Cluster Ion Formation from Alcohol Solutions of CaI_2

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Received: August 28, 1998; In Final Form: January 13, 1999

A liquid beam (continuous liquid flow in a vacuum) of a calcium iodide (CaI_2) solution in ethanol (EtOH) was irradiated with a 220 nm laser, and ions ejected from the surface following multiphoton ionization were observed by a time-of-flight mass spectrometer. Cluster ions, $CaOEt^+(EtOH)_m$ ($m = 2-9$), $CaI^+(EtOH)_m$ ($m = 1-7$), and $H^+(EtOH)_m$ ($m = 3-5$) were found to be produced. The measurement of the velocities of the product cluster ions indicates that two mechanisms are operative; ions formed on the liquid surface are ejected with accompanying solvent molecules, and ions generated by Coulomb explosion of a divalent cluster ion, $Ca^{2+}(EtOH)_m$, are repelled with gaining a sizable translational energy.

1. Introduction

Solvation structures and reaction dynamics of divalent metal ions, M^{2+}, have been studied extensively in various media, such as gas, solution, and cluster. Collisions of M^{2+} with various reactant molecules in the gas phase have been undertaken in a flowing aftergrow[1−3] and in an ion-trap.[4] It is often the case that charge transfer occurs between the collision partners and as a result two singly charged ions are formed, because the energy for M^{2+} formation from M^+ (second ionization potential of M) is larger than the ionization energy of the reactant molecule (first ionization potential). This simple energetic consideration is also applicable to a divalent ion in a solution. The ion is stabilized by an ion−dipole interaction between the ion and its solvent molecules in the vicinity of the ion so that the charge transfer between the divalent ion and a solvent molecule is not favored. In some cases, however, such charge transfer proceeds between a divalent ion and a solvent molecule, although the theoretical basis of the charge transfer is not fully established. One typical example is hydrolysis of a divalent metal ion, M^{2+}, (M = Be, Cd, and Cu) in an aqueous solution of $M(ClO_4)_2$.[5−8] The hydrolysis reaction is considered to take place in a location where its local structure specifically favors the reaction.

Behaviors of a divalent metal ion in a cluster medium have also been investigated extensively because the properties of the cluster medium can be changed by varying its size. Combinations of alkaline earth metal ions and polar molecules have been studied the most extensively by mass and laser spectroscopy. In a singly charged strontium−ammonia cluster, $[Sr(NH_3)_m]^+$, the strontium is present as a divalent form, that is, $Sr^{2+}(NH_3)_m{}^-$.[9] On the other hand, a cluster ion, $[Mg(H_2O)_m]^+$, is considered to have a form, $Mg^+(H_2O)_m$ as well as $Mg^{2+}OH^-(H_2O)_m$.[10−12] Blades et al.[13] have revealed by use of an electrospray technique that cluster ions, $Ca^{2+}(H_2O)_m$ ($m > 2$) and $Sr^{2+}(H_2O)_m$ ($m > 2$) are stable in the gas phase and dissociate into $MOH^+(H_2O)_p$ (M = Ca and Sr) and $H^+(H_2O)_q$ by collision of rare gas atoms. The reactivity correlates to the difference of the second ionization potential of M and the first ionization potential of H_2O. A similar question arises on how M^{2+} behaves on the surface of a liquid solution, because M^{2+} is not completely solvated on the liquid surface. The dynamics of M^{2+} on the solution surface is studied most appropriately by use of the liquid beam technique, since the technique enables us to prepare the solution surface in a vacuum. The ion produced by laser irradiation and ejected from the surface is characterized by a time-of-flight mass spectrometer.

Let us consider that a calcium iodide (CaI_2) solution in ethanol (EtOH) is introduced into a vacuum as a liquid beam. Ions, Ca^{2+}, CaI^+, and I^-, are considered to be present on the solution surface, because CaI_2 is partly ionized in the ethanol solution into Ca^{2+}, CaI^+, and I^-. The divalent ion, Ca^{2+}, is expected to be repelled from the surface with several accompanying EtOH molecules when the counterion, I^-, is neutralized by irradiation of the surface with a UV laser. Consulting with the behaviors of M^{2+} in the gas phase and in the cluster medium, one infers that a nascent cluster ion, $Ca^{2+}(EtOH)_n$, leaving from the surface dissociates into fragment ions having a sizable translational energy, namely,

$$Ca^{2+}(EtOH)_n \rightarrow CaOEt^+(EtOH)_m + H^+(EtOH)_{m'} + (n\text{-}m\text{-}m')EtOH \quad (1)$$

In the present paper, ions produced by irradiation of a UV laser on the liquid beam of a CaI_2 ethanol solution were measured mass spectroscopically. The measurement of the translational energy of each ion shows that two mechanisms are operative for the production of the ions.

2. Experimental Section

The description related merely to the present experiment was made here, as the apparatus and experimental procedures have been given previously in detail.[14−17] A continuous laminar liquid flow of an ethanol solution of CaI_2 was introduced into a vacuum chamber from a nozzle having an aperture 20 μm in diameter. The flow rate was maintained at 0.2 mL/min with a pressure of typically 20 atm inside the nozzle. The liquid beam was trapped at 5 cm downstream from the nozzle by a cylindrical cryopump cooled by liquid N_2. The source chamber was evacuated by a

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10.1021/jp983559i CCC: $18.00 © 1999 American Chemical Society
Published on Web 03/02/1999

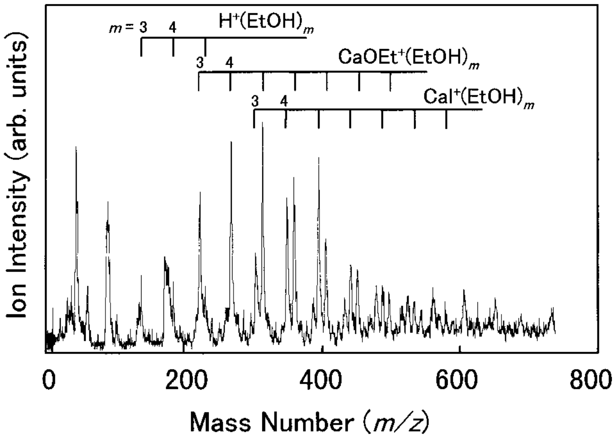


Figure 1. Mass spectrum of ions produced by irradiation of a 220 nm laser on a liquid beam of a 0.5 M CaI_2 solution in ethanol.

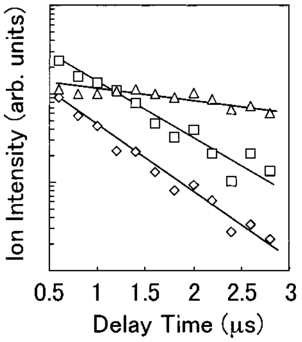


Figure 2. Intensities of $H^+(EtOH)_3$ (◇), $CaOEt^+(EtOH)_2$ (□), and $CaI^+(EtOH)_4$ (△) as a function of the delay time from the laser ionization to the pulse extraction. The solid lines give decay constants of 2.84, 2.28, and 1.03 μs^{-1} for $H^+(EtOH)_3$, $CaOEt^+(EtOH)_2$, and $CaI^+(EtOH)_4$, respectively.

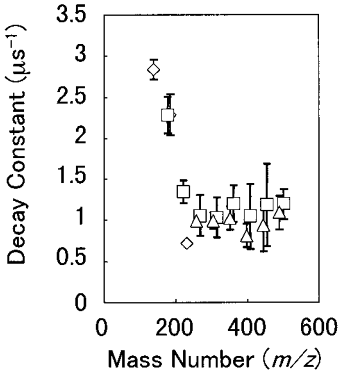


Figure 3. Decay constant of a product ion plotted as a function of its mass: $H^+(EtOH)_n$ (◇); $CaOEt^+(EtOH)_n$ (□); $CaI^+(EtOH)_n$ (△).

1200 L s^{-1} diffusion pump down to 10^{-5}−10^{-6} Torr during injection of the liquid beam. Commercially available ethanol and CaI_2 (n hydrate > 99.5%) were used without any further purification. A small amount of insoluble impurity in the CaI_2−ethanol solution was removed by filtration before the experiment to prevent the nozzle from being clogged.

After traveling a distance of 5 mm from the nozzle, the liquid beam was crossed with a 220 nm laser beam in the first acceleration region of the TOF mass spectrometer. The UV laser beam was obtained by frequency-doubling of the output of a Quanta-ray PDL-3 dye laser (440 nm) pumped by the third harmonics of a Quanta-ray GCR-3 Nd:YAG laser. The laser power (200 μJ/pulse) was monitored by a LAS PM-200 energy meter. The laser was focused into the liquid beam by a lens with a focal length of 450 mm.

The mass-to-charge ratios, m/z, of the ions produced in the gas phase were analyzed by a reflectron TOF mass spectrometer as follows. Ions ejected from the liquid beam were accelerated by a pulsed electric field in the first acceleration region in the direction perpendicular to both the liquid and the laser beams with a time delay from the photoionization. The delay time was varied in the range of 0.6−2.8 μs in order to measure the velocities of cluster ions leaving from the liquid beam surface. It was necessary to apply at least a 0.6 μs delay because the ions need the time to escape from the liquid surface after the production by laser ionization. The ions were then steered and focused by a set of vertical and horizontal deflectors and an einzel lens. The reflectron provided a reversing field tilted by 2° off the beam axis. After traveling a 0.5 m field-free region, a train of spatially mass-selected ions were detected by a Murata EMS-6081B Ceratron electron multiplier. Signals from the multiplier were amplified and processed by a Yokogawa DL 1200E digital oscilloscope based on an NEC 9801 microcomputer. The mass resolution, defined as $m/\Delta m$, was 300 at a delay time of 2.8 μs. The absolute ion intensity was measured by a gated photon counter (model SR400, Stanford Research Systems). Ions were found to arrive at the detector with a typical rate of 10^3 particles/laser shot.

3. Results

3.1. Ions Produced by Laser Irradiation on Liquid Beam. Figure 1 shows a mass spectrum of ions produced by irradiation of a 220 nm laser on a liquid beam of a 0.5 M CaI_2 ethanol solution. Peaks in the mass spectrum are assigned as $CaI^+(EtOH)_m$ (m = 1−7), $CaOEt^+(EtOH)_m$ (m = 2−9), and $H^+(EtOH)_m$ (m = 3−5) (see Figure 1). The mass assignment was confirmed by replacement of ethanol with methanol or n-propanol. By this replacement, the mass of each cluster ion containing m solvent molecules was found to shift by 14(m + 1), where 14 corresponds to the mass difference between methanol and ethanol and ethanol and n-propanol. In addition, there are several peaks assignable to $[Ca_2I(OEt)_2]^+(EtOH)_m$ (m = 2−5) and $[Ca_3I(OEt)_4]^+(EtOH)_m$ (m = 1−2). The mass spectra also showed that no doubly charged species are produced in the present experiment. In summary, cluster ions, $CaI^+(EtOH)_m$ (m = 1−7), $CaOEt^+(EtOH)_m$ (m = 2−9), and $H^+(EtOH)_m$ (m = 3−5) in addition to a small amount of $[Ca_2I(OEt)_2]^+(EtOH)_m$ (m = 2−5) and $[Ca_3I(OEt)_4]^+(EtOH)_m$ (m = 1−2) are produced by laser irradiation on the liquid beam of a CaI_2−ethanol solution.

3.2. Slow and Fast Product Ions. Figure 2 shows the intensities of $H^+(EtOH)_3$, $CaOEt^+(EtOH)_2$, and $CaI^+(EtOH)_4$ as a function of the delay time from the laser ionization to the pulse extraction. The intensity, I, of each ion decreases exponentially with the delay time, t, with a decay constant, λ, as

$$I = I_0 \exp(-\lambda t) \qquad (1)$$

where I_0 represents the ion intensities at t = 0. Evidently, an ion escaping from the acceleration region with a higher velocity has a larger decay constant. Figure 3 shows that the decay constants of the ions observed are plotted against their mass numbers. The intensities, I, of the other observed ions exhibit almost the same $I - t$ dependence. As shown in Figure 3, most of the ions have almost the same decay constants, but the ions $H^+(EtOH)_m$ and $CaOEt^+(EtOH)_{m'}$ with $m \leq 4$ and $m' \leq 2$ have larger decay constants; that is, these ions escape from the acceleration region with higher velocities than the others. This finding indicates that there exist at least two different paths for production of the ions. As argued in our previous papers,[14−16] ions are ejected from liquid beam surfaces by repulsion of a surface charge built by neighboring ions produced by multiphoton ionization (Coulomb ejection scheme). The slower ions from the surface are likely to be produced in this way. On the other hand, the faster ions must be produced by a different manner during which the ion gains more translational energy. In the following section, these two different paths are shown.

4. Discussion

4.1. Reaction Scheme. As described in section 3, at least two different mechanisms operate for the production of the ions having lower and higher velocities. It is highly likely that the slower ions are produced via the Coulomb ejection scheme, as mentioned in the previous section. In addition to it, there exists the other path in which the product ions gain much larger translational energy; the translational energy gain is substantiated by Coulomb explosion of a divalent cluster ion $Ca^{2+}(EtOH)_n$ produced nascently from the solution surface.

4.2. Formation of Slow Ions: Coulomb Ejection Scheme. The solute molecule, CaI_2 in its ethanol solution, is partly dissociated into CaI^+ and I^- and further into Ca^{2+} and $2I^-$. The UV absorption band associated with electron transfer from I^- to the solvent is known as the CTTS (charge transfer to solvent) band. As the absorption maximum of the broad CTTS band in the ethanol solution is at 218.5 nm, the 220 nm laser excites I^- into I and a solvated electron, e_s^-.[17] The solvated electron is ejected into the vacuum as a free electron by absorbing one more photon in the same pulse duration.[18] This process is expressed as

$$I^- \text{ (sol)} + h\nu \rightarrow I^{-*} \text{ (sol)} \rightarrow I \text{ (sol)} + e_s^- \text{ (sol)} \quad (2)$$

$$e_s^- \text{ (sol)} + h\nu \rightarrow e_f^- \quad (3)$$

where e_f^- is a free electron and (sol) represents solution.

Thus, the laser irradiation results in the preparation of an electron-depleted region in the vicinity of the liquid beam surface owing to the electron ejection into the vacuum by the multiphoton excitation. Ions such as CaI^+, $CaOEt^+$, and H^+ generated by various processes in the solution are ejected with several accompanying ethanol molecules by Coulomb repulsion exerted from the depleted region.[14−16] The nascent cluster ions ejected from the surface release several solvent molecules as they travel in the gas phase due to evaporative cooling. These processes are described as follows:

$$X^+\text{(sol)} \rightarrow X^+(EtOH)_n \text{ (g)} \quad (4)$$

$$X^+(EtOH)_n \text{ (g)} \rightarrow X^+(EtOH)_m \text{ (g)} + (n\text{-}m)EtOH \quad (5)$$

where X^+ represents an ion produced in the solution and (g) represents the gas phase.

As stated above, the ion, X^+, is generated through various processes. The cluster ion, $CaI^+(EtOH)_m$, is formed by a simple combination of CaI^+ with EtOH. On the other hand, $CaOEt^+$, which is the core ion of $CaOEt^+(EtOH)_m$, is produced by reactions initiated by an encounter of a solvated electron, e_s^-, with a solvent molecule as

$$e_s^- + EtOH \text{ (sol)} \rightarrow EtO^- \text{ (sol)} + H \text{ (sol)} \quad (6)$$

$$Ca^{2+} + EtO^- \text{ (sol)} \rightarrow CaOEt^+ \text{ (sol)} \quad (7)$$

$$CaI^+ + EtO^- \text{ (sol)} \rightarrow CaOEt^+ \text{ (sol)} + I^- \text{ (sol)} \quad (8)$$

Efficient formation of EtO^- by the reaction of e_s^- with EtOH is also observed in an ethanol solution of sodium iodide (NaI).[17] The involvement of e_s^- in the formation of EtO^- is proved further by disappearance of EtO^- by addition of an electron scavenger in the solution.[17] The species, EtO^-, is also contained in other ions, such as $[Ca_2I(OEt)_2]^+$ or $[Ca_3I(OEt)_4]^+$.

Our previous study on an anisole solution in ethanol shows that ions emerging from the liquid surface via the Coulomb ejection have almost the same velocity of about 700 m/s within the experimental errors,[16] because the observed ions are produced by unimolecular dissociation of a single nascent cluster ion in the gas phase and the ions produced by the unimolecular dissociation have the same velocity. Assuming that every nascent cluster ion concerned has the same velocity as that of the ions observed in the anisole study,[19] one can conclude that the product ions have a velocity of ∼700 m/s.

4.3. Formation of Translationally Hot Ions: Coulomb Explosion of Divalent Ions. As described in section 3, $H^+(EtOH)_3$, $H^+(EtOH)_4$, and $CaOEt^+(EtOH)_2$ escape from the first acceleration region of the TOF mass spectrometer with much larger velocities than the other ions (see Figure 3). This finding indicates that a different mechanism should operate in the formation of these cluster ions. Although Ca^{2+} is a stable entity in a water cluster,[13] no such ion is present in an ethanol cluster; that is, $Ca^{2+}(EtOH)_m$ is not observed in the present experiment. However, Ca^{2+} is present in an ethanol solution as a stable entity as stated in the Introduction section. The comparison of the two results leads us to conclude that Ca^{2+} is present as a stable entity on the liquid surface and then ejected with accompanying several ethanol molecules as a form of $Ca^{2+}(EtOH)_n$ (nascent cluster ion). Just after leaving from the surface, $Ca^{2+}(EtOH)_n$ dissociates into $CaOEt^+(EtOH)_m$ and $H^+(EtOH)_n$ by Coulomb explosion as

$$Ca^{2+} \text{ (sol)} \rightarrow Ca^{2+}(EtOH)_n \text{ (g)} \quad (9)$$

$$Ca^{2+}(EtOH)_n \text{ (g)} \rightarrow CaOEt^+(EtOH)_m \text{ (g)} + H^+(EtOH)_{m'} \text{ (g)} + (n\text{-}m\text{-}m')EtOH \quad (10)$$

The energetics also favors the reaction

$$Ca^{2+} + EtOH \rightarrow Ca^+ + EtOH^+ \quad (11)$$

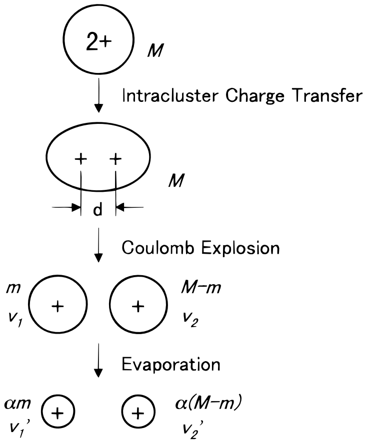
because the second ionization potential of Ca (11.9 eV) is larger than the first ionization of EtOH (10.7 eV). The ion, $EtOH^+$, thus produced further dissociates into EtO and H^+, and as a whole, the reaction of Ca^{2+} with EtOH makes $CaOEt^+ + H^+$ as

$$Ca^{2+} + EtOH \rightarrow CaOEt^+ + H^+ \quad (12)$$

The Coulomb explosion causes the product cluster ions to gain a sizable translational energy.

Scheme 1 illustrates the process related to Coulomb explosion of the divalent cluster ion: (1) charge separation in $Ca^{2+}(EtOH)_n$ (process (12)); (2) Coulomb explosion of $Ca^{2+}(EtOH)_n$ into $CaOEt^+(EtOH)_m$ and $H^+(EtOH)_{m'}$; (3) evaporative cooling of

SCHEME 1



these cluster ions by leaving several EtOH molecules before detection. The energy, E_c, of the Coulomb repulsion between the two charges separated by a distance, d, is given by

$$E_c = \frac{e^2}{4\pi\epsilon_0 d} \tag{13}$$

where e is the elementary electric charge and ϵ_0 is the dielectric constant. On the assumption of full conversion of E_c into the translational energy of the product ions, one obtains the following relations by taking into consideration the energy and momentum conservation.

$$E_c = \frac{1}{2} m v_1^{\,2} + \frac{1}{2}(M - m) v_2^{\,2} \tag{14}$$

$$m v_1 = (M - m) v_2 \tag{15}$$

where M is the total mass of the divalent cluster ion, m and $M - m$ are the masses of the product ions, and v_1 and v_2 are the velocities of the ions whose masses are m and $M - m$, respectively. Assuming that the mass after the evaporation is α times as large as that before, the velocity of the ion after the evaporation, v_1', remains unchanged.

$$v_1'(\alpha m) = v_1(m) \tag{16}$$

Equations 14−16 are reduced to give

$$v_1' = \left(\frac{\alpha M - m}{m} \frac{2E_c}{M}\right)^{1/2} \tag{17}$$

The maximum possible velocity, v_1', gained by the Coulomb explosion should be added to the velocity gained under the Coulomb ejection scheme, so as to obtain the maximum possible velocity of the product ions, $CaOEt^+(EtOH)_m$ and $H^+(EtOH)_{m'}$. The mass, M, is assumed to be 408 amu; that is, the nascent divalent cluster ion is $Ca^{2+}(EtOH)_8$. This assumption is based on the conjecture that Ca^{2+} accompanies almost the same number of the solvent molecules as CaI^+ since Ca^{2+} is smaller in size but more in charge than CaI^+, and hence these two factors compensate each other to give almost the same solvent number to these ions; the solvent number of CaI^+ is 7 so that the number of the solvent molecules given to Ca^{2+} is within a reasonable range. X-ray diffraction of an aqueous solution of $Ca(NO_3)_2$ shows that Ca^{2+} and the O atom of a H_2O molecule in the nearest-neighbor position is separated by 0.25 nm.[20] As the local structure around Ca^{2+} in the aqueous solution of $Ca(NO_3)_2$ is considered to be similar in nature to the arrangement of the solvent molecules around Ca^{2+} in $Ca^{2+}(EtOH)_n$, d is approximated by the distance (0.25 nm) between Ca^{2+} and O in the $Ca(NO_3)_2$ solution. As argued in the previous subsection, one can conclude that the product ions gain a velocity by the Coulomb explosion in addition to the velocity gain of 700 m/s by the Coulomb ejection of the nascent cluster ion of interest. It follows that the product ions have a velocity of $700 + v_1'$ m/s. Substituting all these values into eq 17 leaving α as the variable parameter, one obtains the velocity of a product ion as a function of its mass number as shown in Figure 4 (solid curve). The calculation reproduces the experimental values reasonably well when α is set to be 0.57. The number of ethanol molecules accompanied by Ca^{2+} ($n = 8$) and the average fraction of the evaporation ($\alpha = 0.57$) are consistent with the observation that the maximum number of solvent ethanol molecules of $H^+(EtOH)_m$ is about 5 while the most probable number of solvent molecules of $H^+(EtOH)_m$ is about 3 (see Figure 1).

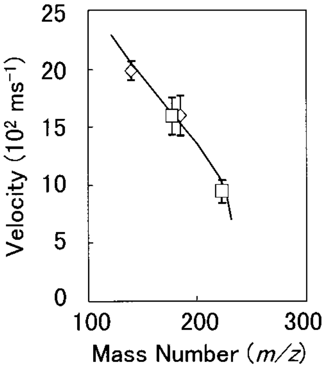


Figure 4. Velocity of a product ion plotted as a function of its mass: $H^+(EtOH)_n$ (◇); $CaOEt^+(EtOH)_n$ (□). The solid curve represents the prediction based on the Coulomb explosion scheme.

5. Conclusion

Ion formation processes followed by laser excitation of CaI_2 in ethanol solution were revealed by using the liquid beam multiphoton ionization mass spectroscopic technique. The observed ions were $CaOEt^+(EtOH)_m$ ($m = 2-9$), $CaI^+(EtOH)_m$ ($m = 1-7$), and $H^+(EtOH)_m$ ($m = 3-5$). The velocity of these ions were almost the same, except for $CaOEt^+(EtOH)_m$ and $H^+(EtOH)_m$ which have small m values. This shows that the ions, $CaOEt^+(EtOH)_m$, are formed via two different channels: EtO^- capture by Ca^{2+} or CaI^+ and Coulomb explosion reaction of a doubly charged cluster ion, $Ca^{2+}(EtOH)_m$. The analysis revealed that Coulomb explosion of a nascent divalent cluster ion, $Ca^{2+}(EtOH)_8$, takes place after it is repelled from the surface by the Coulomb ejection.

Acknowledgment. The authors are grateful to Mr. Yoshihiro Takeda for his assistance in the early stage of the liquid beam studies and also to Mr. Hisashi Matsumura for his helpful discussion. This research was supported by the International Joint Research of NEDO and the Special Cluster Research Project of Genesis Research Institute, Inc.

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