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Ion–Molecule Reaction between Ionized Photochemical Intermediates of Acetophenone and Alcohol Following Multiphoton Excitation in a Liquid Beam

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Ion–molecule reactions on the surface of a liquid solution are expected to be specific and different from those occurring inside the solution. The ionic species on the liquid surface involved in the reactions are not completely surrounded with the solvent molecules although the density of the reactants is sufficiently high that the reactions proceed efficiently and effectively as occurring inside the solution. It is also conceivable that the ionic species emerging during the course of the reactions could be ejected into vacuum, since they are repelled from each other by Coulomb interaction but are attracted relatively weakly by the solvent molecules due to the insufficient solvation. In order to investigate this type of reaction, we have explored a technique of introducing a continuous liquid flow into vacuum (liquid beam) and combined this technique with multiphoton ionization (MPI) and time-of-flight (TOF) mass spectrometry.[1–3] Upon laser irradiation on the liquid beam, ions are ejected directly from the liquid surface following multiphoton ionization without any significant secondary collision with the background gas molecules.[2] Along with this study, intensive investigations have been performed to characterize the beam surface: UPS, XPS, and Penning ionization electron spectrometry[4,5] have shown that a clean liquid surface is exposed in the vacuum. A kinetic energy distribution of molecules evaporating from the liquid surface has revealed that the molecules evaporate directly from the surface into vacuum without suffering any significant secondary collision;[6,7] this finding and our result mentioned above[2] imply that there is no dense gas layer above the surface of the liquid beam.[8] Further, the liquid beam is laminar in the vacuum because the laser passes through the inside of the beam without any observable scattering when the laser is introduced collinearly with the liquid beam.[6] The characterization of the liquid beam facilitates the application of our liquid beam–MPI–TOF mass spectrometry to the studies of ion–molecule reactions on liquid surfaces.

We applied this technique to the study of a typical ion–molecule reaction, the acetal formation reaction in an ethanol solution of acetophenone.[9] When an alcohol solution of acetophenone ($C_6H_5COCH_3$) is irradiated with unfocused ultraviolet light, acetophenone is excited to the T_1 state via an S_n state. Acetophenone in the T_1 state abstracts hydrogen to form the radical, $C_6H_5C(OH)CH_3$, in an alcohol solution, and pinacol is formed by the subsequent dimerization reaction.[10–13] Under irradiation of focused laser light,[14,15] it is expected that the radical, $C_6H_5C(OH)CH_3$, is ionized by further absorbing photons before the dimerization, and $C_6H_5C(OH)CH_3^+$ is formed; this ionic species is an intermediate of the acetal formation reaction. This means that a reaction intermediate can be selectively produced by laser irradiation instead of acid being added to the solution.

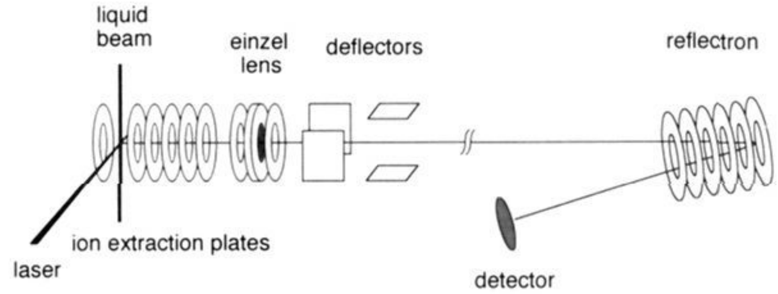

Figure 1. Schematic diagram of the experimental setup.

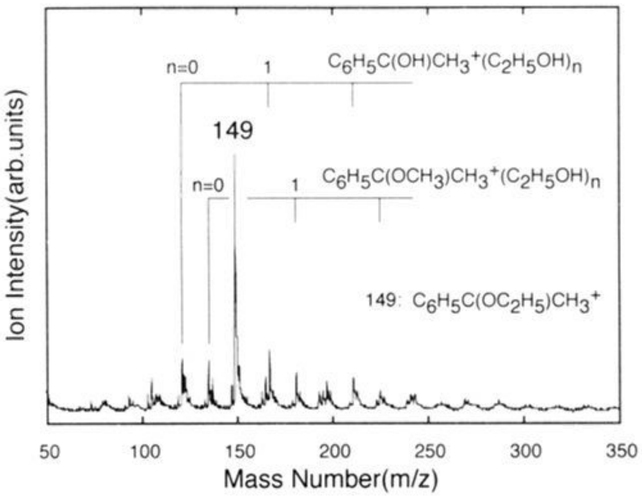

Figure 2. TOF mass spectrum of the ions produced from a 0.5 M solution of acetophenone in ethanol by irradiation of a 250 nm laser. The peak with $m/z = 149$ is assigned as $C_6H_5C(OC_2H_5)CH_3^+$, and the other peaks are assigned as $C_6H_5C(OH)CH_3{\cdot}(C_2H_5OH)_n^+$ ($n \geq 0$) and $C_6H_5C(OCH_3)CH_3{\cdot}(C_2H_5OH)_n^+$ ($n \geq 0$).

A schematic diagram of the experimental setup is shown in Figure 1. A sample solution of acetophenone or propiophenone in ethanol or 1-propanol was injected into a main vacuum chamber from a nozzle at a flow rate of 0.2 mL/min. Commercially available acetophenone (Kanto Chem. Co., 99%) or propiophenone (Tokyo Kasei Kogyo Co., 99%) was used without further purification. The vacuum chamber was evacuated down to 10^{-5} Torr by a 1200 L/s diffusion pump and a cylindrical cryopump cooled by liquid N_2. A laser beam was introduced perpendicularly *to the liquid beam in the first acceleration region of the TOF* mass spectrometer. The laser beam (500 or 560 nm) was obtained from a Quanta-Ray PDL-3 dye laser pumped by the third harmonics of a Quanta-Ray GCR-3 Nd:YAG laser. The visible output of the dye laser was frequently-doubled with an angle-tuned BBO crystal. In the experiment using a 355 nm laser, the third harmonics of the Nd:YAG laser was directly introduced into the vacuum chamber. The output was focused into the liquid beam by a lens with a focal length of 450 mm. The fluence of the incident laser was typically 10^5 W/cm^2.

Ions produced by multiphoton ionization and ejected from the liquid beam were mass-analyzed by a reflectron TOF mass spectrometer. The ions were extracted by a pulsed electric field delayed by ∼1 μs with respect to the ionization laser pulse in the direction perpendicular to both the liquid and the laser beams. The mass resolution ($m/\Delta m$) exceeds 250 in a typical experimental condition.

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(8) An effective pressure in the gas layer above the liquid with a thickness of ∼100 μm was found to be ∼10^{-3} Torr or less, by treating the liquid beam as a cylindrical effusive source. The rate of the gas flow from the source was estimated from the background pressure and a known pumping speed of the system. Under this condition, an ion–molecule reaction with a cross section as large as a Langevin cross section does not proceed significantly even within the gas layer having the highest density in vacuum.

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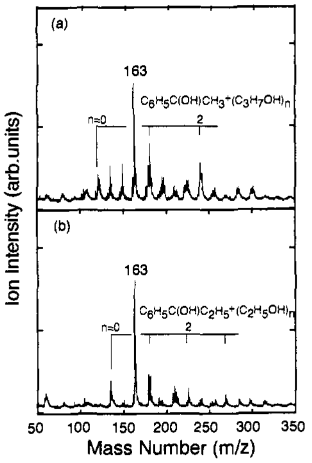


Figure 3. TOF mass spectra of ions produced from 0.5 M solutions of (a) acetophenone in 1-propanol and (b) propiophenone in ethanol. The peaks with $m/z = 163$ in panels a and b are ascribable to $C_6H_5C(OC_3H_7)CH_3^+$ and $C_6H_5C(OC_2H_5)C_2H_5^+$, respectively.

Figure 2 shows a typical TOF mass spectrum of ions produced from a 0.5 M solution of acetophenone in ethanol by irradiation of a 250 nm laser. In this spectrum, one intense peak appears at $m/z = 149$ together with other small peaks. The mass number of this intense peak agrees with the sum of those of acetophenone (120) and the ethyl group (29), while the small peaks are assignable to $C_6H_5C(OH)CH_3^+ \cdot (C_2H_5OH)_n$ ($n \geq 0$) and $C_6H_5C(OCH_3)CH_3^+ \cdot (C_2H_5OH)_n$ ($n \geq 0$).

In order to identify each peak, acetophenone was replaced with propiophenone in ethanol and its m/z value was observed. As shown in Figure 3, the most intense peak shifts by $m/z = 14$, the mass difference between acetophenone and propiophenone. When a 1-propanol solution of acetophenone is used instead of an ethanol solution of acetophenone, the most intense peak shifts by $m/z = 14$, the mass difference between ethanol and 1-propanol. These results indicate that the most intense peak in the mass spectrum for the ethanol solution of acetophenone is identified to be $C_6H_5C(OC_2H_5)CH_3^+$ produced by the reaction of one acetophenone molecule and one ethanol molecule.

Figure 4 shows typical TOF mass spectra of ions produced from the solution of acetophenone in ethanol by laser irradiation at wavelengths of 250 nm (panel a), 280 nm (panel b), and 355 nm (panel c), at which the S_3, S_2, and S_1 states are expected to be excited, respectively. The spectra do not change significantly with the excitation wavelength; the intensities of the small peaks increase only slightly with the excitation wavelength. This finding indicates that each ion is produced through the same excited state. It is highly likely that the radical, $C_6H_5C(OH)CH_3$, is produced from an acetophenone molecule in the T_1 state by hydrogen abstraction from ethanol and is ionized into $C_6H_5C^+(OH)CH_3$ by absorbing photons before the dimerization reaction. In this ion, the carbon atom bonded to the OH group is positively charged and is readily attacked by the oxygen atom of an alcohol molecule having a lone pair electron as a nucleophile, and $C_6H_5C(OC_2H_5)CH_3^+$ is generated as a result. As shown in Figure 2, both $C_6H_5C(OH)CH_3^+$ and $C_6H_5C(OC_2H_5)CH_3^+$ are observed in the mass spectrum. The photochemical reactions described above are summarized in Scheme 1. The pinacol ion, $(C_6H_5CH_3COH)_2^+$, is hardly observed probably because of a small probability of a bimolecular encounter of the radicals, $C_6H_5C(OH)CH_3$, in the time window of photoionization (<10 ns).

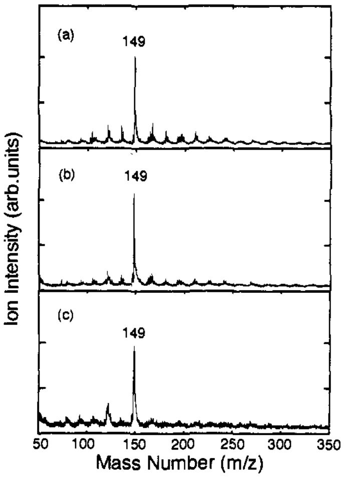
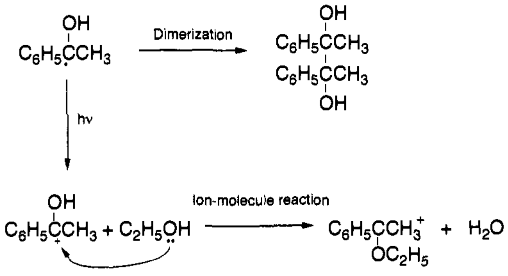


Figure 4. TOF mass spectra for a 0.5 M solution of acetophenone in ethanol by irradiation of (a) 250 nm, (b) 280 nm, and (c) 355 nm laser beams. The assignments of the peaks are given in the caption of Figure 2.

Scheme 1



In a usual reaction, acids must be added to a solution of acetophenone in ethanol so as to prepare $C_6H_5C(OH)CH_3^+$ acting as a reaction intermediate of the acetal formation. However, the acids very often disturb other major reaction processes involved and are not selective for the protonation of acetophenone. In this regard, the photochemical reaction under intense laser light is particularly advantageous for dealing with a compound which has functional groups vulnerable to acids. In summary, this is a new method of inducing and probing multiphoton chemical reactions on a liquid surface, which allows selective ionization of a given functional group of a molecule in solution and initiation of specific ion–molecule reactions.

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