

Microhydration Effects on the Intermediates of the ($\text{I}^- + \text{CH}_3\text{I}$) $\text{S}_{\text{N}}2$ Reaction

Keisuke Doi, Eijiro Togano, Sotiris S. Xantheas, Ryuzo Nakanishi, Takashi Nagata, Takayuki Ebata, and Yoshiya Inokuchi*

Reactions of halide anions with methyl halides ($\text{X}^- + \text{CH}_3\text{Y} \rightarrow \text{XCH}_3 + \text{Y}^-$) are bimolecular nucleophilic substitution ($\text{S}_{\text{N}}2$) reactions that have been well investigated in the last few decades.^[1] Figure 1 shows typical potential energy surfaces (PESs) proposed for symmetric ($\text{X}^- + \text{CH}_3\text{X} \rightarrow \text{XCH}_3 + \text{X}^-$) $\text{S}_{\text{N}}2$ reactions along the reaction coordinate. In the gas phase, the PES has two minima corresponding to the stable $\text{X}^-(\text{CH}_3\text{X})$ complexes.^[2] The PES is substantially distorted by the solvation. Since the negative charge is delocalized over the $[\text{X}\cdots\text{CH}_3\cdots\text{X}]^-$ moiety at the transition state the stabilization energy gained by the solvation is smaller for the transition state than that for the ($\text{X}^- + \text{CH}_3\text{X}$) reactants or the $\text{X}^-(\text{CH}_3\text{X})$ 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 ($\text{Cl}^- + \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 + \text{Cl}^-$) $\text{S}_{\text{N}}2$ reaction with a few H_2O molecules. The attachment of H_2O molecules to the $\text{Cl}^-(\text{CH}_3\text{Cl})$ reactive system produces metastable isomers, which affect the reaction mechanism.^[4] Johnson and co-workers extensively investigated the structure and reactions of halide anion complexes in the gas phase using photodissociation spectroscopy.^[5] In this study we report the results of IR

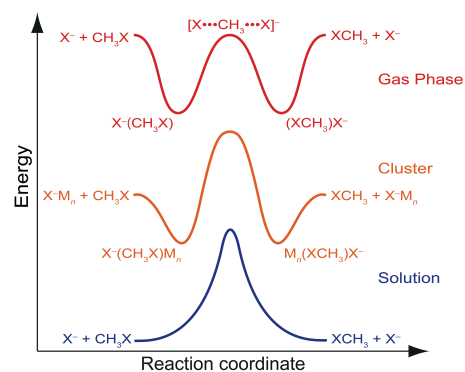


Figure 1. Potential energy surfaces of ($\text{X}^- + \text{CH}_3\text{X} \rightarrow \text{XCH}_3 + \text{X}^-$) $\text{S}_{\text{N}}2$ reactions in the gas phase, in clusters, and in solution.

photodissociation (IRPD) spectroscopy of the $\text{I}^-(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$ ($n = 1-3$) clusters. The analysis of the IRPD spectra with the aid of theoretical calculations provides valuable information about the stable structures of these complexes. From these stable structures

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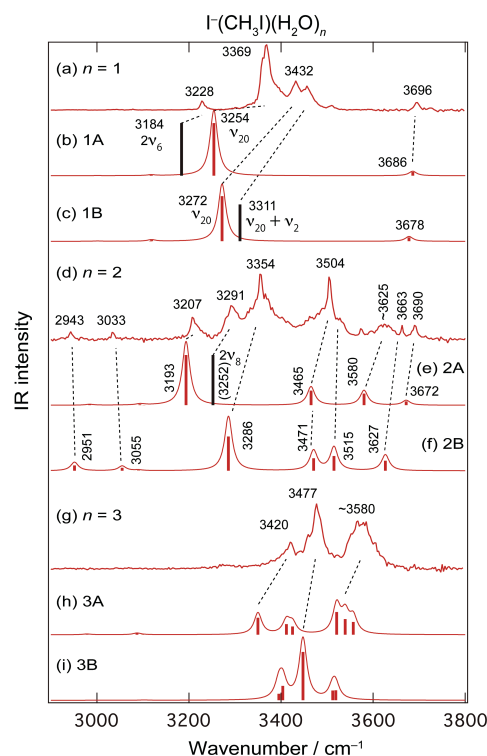


Figure 2. The IRPD (a, d, and g) and calculated IR spectra of the $\text{I}^-(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$ ($n = 1-3$) clusters in the CH and OH stretching region. Black bars show the position of overtone or combination vibrations. No scaling factor is used for the calculated anharmonic frequencies.

we obtain information about the deformation of the PES along the ($\Gamma + \text{CH}_3\text{I} \rightarrow \text{ICH}_3 + \Gamma$) $\text{S}_{\text{N}}2$ reaction coordinate caused by microhydration. The rate constant of this reaction was measured in water, methanol, ethanol, and acetone; the rate constant in water is four orders of magnitude smaller than that in acetone.^[3,6] The binding energy between Γ ion and H_2O is 43 kJ/mol, a value that is comparable to that of Γ with CH_3I (35 kJ/mol).^[7] Other previous important studies related to this subject are discussed in the Supporting Information.

Figure 2 shows the measured IRPD and calculated IR spectra of the $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_{1-3}$ clusters in the CH and OH stretching regions. The strong bands in the 3200–3700 cm^{-1} region are due to the OH stretching vibrations of the H_2O constituents. We have performed anharmonic analysis with a large basis set [MP2/aug-cc-pVDZ-PP(for I)/aug-cc-pVDZ(for C, H, O)] in order 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 $\Gamma(\text{H}_2\text{O})$ 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 $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_{1-3}$ complexes determined by 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(H)-bonded and free OH stretching vibrations of isomer 1A, which is the most stable form for $n = 1$. The weak band at 3228 cm^{-1} is the first overtone of the bending vibration of H_2O in 1A, whose frequency 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 a H-bonded OH 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, indicating 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 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 CH stretching bands appear only for the $n = 2$ complex at 2943 and 3033 cm^{-1} . This is due to the relative arrangement between Γ and CH_3I characteristic of the $n = 2$ complex. For better visualization of the relation between the configuration and the IR absorption intensity of the CH stretches, the position of the Γ anion with respect to the CH_3I component in the $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$ isomers is displayed in Figure 4b with the structure of the non-hydrated $\Gamma(\text{CH}_3\text{I})$ 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 the H_2O molecules are omitted, and the position of the Γ anion relative to the CH_3I component is shown with spherical markers. The color of the markers indicates the IR intensity of the CH stretching vibrations of the isomers; the IR intensity of each isomer is obtained by the summation of the IR intensity for all the three CH stretching vibrations. The $n = 0$ ion has the Γ anion in the C_3 axis and a very weak IR intensity for the CH stretching vibrations. In isomers 1A and 1B, the Γ ion is close to the C_3 axis, similar to the non-hydrated $\Gamma(\text{CH}_3\text{I})$ ion. For the $n = 2$ complex, the Γ anion is located around the extended line of the CH bond in isomer 2B, which results in an enhanced IR intensity of the CH stretching

Figure 3 shows the structure of the $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_{1-3}$ complexes determined in this study. The numbers in the figure correspond to the C–I distance in Å. The numbers in parentheses are the charge on the I atoms. ΔE stands for the Gibbs energy at 298.15 K relative to that of the most stable ones.

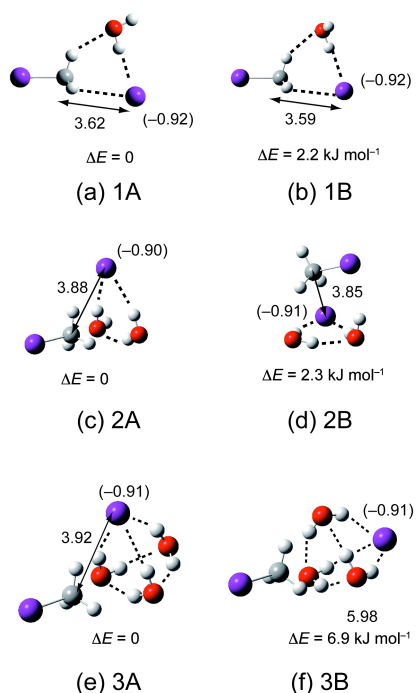


Figure 3. The structure of (a, b) $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_1$, (c, d) $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_2$, and (e, f) $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_3$ determined in this study. The numbers in the figure correspond to the C–I distance in Å. The numbers in parentheses are the charge on the I atoms. ΔE stands for the Gibbs energy at 298.15 K relative to that of the most stable ones.

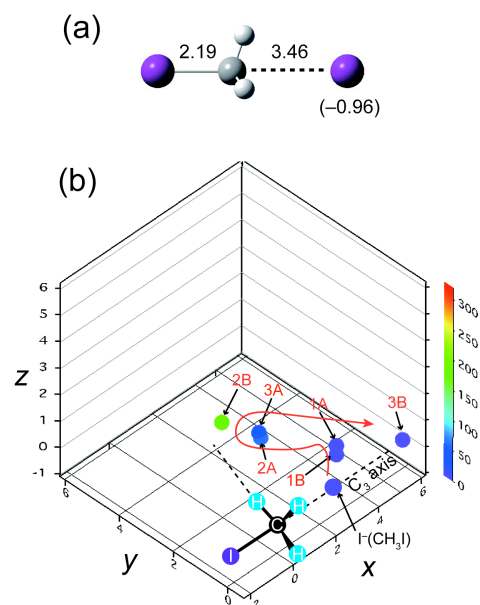


Figure 4. (a) The optimized structure of the $\Gamma(\text{CH}_3\text{I})$ ion. (b) Positions of the Γ anion with respect to the CH_3I component (in Å) in the structure of the $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$ ($n = 0-3$) complexes (Figure 3). Spherical markers show the position of the Γ anion (in Å). The color of the markers represents the IR intensity of the CH stretching vibrations in km/mol .

vibrations for 2B. The calculated result is consistent with the experimental one, namely that the $n = 2$ complex shows noticeable CH bands in the IRPD spectrum. Isomer 2A has the Γ anion slightly off from the extended line of the CH bond, having a weaker IR intensity than that of 2B. In isomer 3A, the position of the Γ anion is similar to that in 2A. For isomer 3B, the Γ anion is located close to the C_3 axis, but the distance between C and Γ is very long (5.98 Å) because of the hydration shell formed between the Γ anion and the CH_3I moiety. The IR intensities of the CH stretching vibrations of 3A and 3B are very weak. The red curve in Figure 4b shows the trend of the position of the Γ anion with increasing the number of H_2O molecules. Solvation with just two or three H_2O molecules moves the Γ anion away from the CH_3I moiety, a fact that will effectively suppress the $\text{S}_{\text{N}}2$ reaction.

The energetics of the $\Gamma(\text{H}_2\text{O})_n$ and $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$ complexes also predict a considerable inhibition of the ($\Gamma + \text{CH}_3\text{I} \rightarrow \text{ICH}_3 + \Gamma$) $\text{S}_{\text{N}}2$ reaction by microhydration. Figure 5 shows the energy levels of the $[\Gamma(\text{H}_2\text{O})_n + \text{CH}_3\text{I}]$ reactants, $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$ complexes, and the transition state of the reaction with $n = 0-3$. For the energy levels of $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$, 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 ($\Gamma + \text{CH}_3\text{I}$) reactants is higher than that of the $[\text{I}\cdots\text{CH}_3\cdots\text{I}]^-$ transition state by 1.0 kJ/mol; there exists no potential barrier for the $n = 0$ system from the reactant level. Solvation with one H_2O molecule stabilizes the Γ ion by 47.0 kJ/mol, whereas the energy of the transition state is lowered by 40.0 kJ/mol. As a result, the energy of the $[\text{I}\cdots\text{CH}_3\cdots\text{I}]^-(\text{H}_2\text{O})_1$ transition state becomes higher than that of the $[\Gamma(\text{H}_2\text{O})_1 + \text{CH}_3\text{I}]$ reactants by 6.0 kJ/mol. In the case of the $n = 2$ system, the energy of the $[\text{I}\cdots\text{CH}_3\cdots\text{I}]^-(\text{H}_2\text{O})_2$ transition state is higher than that of the $[\Gamma(\text{H}_2\text{O})_2 + \text{CH}_3\text{I}]$ reactants by 15.8 kJ/mol. For the $n = 3$ system, the barrier height is predicted to be 27.0 kJ/mol, larger than that of the $n = 2$ system. These results suggest that solvation with just one H_2O molecule will substantially inhibit the ($\Gamma + \text{CH}_3\text{I} \rightarrow \text{ICH}_3 + \Gamma$) reaction due to the increase of the barrier height. The rate constant has not been reported for the (Γ

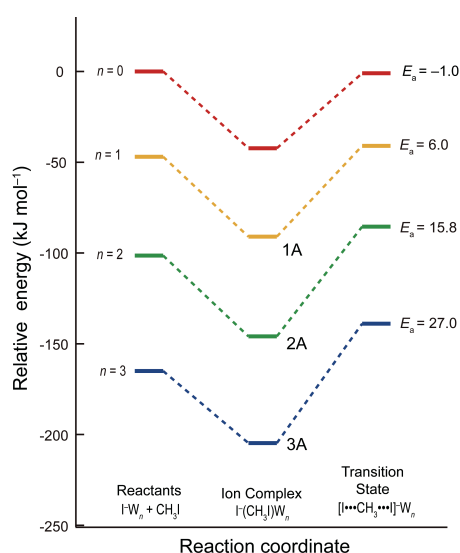


Figure 5. The energy levels of the reactants $[\Gamma(\text{H}_2\text{O})_n + \text{CH}_3\text{I}]$, ion complexes $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$, and transition states $[\text{I}\cdots\text{CH}_3\cdots\text{I}]^-(\text{H}_2\text{O})_n$ calculated at the MP2/aug-cc-pVDZ-PP(I)/aug-cc-pVDZ(C, H, O) level of theory. E_a is the barrier height (kJ/mol), which is obtained by subtracting the energy of the $[\Gamma(\text{H}_2\text{O})_n + \text{CH}_3\text{I}]$ reactants from that of the $[\text{I}\cdots\text{CH}_3\cdots\text{I}]^-(\text{H}_2\text{O})_n$ transition states.

+ $\text{CH}_3\text{I} \rightarrow \text{ICH}_3 + \Gamma$) 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 $[\text{X}^-(\text{H}_2\text{O})_n + \text{CH}_3\text{Y}]$ systems.^[8] The $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$ complexes are trapped in deep potential minima between the $[\Gamma(\text{H}_2\text{O})_n + \text{CH}_3\text{I}]$ reactants and the $[\text{I}\cdots\text{CH}_3\cdots\text{I}]^-(\text{H}_2\text{O})_n$ transition states. The depth of the potential wells from the transition state becomes deeper with increasing the number of H_2O molecules (41.3 and 69.3 kJ/mol for $n = 0$ and 3), but it becomes shallower from the $[\Gamma(\text{H}_2\text{O})_n + \text{CH}_3\text{I}]$ reactants (42.3 and 39.7 kJ/mol for $n = 0$ and 3). This modulation of the PES by the hydration will result in the disappearance of the deep potential minima of $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$ and the appearance of a large potential barrier between the reactants and products in solution, as schematically shown in Figure 1.

Figure 6 shows schematic PESs of the $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$ ($n = 0$ and 3) complexes along the ($\Gamma + \text{CH}_3\text{I} \rightarrow \text{ICH}_3 + \Gamma$) reaction coordinate based on the stable structures determined in this study. R_1 and R_2 are the distance between the I and C atoms. For the $n = 0$ system, the potential minimum of the $\Gamma(\text{CH}_3\text{I})$ complex is located at $R_1 - R_2 = 1.28$ Å. In the $n = 3$ case, the pyramidal-type hydration shell is formed around the Γ anion, and the CH_3I molecule is preferentially bonded to the hydration network rather than the Γ anion. Since 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 Γ anion to promote the reaction. In our calculations, no stable isomer is found for the $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_3$ complex in which the CH_3I component is directly bonded to the Γ anion at the apex of the $\Gamma(\text{H}_2\text{O})_3$ pyramid. Therefore, the CH_3I moiety and the H_2O molecules move simultaneously to reach the transition state. The position of the potential minima of 3A and 3B ($R_1 - R_2 = 1.76$ and 3.82 Å, respectively) is more distant from the transition state than that in the $\Gamma(\text{CH}_3\text{I})$ complex ($R_1 - R_2 = 1.28$ Å). In the ($\Gamma + \text{CH}_3\text{I} \rightarrow \text{ICH}_3 + \Gamma$) reaction for the $n = 3$ cluster, therefore, the Γ anion will be trapped further away from the CH_3I molecule, something that will result in a further inhibition of the $\text{S}_{\text{N}}2$ reaction.

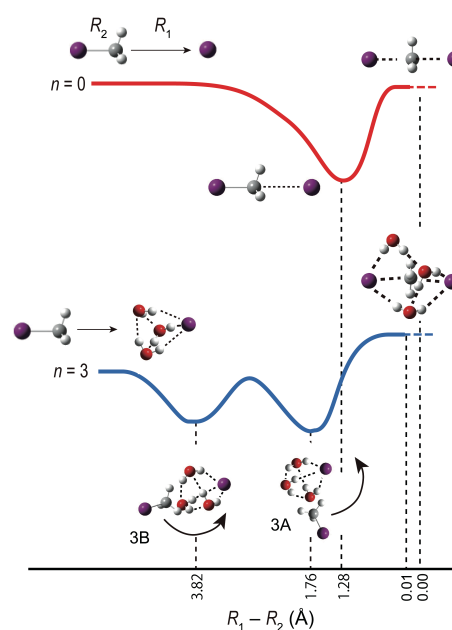


Figure 6. Potential energy surfaces of the ($\Gamma + \text{CH}_3\text{I} \rightarrow \text{ICH}_3 + \Gamma$) $\text{S}_{\text{N}}2$ reaction with no water ($n = 0$) and with three water molecules ($n = 3$) as a function of the difference in the C-I distances, $R_1 - R_2$.

As mentioned above, the binding energy of the Γ^- anion with CH_3I (35 kJ/mol) is comparable to that with H_2O (43 kJ/mol). Nevertheless, three H_2O molecules in the $n = 3$ complex are likely to shield the Γ^- anion from the CH_3I component quite effectively.

In summary, we have measured IR photodissociation (IRPD) spectra of the $\Gamma^-(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$ ($n = 1-3$) complexes in order to elucidate the effect of the microsolvation of water to the ($\Gamma^- + \text{CH}_3\text{I} \rightarrow \text{ICH}_3 + \Gamma^-$) $\text{S}_{\text{N}}2$ reaction. On the basis of the stable forms of the $\Gamma^-(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$ complexes determined in this study, just two or three H_2O molecules can effectively inhibit the ($\Gamma^- + \text{CH}_3\text{I} \rightarrow \text{ICH}_3 + \Gamma^-$) $\text{S}_{\text{N}}2$ reaction. In addition, the calculated energetics suggest that the suppression of the reaction occurs from $n = 1$ as the barrier height of the reaction becomes positive already for that cluster size.

Experimental and Computational Section

The details of our experiment used to measure the IRPD spectra have been given in our previous report^[9] and in the Supporting Information. In brief, the $\Gamma^-(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$ ions produced in a vacuum chamber with electron impact are mass analyzed by a time-of-flight mass spectrometer. Parent ions of interest are isolated by a mass gate and irradiated by an output of an IR laser. Resulting fragment $\Gamma^-(\text{H}_2\text{O})_n$ ions are mass-analyzed by a reflectron and detected by a multichannel plate. The IRPD spectra of the parent ions are obtained by plotting yields of the fragment ions as a function of the wavenumber of the IR laser. In order 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 $\Gamma^-(\text{CH}_3\text{I})(\text{H}_2\text{O})_{0-3}$ complexes are done at the MP2/aug-cc-pVDZ-PP(I)/aug-cc-pVDZ(C, H, O) level. The anharmonic frequencies were obtained via vibrational second order perturbation theory.

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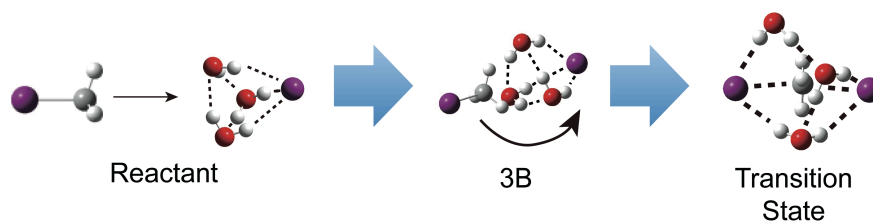
Entry for the Table of Contents

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Solvent Effect

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Microhydration Effects on the Intermediates of the ($\text{I}^- + \text{CH}_3\text{I}$) $\text{S}_{\text{N}}2$ Reaction



Hydrated $\text{I}^-(\text{CH}_3\text{I})$ complexes, $\text{I}^-(\text{CH}_3\text{I})(\text{H}_2\text{O})_{1-3}$, are investigated by IR photodissociation spectroscopy for examining the stable structures of the intermediates of the ($\text{I}^- + \text{CH}_3\text{I} \rightarrow \text{ICH}_3 + \text{I}^-$) $\text{S}_{\text{N}}2$ reaction under hydrated conditions. The structures and the energetics of the complexes suggest that just one or two H_2O molecules will effectively inhibit this $\text{S}_{\text{N}}2$ reaction.