Ionization Capabilities of Hydronium Ions and High Electric Fields Produced by Atmospheric Pressure Corona Discharge

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Atmospheric pressure corona discharge (APCD) was applied to the ionization of volatile organic compounds. The mass spectra of analytes having aromatic, phenolic, anilinic, basic and aliphatic in nature were obtained by using vapor supply and liquid smear supply methods. The vapor supply method mainly gave protonated analytes \([A+H]^+\) caused by proton transfer from hydronium ion \(H_3O^+\), except for benzene, toluene and \(n\)-hexane that have lower proton affinity. The use of the liquid smear supply method resulted in the formation of molecular ion \(A^+\) and/or dehydride analyte \([A−H]^−\), according to the nature of analytes used. The formation of \(A^+\) without fragment ions could be explained by the electron tunneling via high electric fields \(10^8\,\text{V/m}\) at the tip of the corona needle. The dehydride analytes \([A−H]^−\) observed in the mass spectra of \(n\)-hexane, di- and tributylamines may be explained by the hydride abstraction from the alkyl chains by the hydronium ion. The hydronium ion can play the two-roles for analytes, i.e., the proton donor to form \([A+H]^+\) and the hydride acceptor to form \([A−H]^−\).

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INTRODUCTION

Although ambient mass spectrometry (AmbiMS)1–3 has been increasingly grown up to be a practical tool for easily detecting widespread chemicals, the ion source for AmbiMS is build up from conventional ionization devices. Among the devices the needle electrode for corona discharge is simplest device and has been used for atmospheric pressure chemical ionization (APCI). We have used a needle electrode for studying the mechanism of negative-ion formation and negative-ion/molecule reactions under ambient air conditions,4–14 while the corona needle are exclusively used for positive-ion APCI with solvent chemicals as the reagent gas. The corona discharge under ambient air conditions produces micro-plasma consisting of short- and long-lifetime ionic species called as atmospheric ions, \(X^+\) and \(Y^−\), according to the polarity of voltage applied to the electrode. The atmospheric ions \(X^+\) and \(Y^−\) are formed via so-called “ion-evolution,”6–8 which occurs by discharge-induced ion/molecule reactions in the glow region at the tip of the needle with ca. 1 \(\mu\text{m}\) in radius (Fig. 1 left) and the drift region between the tip of the needle and the orifice of mass spectrometer (Fig. 1 right). It is of importance to clarify the fundamental processes of the ion formation for the application of atmospheric pressure corona discharge ionization (APCDI) to the AmbiMS of organic compounds having various physicochemical properties.

Here we examine the analyte ion formation of volatile organic compounds such as benzene and its derivatives, butylamines and hexane, by using positive-ion APCDI MS. The analytes were selected from the points of the ionization properties such as electron transfer to form molecular ion \(A^+\), proton transfer to form protonated analyte \([A+H]^+\) and hydride transfer to form dehydride analyte \([A−H]^−\).

MATERIALS AND METHODS

Materials

The liquid phase analytes benzene, toluene, phenol, benzylamine, butylamine, dibutylamine, tributylamine, 2,6-xylidine and \(n\)-hexane were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Aniline was purchased from Tokyo Chemical Industry (Tokyo, Japan). The analytes used have aromatic, phenolic, anilinic, basic and aliphatic in nature. The chemicals were used without further purification.

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Mass spectrometry

Mass spectra were acquired on a reversed geometry double-focusing mass spectrometer JMS-BU30 (JEOL, Tokyo, Japan). The mass spectrometer was operated at positive-ion mode. The ion source contained a discharge needle made of stainless steel with a diameter of 200 µm and 20 mm in length (Fig. 1 left), which is an insect pin with headless (Shiga, Tokyo, Japan). The needle tip with glossy surface as a point electrode has ca. 1 µm in radius (Fig. 1 left). The gap distance between the needle tip and the orifice plate was 3 mm (Fig. 2). The orifice hole was 320 µm in diameter and 2 mm in length. The orifice temperature was 40°C. Discharge voltage +3.9 kV was applied to the needle relative to the orifice plate. The current value between the needle and orifice plate were 10 µA. The ions entered into vacuum region were accelerated to 2.5 kV at the focusing lens electrode and separated by the reversed geometry double-focusing mass spectrometer. The scan speed was 5 s/scan. The analyte was supplied as vapor molecules into a glow or drift region between the tip of the needle and the orifice of mass spectrometer (Fig. 1a), while the liquid analyte (approximately 0.5 µL) was directly smeared on the surface of the vicinity of the tip of the needle by using a micro-pipet (Fig. 1b).

Corona discharge

The positive atmospheric ions X⁺ as reactant ion in APCI were produced by the corona discharge with a needle elec-

Fig. 1. Corona needle used (left) and the methods for supplying analyte (right). (a) The vapor supply method and (b) liquid smear supply method under ambient air conditions.

Fig. 2. Schematic illustration of the experimental apparatus containing a needle electrode.

Scheme 1. Positive-ion evolution of atmospheric pressure corona discharge to form terminal ions H₃O⁺ and H₃O⁺(H₂O)₆–8)
trode, under ambient air. The ions $X'$ are formed via a series of ion/molecule reactions called as "ion-evolution," as shown in Scheme 1. The terminal stable ions $X'$ produced under ambient air conditions are typically hydronium ion $\text{H}_3\text{O}^+$ and its hydrate $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{6-8}$. These ions act as the reactant ions to form positive analyte ions $[\text{A}+\text{H}]^+$ via collisional interactions with air components such as $\text{N}_2$, $\text{O}_2$ and $\text{H}_2\text{O}$ as third body.

RESULTS AND DISCUSSION

Mass spectra of benzene and its derivatives by positive-ion APCDI

Positive-ion APCDI mass spectra of benzene, toluene, phenol, aniline, 2,6-xylidine and benzylamine are shown in Fig. 3. In each data, the upper represents the mass spectrum obtained by supplying the analyte vapor (Fig. 1a), while the lower spectrum was obtained with liquid analyte smeared on the surface in the vicinity of the tip of corona needle (Fig. 1b). In the case of the vapor supply in all the spectra (upper), the ion peaks corresponding to protonated analyte $[\text{A}+\text{H}]^+$ were observed, except for benzene and toluene. In the atmospheric pressure ion evolution of corona discharge in positive polarity$^{6-8}$ (Scheme 1), the stable and abundant terminal ions such as $\text{H}_3\text{O}^+$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ are produced and staying in drift region between the tip of needle and orifice of mass spectrometer. Consequently, the vapor analytes A arrived at the drift region collide or interact with those hydronium ions $\text{H}_3\text{O}^+$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})$. If the proton affinity of analyte PA (A) is larger than that of water (PA $\text{H}_2\text{O}=691.0$ kJ/mol or 7.16 eV)$^{15}$, the proton transfer takes place from hydronium ions to analyte molecules as follows:

$$\text{A} + \text{H}_3\text{O}^+ \rightarrow [\text{A} + \text{H}]^+ + \text{H}_2\text{O} \quad (1)$$
Among the analytes used here, benzene and toluene having the difference in PA between water and analyte, ∆PA values, lower than 0.97 eV did not show any analyte ions under the vapor supply condition (Table 1). Aniline and 2,6-xylidine lower than 0.97 eV did not show any analyte ions under the vapor supply condition (Table 1). Aniline and 2,6-xylidine gave an extraordinarily stable fragment ions such as A_113, 130 and 131 in Fig. 3c, whereas benzylamine gave an extraordinarily stable fragment ion at m/z 91 corresponding to the tropolium ion C_7H_5_+. 16) though the ion at m/z 91 is originated from both a water cluster H_3O^+(H_2O)_4 and analyte tropolium ion C_7H_5_+. The tropolium or benzylium ion at m/z 91 observed in Fig. 3f is a fragment ion originated from the loss of ammonia NH_3 from protonated benzylamine [A_+H]^+ at m/z 108, as shown in Scheme 2. The [A_+H]^+ ion at m/z 106 observed in Fig. 3f may be formed by the hydride transfer from benzylamine to benzylium ion accompanied with the formation of tropolium C_7H_5_+ as follows:

C_6H_5NH_2 + C_7H_5_+ (benzylium ion) → [A_−]_+ + C_6H_5_+  
(2)

Furthermore, the mass spectra obtained with vapor and/or liquid smear supply methods showed hydrated analyze ions such as A_+H^+(H_2O)_n and/or [A_+H]^+(H_2O)_n, e.g., m/z 112, 113, 130 and 131 in Fig. 3c, m/z 112 and 130 in Fig. 3d, m/z 140 in Fig. 3e, and m/z 126 in Fig. 3f. The water cluster H_3O^+(H_2O)_n and hydrated analyze ions described above are produced via hydration reactions between hydronium ion H_3O^+ or analyte ions (A_+ and [A_+H]^+) and water molecules in the atmospheric pressure drift region (10^5 Pa), the inside of the orifice hole (=10^3 Pa) and/or adiabatic expansion in the vacuum region (270 Pa). 17) as sown in Fig. 2. It is of interest to note that the corona discharge ionization produced molecular ions M_+ which need electronic excitation like in electron ionization (EI).

It has been reported that the high electric fields (10^8 V/m) on the tip surface of the needle (Fig. 1 left) bring about the electrons accelerated to 100 eV or above in kinetic energy. 7,14) The first step of the ion evolution in Scheme 1 starts from such EI like process in the vicinity of the surface of the tip. Although the EI mass spectra of the compounds used here give intense and abundant fragment ions,15,18) the APCDI mass spectra obtained did not show any fragment ions except for tropolium ion at m/z 91. This suggests that the formation of molecular ions A_+ is due to the energy of thresholds near to the ionization energy (IE) listed in Table 1. From this, the A_+ ion formation can be explained by the mechanism of field ionization (FI) with an effect of electron tunneling, 19,20) because the EI mass spectra are generally lacking in fragment ions. 21,22) The influence of positive-polarity high electric field (+hef) on analyte molecules A may result in the induction effects such as molecular orbital distortion and polarization. These effects may be leading to electron transfer reaction (3) from analyte to the tip of needle electrode without excess energy depositions for the analyte molecular ions formed.

A_+ + (hef) → A_+ (without excess internal energy)  
(3)

**Table 1.** Ionization energy (IE), proton affinity (PA) and the difference in proton affinity (ΔPA) between water and volatile organic compounds.

| Analyte (M_0) | IE (eV)* | PA (kJ/mol)*/ | ΔPA (eV)* |
|--------------|----------|---------------|-----------|
| Water (18)   | 12.62    | 691.0/7.16    | 0.62      |
| Benzene (78) | 9.24     | 750.4/7.78    | 0.62      |
| Toluene (82) | 8.83     | 784.0/8.13    | 0.97      |
| Phenol (94)  | 8.49     | 817.8/8.47    | 1.31      |
| Aniline (93) | 7.72     | 882.5/9.15    | 1.99      |
| 2,6-Xyldine (121) | 7.33 | 901.7/9.35    | 2.19      |
| Benzylamine (107) | 8.49 | 913.9/9.47    | 2.31      |
| Butylamine (73) | 8.73   | 921.5/9.55    | 2.39      |
| Dibutylamine (129) | 7.69   | 968.5/10.03   | 2.87      |
| Tributylamine (185) | 7.4   | 998.5/10.35   | 3.19      |
| n-Hexane (86) | 10.13    | 672.5/6.97    | −0.19     |

*1 Thermochemical data from NIST Webbook. 15)
*2 PA (analyte)−PA (water) in eV.

[Diagram of Scheme 2: The formation of benzylium ion and tropolium ion from protonated benzylamine.]
of the [A−H]+ ions for di- and tributylamines might be explained by the hydride abstraction from methylene chains. Although the formation of the [A−H]+ ion for n-alkane has been explained by the hydride transfer reaction (4) with the formation of H₂ and a neutral product using a methane/CIMS, the detailed mechanism(s) with energetics remains unknown at present.

\[
A + H_2O^+ \rightarrow [A - H]^+ + H_2 + H_2O \quad (4)
\]

For the butylamines here, consequently, the competitive reactions of the proton transfer (1) and the hydride abstraction (4) take place due to its high proton affinity and the interaction between the butyl groups and hydronium ions under APCDI conditions. The lack in the molecular ions A− of di- and tributylamines, in spite of the lower ionization energy, may be due to the preferential interaction of butyl groups with the hydronium ions H₃O⁺ and H₃O⁺(H₂O) which largely exist in the drift region.
CONCLUSION

Positive-ion atmospheric pressure corona discharge ionization mass spectrometry (APCDI MS) was applied to volatile organic compounds which have aromatic, phenolic, anilinic, basic and aliphatic in nature, by using the vapor supply and liquid smear supply methods. The mass spectra obtained with the vapor supply method mainly gave protonated analytes \([A\cdot H]^+\) caused by the proton transfer from hydronium ions \(H_3O^+\) and/or \(H_3O^+\)(H\(_2\)O)\(_n\) as the reactant ions generated by the positive corona under ambient air conditions, except for benzene, toluene and \(n\)-hexane that have lower proton affinity. On the other hand, the use of the liquid smear supply method resulted in the formation of molecular ions \(A\cdot\) and/or dehydride analytes \([A\cdot H]^+\). The resulting analyte ions \(A\cdot\), \([A\cdot H]^+\) and \([A\cdot H]^+\) were without fragment ions, except for the formation of the tropylation ion at \(m/z\) 91 originated from the analyte ions of toluene and benzylamine. The formation of molecular ions \(A\cdot\) without fragment ions could be explained by the electron tunneling that occurs by high electric field (10\(^8\) V/m) at the tip of the corona needle. The dehydride analytes \([A\cdot H]^+\) observed in the mass spectra of \(n\)-hexane, di- and tributylamines may be explained by the hydride abstraction from the alkyl chains by the hydronium ions \(H_3O^+\) and \(H_2O^+(H_2O)\). From this, it can be expected that the hydronium ions can play the two-roles for the analyte ionization, i.e., the proton donor and hydride acceptor, according to the proton affinity of analytes. Further study is needed to clarify the detailed mechanism(s) of the ion formation with energetics in the APCDI MS.

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