Scavenging Reaction of Solvated Electron Produced by UV Laser from Iodide Anion in Liquid Beam

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A sodium iodide (NaI) solution in ethanol was introduced into vacuum as a continuous liquid flow (liquid beam) and irradiated with a 220 nm UV laser. Cluster cations containing ethoxide such as Na⁺(NaOEt), Na⁺(NaI)_n(NaOEt) (n = 1-4), and Na⁺(NaI)_n(NaOEt)₂ (n = 1-4) were observed by a time-of-flight (TOF) mass spectrometer. Furthermore, addition of NH₄⁺ or *n*-BuOH into the NaI ethanol solution resulted in suppressing the intensities of the peaks associated with these cluster ions. It is concluded that the ethoxide is produced by a scavenging reaction of a solvated electron with an ethanol molecule, and the reaction of the ethoxide formation competes with a scavenging reaction by NH₄⁺ or *n*-BuOH. The rate equations of these competing processes predict the dependence of the ethoxide formation on the concentration of NH₄⁺ or *n*-BuOH. Similar reaction products were observed from alcohol solutions of several iodides.

Introduction

Solvated electrons in liquid have long been of interest from the viewpoint of their energetics, structure, generation, and reactivity.¹⁻¹³ In an alcohol solution of an alkali halide, the absorption band associated with electron transfer from the halide anion to the solvent ("charge transfer to solvent" band or CTTS band) is observed, and solvated electrons are liberated by the excitation of this band.¹⁴ The solvated electrons thus liberated are decayed in two ways:¹⁵ geminate neutralization or reaction with nearest-neighbor neutral species in typical half-lives of a fraction of a microsecond, and reaction with the solvent molecules in typical half-lives of several microseconds.¹⁵ For example, in the reaction of a solvated electron with an ethanol molecule, an ethoxide anion, EtO⁻, is considered to be produced:

$$e_s^- + EtOH \rightarrow EtO^- + H$$
 (1)

in analogy to the reaction of a hydrated electron with a water molecule.¹⁵ The electric conductivity and the diffusion coefficient measurements^{12,16} indicate that solvated electrons in ethanol are converted partly to EtO^- through process 1. Kinetic studies on photobleaching of trapped electrons in protiated and deuterated ethanol glass at 77 K suggest formation of EtO^- by dissociative electron attachment to ethanol.¹⁷ Furthermore, EtO^- formation is postulated for explanation of the result on laser-induced electron transfer (LIET) in ethanol containing solvated electrons produced by photoionization of pyrene.^{18,19}

To clarify the reaction mechanism, chemical species involved in the reaction should be identified. To this end, the liquid beam technique²⁰⁻²³ is appropriate, because this technique enables us to introduce a liquid sample directly into vacuum as a continuous liquid flow and ionic species released from the surface can be detected by a mass spectroscopic technique. In the present study, an NaI ethanol solution was introduced into vacuum as a liquid beam and was irradiated with a UV laser in the wavelength range of the CTTS band of the NaI solution. Ionic species composed of NaOEt were observed in the mass spectrum of ions ejected after the laser irradiation and were identified to originate from the reaction of ethanol molecules with solvated electrons produced by single-photon ionization of I⁻ in ethanol.



Figure 1. Schematic diagram of a liquid beam apparatus with a TOF mass spectrometer.

More efficient scavengers, such as NH_4^+ and *n*-BuOH, were added to the NaI solution to attest the reaction mechanism proposed.

Experimental Section

A schematic diagram of a liquid beam source and a TOF mass spectrometer²⁰ is shown in Figure 1. A continuous liquid flow of a sample solution was supplied by a pump designed for a liquid chromatograph and was introduced into a source chamber through a nozzle (20 μ m in diameter) with a typical flow rate of 0.2 mL/min.

The source chamber was evacuated by a diffusion pump and a liquid nitrogen cryopump. The ambient pressure was typically 10^{-5} Torr when the liquid beam was introduced into the vacuum chamber. The flight tube of the TOF mass spectrometer was evacuated differentially by a diffusion pump down to 10^{-6} — 10^{-7} Torr. A 220 nm laser was obtained by frequency doubling the output of a Quanta-ray PDL-3 dye laser (440 nm) pumped by the third harmonics of the Nd:YAG laser. The laser power was monitored by a photodiode which was calibrated by a power meter. The ions ejected from the liquid beam were extracted by a pulsed electric field about 1 μ s after the laser irradiation. The ions steered and focused by a set of vertical and horizontal

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Figure 2. (a) Mass spectrum of ions ejected from ethanol solution of NaI (0.5 M) by 220 nm laser irradiation. Ions consisting of EtOH, NaI, NaOEt are observed. (b) The peaks appearing in the m/z range 0-120 are assigned as follows in addition to Na⁺(EtOH)_m (m = 1, 2): Na⁺(m/z = 46), Na⁺(NaH) (m/z = 47), Na⁺(NaOH) (m/z = 63), Na⁺(C₂H₃ONa) (m/z = 89), Na⁺(NaOEt) (m/z = 91), and Na⁺(C₂H₃OH)(EtOH) (m/z = 113).

deflectors and an einzel lens were reversed by a reflectron and detected by a Ceratron electron multiplier (Murata EMS-6081B). Signals from the multiplier were registered and processed by a Yokogawa DL 1200E transient digital oscilloscope based on an NEC 9801 microcomputer. All the ions observed are considered to be ejected from the liquid beam, because no ion signal was detected when the laser beam was moved away from the liquid beam.²³ Halides (NaI, KI, NH₄I, NH₄Br) and alcohols (methanol, ethanol, *n*-propanol, and *n*-butanol, >99.5%, Wako Pure Chemical Ind., Ltd.) were used as samples without any further purification. Uncertainties in the relative intensities of the ions were estimated from reproducibilities of different experimental runs; a typical uncertainty was about 2%.

Results

Figure 2a shows a mass spectrum of ions produced by irradiation of a 220 nm laser (~30 μ J/pulse) on a liquid beam of a 0.5 M NaI solution in ethanol. Ions Na⁺, Na⁺(EtOH)_m (m = 1-3), and Na⁺(NaI)_n (n = 1-5) are observed, in addition to cluster ions composed of NaOEt, Na⁺(NaI)_n(NaOEt), and Na⁺(NaI)_n(NaOEt)₂ (n = 1-4). For the sake of clarity, the mass range of m/z = 0-120 is expanded in Figure 2b. The peaks at m/z = 46, 47, 63, 67, 89, 91, and 113 are assignable to Na₂⁺, Na⁺(NaH), Na⁺(NaOH), Na⁺(C₂H₃OH), Na⁺(C₂H₃ONa), Na⁺(NaOEt), and Na⁺(C₂H₃OH)(EtOH), respectively. When



Figure 3. (a) Relative intensity of Na⁺(NaOEt) as a function of the NH₄Br concentration. The solid curve shows the prediction given with $[e_s^-]_{r=0} = 0.07$ M. (b) Relative intensity of Na⁺(NaOEt) as a function of the *n*-BuOH concentration. The solid curve shows the calculation. The ions observed are produced from an ethanol solution of NaI (0.5M) by irradiation of a 220 nm laser.

ethanol was replaced by a different alcohol, the mass peaks at m/z = 67, 89, 91, and 113 in the spectrum for the ethanol solution shift by the mass difference between the ethanol molecule and the alcohol molecule replaced. On the other hand, mass peaks at m/z = 46, 47, and 63 peaks did not shift by the replacement. The shift of the m/z = 91 peak by the replacement enables us to assign this peak as Na⁺(NaOEt), which contains an ethoxy group. The peaks at m/z = 67, 89, and 113 are assignable to Na⁺(C₂H₃OH), Na⁺(C₂H₃ONa), and Na⁺(C₂H₃-OH)(EtOH), respectively, and are formed by abstraction of two hydrogen atoms from Na⁺(EtOH), Na⁺(NaOEt), and Na⁺(EtOH)₂, respectively. On the other hand, the m/z = 46, 47, and 63 peaks are assignable to Na2⁺, Na⁺(NaH), and Na⁺(NaOH), respectively, as these peaks do not shift by the replacement. These assignments are also supported by comparison of the results on the KI solution with those on the NaI solution; the peaks shift by the mass difference between Na and K. As these ions do not exist initially in the solution, they must be produced from chemical reactions following photoabsorption.

To examine involvement of the solvated electrons for the formation of EtO⁻ or NaOEt, a more efficient scavenger for the solvated electrons, such as NH₄⁺ or *n*-BuOH,^{10,24} were introduced into the NaI ethanol solution. Figure 3a shows the relative intensity of Na⁺(NaOEt) produced from a 0.5 M NaI solution in ethanol, as a function of the NH₄Br concentration. The intensity of Na⁺(NaOEt) decreases with increase in the NH₄Br concentration. Figure 3b shows the relative intensity of Na⁺(NaOEt) decreases with an increase in the nH₄Br concentration. Figure 3b shows the relative intensity of Na⁺(NaOEt) decreases with an increase in the *n*-BuOH concentration. Figure 4 shows a mass spectrum of ions produced from an ethanol solution of NH₄I (0.5 M) by irradiation of a 220 nm laser. As shown in Figure 4, NH₄⁺(EtOH)_n (n = 0-8) and NH₄⁺(NH₃)(EtOH)_n (n = 1-5) are observed.

Discussion

Reaction Processes. It is well-known that the absorption band associated with electron transfer from the iodide ion to the solvent ("charge transfer to solvent" band or CTTS band) is observed in an alcohol solution of an iodide ion in the UV region. Accordingly, the solvated electrons are considered to be produced by the excitation of this band.¹⁴ Solvated electrons are generated by irradiation of a 220 nm laser on an ethanol solution containing $I^{-,25}$ as evidenced by formation of ions



Figure 4. Mass spectrum of ions produced from an ethanol solution of NH_4I (0.5M) by irradiation of a 220 nm laser. Cluster ions consisting of NH_3 are observed.

composed of NH₃ from an ethanol solution of NH₄I by irradiation of a 220 nm laser (see Figure 4); in the NH₄I solution, NH₄I is ionized into NH₄⁺ + I⁻ and solvated electrons liberated from I⁻ by the laser irradiation react with NH₄⁺ to form NH₃. It is therefore concluded that in the NaI solution solvated electrons are generated by excitation of its CTTS band with the 220 nm laser irradiation as NaI in the solution is ionized as Na⁺ + I⁻. The generation of the solvated electrons along with ejection of ions composed of NaOEt lead us to conclude that the solvated electrons react with ethanol, and EtO⁻ or NaOEt is formed as a result (see process 1). The solvated electrons can also recombine with other I:

$$\mathbf{e}_{\mathbf{s}}^{-} + \mathbf{I} \rightarrow \mathbf{I}^{-} \tag{2}$$

Participation of the solvated electrons in the EtO⁻ formation is confirmed by introduction of an electron scavenger, NH_4^+ or *n*-BuOH, into the NaI solution. The additional process competing with processes 1 and 2 is

$$\mathbf{e}_{\mathrm{s}}^{-} + \mathrm{NH}_{4}^{+} \rightarrow \mathrm{NH}_{3} + \mathrm{H}$$
(3)

or

$$e_{s}^{-} + n - BuOH \rightarrow n - BuO^{-} + H$$
 (4)

As shown in Figure 3, the intensities of the ions composed of NaOEt decrease with increase in the concentration of each scavenger.

Other product ions containing C_2H_3OH , C_2H_3ONa , and NaH could originate from secondary reactions such as photodissociation of NaOEt. Ions composed of NaOH are likely to be produced from a reaction of the solvated electrons with water molecules contained as impurity. In fact, the intensities of the ions composed of NaOH increase proportionally to the square root of the water concentration. This dependence also supports the involvement of the water molecules and the solvated electrons for production of the ions composed of NaOH.²⁶

Rate Equations for Scavenging Reactions. To clarify the role of the solvated electrons produced by the photoionization of NaI in ethanol, one introduces a more efficient electron scavenger in the solution and observes how the intensity of a cluster ion composed of NaOEt decreases. To this end, NH₄Br is one of the most suitable scavengers, because NH_4^+ in the ethanol solution scavenges an electron by about 10^5 times more efficient than an ethanol molecule does.¹⁰ Evidently, Na⁺(NaOEt)

decreases with the NH₄Br concentration (see Figure 3a). This decrease is explained kinetically by the rate equations of the three competing reactions, processes 1-3.

In process 1, the pseudo-first-order rate constant, k_1 [EtOH], is obtained to be $1.0 \times 10^5 \text{ s}^{-1.24}$ or the second-order rate constant, k_1 , is obtained to be 7 × 10³ M⁻¹ s^{-1 2} from a pulse radiolysis study in ethanol. In process 2, the solvated electrons react with other iodine atoms produced by photodetachment of I⁻. Self-recombination of a solvated electron²⁵ with its own I is not included explicitly because this recombination simply causes reduction of the initial concentration of the solvated electrons. Process 2 is regarded to be diffusion-controlled,²⁷ so that the rate constant, k_2 , for process 2 should be as large as a diffusion-controlled rate constant of $\sim 2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. In process 3, the reaction of NH₄⁺ with the solvated electrons is diffusion-controlled in the ethanol solution and the rate constant, k₃, for process 3 at 28 °C is 2.0 \times 10¹⁰ M⁻¹ s^{-1,10} The backward rate of process 3 is not significant, because this backward process is endothermic.²⁸ Further, the backward rate of process 1 is ruled out since [EtO⁻][H] is much smaller than $[EtOH][e_s^{-}]$. Then, the rate equations for processes 1-3 are given by

$$d[EtO^{-}]/dt = k_1[EtOH][e_s^{-}]$$
(5)

$$d[I]/dt = -k_2[I][e_s^{-}]$$
(6)

$$d[NH_4^+]/dt = -k_3[NH_4^+][e_s^-]$$
(7)

$$d[e_{s}^{-}]/dt = -k_{1}[EtOH][e_{s}^{-}] - k_{2}[I][e_{s}^{-}] - k_{3}[NH_{4}^{+}][e_{s}^{-}]$$
(8)

where [X] represents the concentration of a species X and t represents the time after laser irradiation. Initially, the concentration of I is equal to that of e_s^- . Further, the initial concentration, $[NH_4^+]_{t=0}$, is determined from the following equilibrium relations:²⁹

$$NaI \rightleftharpoons Na^+ + I^- \tag{9}$$

$$NH_4Br \rightleftharpoons NH_4^+ + Br^- \tag{10}$$

$$\mathbf{NH}_{4}\mathbf{I} \rightleftharpoons \mathbf{NH}_{4}^{+} + \mathbf{I}^{-} \tag{11}$$

$$NaBr = Na^{+} + Br^{-}$$
(12)

Let us consider a particular ion, $Na^+(NaOEt)$, as a representative product ion. The intensity, N, of $Na^+(NaOEt)$ ejected into vacuum is proportional to [EtO⁻]:

$$N = j[\text{EtO}^-] \tag{13}$$

where *j* is a coefficient characteristic of Na⁺(NaOEt). The concentration, [EtO⁻], was calculated by numerical integration of eqs 5–8 with the aid of the Euler method. In this calculation, the initial concentration of the solvated electrons, $[e_s^-]_{r=0}$ (=[I]_{*t*=0}) is the only adjustable parameter used. The calculation was terminated when $[e_s^-]$ was reduced less than 1×10^{-6} M. The absolute value of [EtO⁻] did not change significantly with the parameter, $[e_s^-]_{t=0}$. As is shown in Figure 3a, the calculation reproduces the results with $[e_s^-]_{t=0} = 0.07$ M. This $[e_s^-]_{t=0}$ value of 0.07 ± 0.01 M is reasonable, because this value is comparable to $[I^-]_{t=0}$ of 0.08 ± 0.005 M, which is calculated in NH₄Br concentrations of 0–0.1 M from eqs 9–12. This calculation also shows that processes 1–3 complete within 20–100 ns after the laser irradiation. It is concluded, therefore,

that the product ions are generated in the liquid beam before they are ejected into vacuum.

A similar calculation was performed when *n*-BuOH is used as a scavenger. The rate constant, k_4 , for process 4 is obtained to be 3×10^3 M⁻¹ s⁻¹; the pseudo-first-order reaction rate of the solvated electrons in *n*-BuOH is reported to be 5×10^4 s⁻¹.²⁴ The calculated dependence of the Na⁺(NaOEt) intensity on the concentration of *n*-BuOH is shown in Figure 3b as a solid curve. Similarly, processes 1, 2, and 4 are complete within ~75 ns after the laser irradiation, and hence, ejection of the product ions occurs after the scavenging reaction has finished in the liquid beam.

Furthermore, it is reported that in water, electron transfer from the lowest excited state of an iodide ion to the lowest excited state of a hydrated electron is energetically inaccessible.^{30,31} This finding implies that the solvated electron thus produced in ethanol is in its electronic ground state since the stabilization energy of the solvated electron in water is considered to be comparable to that in the alcohol. Accordingly, it is concluded that the precursor, EtO⁻, is produced by the reaction of the solvated electron in the ground state with ethanol.

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(27) The reaction of a solvated electron with I₂ is diffusion-controlled with its rate constant of 2.1×10^{10} M $^{-1}$ s $^{-1}$. 10 On the other hand, the cross section of electron capture by I is considered to be much larger than by I₂, as the electron affinity of I is larger by about 0.5 eV than I₂. Therefore, it is reasonable to postulate that the reaction between e_s^- and I is also diffusion-controlled and its apparent rate constant is $\sim 2.0\times10^{10}$ M $^{-1}$ s $^{-1}$.

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