figure 6 shows PESs of the $I^-(CH_3I)(H_2O)_n$ ($n=0$ and 3) complexes along the $I^-+CH_3I \rightarrow ICH_3+I^-$ reaction coordinate based on the stable structures determined herein. R_1 and R_2 are the distance between the I and C atoms. For the $n=0$ system, the potential minimum of the $I^-(CH_3I)$ complex is located at R_1–$R_2=1.28$ Å. In the $n=3$ case, a pyramidal-type hydration shell is formed around the I^- anion, and the CH_3I molecule is preferentially bonded to the hydration network rather than the I^- anion. As it seems impossible for the CH_3I molecule to penetrate this hydration shell, the CH_3I molecule has to move around the pyramid to the I^- anion to promote

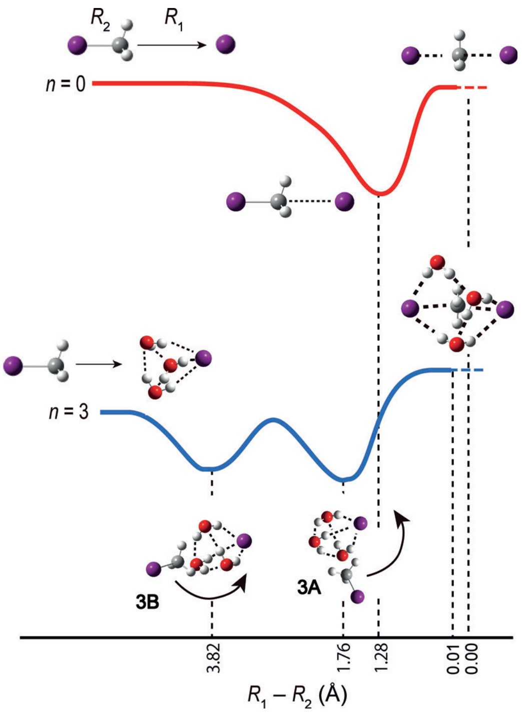

Figure 6. Potential energy surfaces of the $I^- + CH_3I \rightarrow ICH_3 + I^-$ S_N2 reaction without water ($n=0$) and with three water molecules ($n=3$), as a function of the difference in the C–I distances (R_1–R_2).

the reaction. In our calculations, no stable isomer is found for the $I^-(CH_3I)(H_2O)_3$ complex in which the CH_3I component is directly bonded to the I^- anion at the apex of the $I^-(H_2O)_3$ pyramid. Therefore, the CH_3I moiety and the H_2O molecules move simultaneously to reach the transition state. The positions of the potential minima of **3A** and **3B** (R_1–R_2 = 1.76 and 3.82 Å, respectively) are more distant from the transition state than that in the $I^-(CH_3I)$ complex (R_1–R_2 = 1.28 Å). In the $I^- + CH_3I \rightarrow ICH_3 + I^-$ reaction for the $n=3$ cluster, therefore, the I^- anion will be trapped further away from the CH_3I molecule, something that will result in a further inhibition of the S_N2 reaction. As mentioned above, the binding energy of the I^- anion with CH_3I (35 kJ mol^{-1}) is comparable to that with H_2O (43 kJ mol^{-1}). Nevertheless, three H_2O molecules in the $n=3$ complex are likely to shield the I^- anion from the CH_3I component quite effectively.

In summary, we have measured IR photodissociation (IRPD) spectra of $I^-(CH_3I)(H_2O)_n$ ($n=1$–3) complexes to elucidate the effects of the microsolvation of water in the $I^- + CH_3I \rightarrow ICH_3 + I^-$ S_N2 reaction. On the basis of the stable forms of the $I^-(CH_3I)(H_2O)_n$ complexes determined herein, just two or three H_2O molecules can effectively inhibit the $I^- + CH_3I \rightarrow ICH_3 + I^-$ S_N2 reaction. Furthermore, the calculated energetics suggest that suppression of the reaction occurs from $n=1$, as the barrier height of the reaction already becomes positive for that cluster size.

Methods Section

The details of our experiments for measuring the IRPD spectra have been given in our previous report[9] and in the Supporting Information. In brief, the $I^-(CH_3I)(H_2O)_n$ ions are produced in a vacuum chamber by electron impact and are analyzed by a time-of-flight mass spectrometer. Parent ions of interest are isolated by a mass gate and irradiated by the output of an IR laser. The resulting fragment $I^-(H_2O)_n$ ions are mass-analyzed by a reflectron and detected by a multichannel plate. The IRPD spectra of the parent ions are obtained by plotting the yields of the fragment ions as a function of the wavenumber of the IR laser. To analyze the IRPD spectra and determine the complex structure, we performed quantum chemical calculations with the GAUSSIAN09[10] and NWChem[11] program packages. Geometry optimization and vibrational (harmonic and anharmonic) analysis of the $I^-(CH_3I)(H_2O)_{0-3}$ complexes are done at the MP2/aug-cc-pVDZ-PP (for I atoms)/aug-cc-pVDZ (for C, H, O atoms) level. The anharmonic frequencies were obtained by vibrational second order perturbation theory.

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