International Journal of Mass Spectrometry 285 (2009) 95–99

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

A deuterium-labeling study on the reproduction of hydronium ions in the PTR-MS detection of ethanol

Satoshi Inomata[a,*], Hiroshi Tanimoto[b]

[a] Atmospheric Environment Division, National Institute for Environmental Studies, 16–2 Onogawa, Tsukuba, Ibaraki 305-8506, Japan
[b] Asian Environment Research Group, National Institute for Environmental Studies, 16–2 Onogawa, Tsukuba, Ibaraki 305-8506, Japan

ARTICLE INFO

Article history:
Received 15 December 2008
Received in revised form 8 May 2009
Accepted 12 May 2009
Available online 21 May 2009

Keywords:
PTR-MS
H_3O^+ + ethanol reaction
Ethanol
Deuterium-labeling study
Alcohol

ABSTRACT

The reactions of hydronium ions (H_3O^+) with ethanol (C_2H_5OH) and deuterium-labeled ethanols (CD_3CH_2OH and CH_3CD_2OH) were investigated by means of proton transfer reaction mass spectrometry (PTR-MS). Besides the protonation reaction of H_3O^+ with C_2H_5OH, three fragmentation processes yielding $C_2H_5{}^+$, CH_2OH^+, and H_3O^+ ions were previously implied. In this paper, we report the branching ratios for those four channels at six different field strengths (E/N ratios) of the drift tube. The contribution of the channel that reproduces hydronium ions (H_3O^+) was determined by detecting H_2DO^+ ions at m/z 20 produced in reactions of H_3O^+ with deuterium-labeled ethanols (CD_3CH_2OH and CH_3CD_2OH). The reproduction of H_3O^+ ions was found to be significant between 108 and 162 Td of the E/N ratio, however, it did not quantitatively account for the low detection sensitivity of ethanol by PTR-MS, suggesting the presence of unidentified reaction channel(s). The unidentified reaction channel(s) might be the H_3O^+-reproducing channel itself, because the contribution from this channel would be underestimated in this experiment due to loss process(es) such as an H/D exchange between H_2DO^+ and H_2O.

1. Introduction

Proton transfer reaction mass spectrometry (PTR-MS) is a technique that allows for fast and sensitive measurements of volatile organic compounds (VOC) at trace levels in air [1–4]. Proton transfer is an example of chemical ionization: it enables soft ionization of chemical species that have a proton affinity (PA) higher than that of the reagent species (i.e., water):

$$H_3O^+ + VOC \rightarrow VOC^{\bullet}H^+ + H_2O \qquad (1)$$

One of the advantages of PTR-MS is that it does not require any sample treatment such as drying and/or preconcentration, and in particular, it is suitable for oxygenated VOCs, which are difficult to quantify from canister samples.

Although quantitative measurements of methanol have been carried out in ambient air [2–6], there are problems with the detection of other aliphatic alcohols by PTR-MS. A study using selected ion flow tube mass spectrometry (SIFT-MS) [7] reported that the protonation of alcohols such as propanol, butanol, and pentanol by H_3O^+ is followed by the ejection of an H_2O molecule, so that protonated molecules cannot be detected. In addition, the ion signals of the alkyl radical cations that formed overlap with those of protonated alkenes [8,9].

Fragmentation was not observed in ethanol (C_2H_5OH, molecular weight 46) by using SIFT-MS [7], however, quantification of ethanol by PTR-MS seems to be difficult [9–11] because of fragmentation processes [10]. Besides protonated ethanol, $C_2H_5OH^{\bullet}H^+$, at m/z 47, production of a fragment ion, $C_2H_5{}^+$, at m/z 29 was observed in the detection of C_2H_5OH by PTR-MS [10,12–14]:

$$H_3O^+ + C_2H_5O \rightarrow C_2H_5OH^{\bullet}H^+ + H_2O \qquad \Delta H_r{}^{\circ} = -85\,\mathrm{kJ\,mol^{-1}} \qquad (2a)$$

$$H_3O^+ + C_2H_5OH \rightarrow C_2H_5{}^+ + 2H_2O \qquad \Delta H_r{}^{\circ} = +54\,\mathrm{kJ\,mol^{-1}} \qquad (2b)$$

The ratio of (2b)/(2a) under dry conditions was reported to be approximately 0.1 at 119 and 137 Td for the field strength, E/N, of the drift tube ($1\,\mathrm{Td} = 10^{-17}\,\mathrm{cm^2\,V\,molecule^{-1}}$), where E is the electric field strength ($\mathrm{V\,cm^{-1}}$) and N is the buffer gas number density ($\mathrm{molecule\,cm^{-3}}$) [13], and was reported to be 0.07 even at E/N = 165 Td [14].

Recently, our group found a fragmentation process that likely produces a CH_2OH^+ ion at m/z 31 from ethanol:

$$H_3O^+ + C_2H_5OH \rightarrow CH_2OH^+ + CH_4 + H_2O \qquad \Delta H_r{}^{\circ} = +38\,\mathrm{kJ\,mol^{-1}} \qquad (2c)$$

---

* Corresponding author. Tel.: +81 29 850 2403; fax: +81 29 850 2579.
E-mail addresses: ino@nies.go.jp (S. Inomata), tanimoto@nies.go.jp (H. Tanimoto).

1387-3806/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2009.05.001

The ratio of (2c)/(2a) was reported to be 0.045 ± 0.004 at $E/N = 108$ Td [15]. The detection sensitivity of ethanol and its humidity dependency were also determined by PTR-MS in the laboratory for the calibration of data obtained during an intensive field campaign on the summit of Mount Tai, China, in June 2006 [Inomata et al., manuscript in preparation, hereafter referred to as Inomata et al., 2009]. The detection sensitivity of ethanol under dry conditions was determined to be 1.6 ± 0.1 normalized counts per second (ncps)/parts per billion by volume (ppbv), which is almost seven times less than that of methanol (10.6 ± 0.4 ncps/ppbv), although the rate coefficient of the reactions of H_3O^+ with ethanol has been reported to be the same with methanol (2.7×10^{-9} cm^3 molecule^{-1} s^{-1}) [7]. A similarly large difference in detection sensitivities between ethanol and methanol has been reported by Warneke et al. [10] (3 ncps/ppbv for ethanol vs. 15.9 ncps/ppbv for methanol). Since the contributions of the fragmentation processes (2b) and (2c) are not significant in the reaction of ethanol with H_3O^+, it is unlikely that the low detection sensitivity of ethanol is caused by these fragmentation processes.

Warneke et al. [10] have suggested that ethanol has a fragment at m/z 19:

$$H_3O^+ + C_2H_5OH \rightarrow H_3O^+ + C_2H_4 + H_2O \qquad \Delta H_r{}^\circ = +44\,\text{kJ mol}^{-1} \tag{2d}$$

However, they did not confirm it because the ion signal at m/z 19 was not detectable due to an overlap with the H_3O^+ primary ion signal. Therefore, the relative contribution from channel (2d) remains unknown. The production of H_3O^+ as well as $C_2H_5{}^+$ by the unimolecular dissociation of protonated ethanol, $C_2H_5OH{}^\bullet H^+$, has been reported in variable temperature selected-ion-flow-drift tube (VT-SIFDT) experiments [16].

In the present study, we examined the contribution from channel (2d) by detecting H_2DO^+ ions at m/z 20 produced in the reactions of H_3O^+ with deuterium-labeled ethanols (CD_3CH_2OH and CH_3CD_2OH). We report the branching ratios of channels (2a)–(2d).

2. Experimental

We used a commercially available PTR-MS instrument (Ionicon Analytik) [15,17,18]. Briefly, H_3O^+ ions were produced from a pure water vapor flow of 7.8 sccm in a hollow cathode discharge ion source. The sample air was introduced into the drift tube at a flow rate of approximately 22 sccm and the drift tube pressure was held at 2.1 mbar. Temperatures of the sampling inlet and the drift tube were held at 105 °C. The drift tube (9.2 cm long) consisted of stainless steel ring electrodes, separated by Teflon rings for electrical isolation. The ring electrodes were connected to a resistor network, which divided the overall drift voltage into a homogeneously increasing voltage and established a homogeneous electric field inside the drift tube to avoid substantial formation of cluster ions, $H_3O^{+\bullet}(H_2O)_n$ ($n = 1, 2, \ldots$). In the drift tube, trace gases such as VOCs in the sample air were ionized by proton transfer reactions (reaction (1)). A fraction of the reagent ion, H_3O^+, and the product ions was extracted through a small orifice into a quadrupole mass spectrometer. The ions were detected by a secondary electron multiplier for ion pulse counting. The mass dependence of the transmission efficiency of the QMS was calibrated by the manufacturer.

Ethanol vapor was prepared by injecting a liquid sample into a 10-L Tedlar bag, and ion signals were obtained in multi-ion detection (MID) mode at six values of E/N (108, 119, 130, 140, 151, and 162 Td). A small amount of each sample (0.06 μl) was injected into the bag filled with pure air, resulting in a sample mixture of approximately 1 part per million by volume (ppmv).

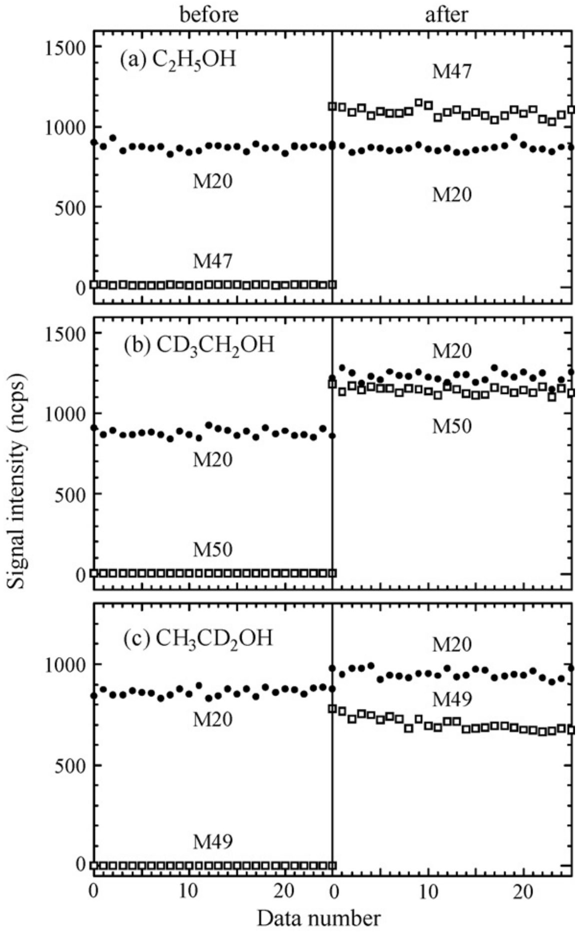

Fig. 1. Differences in the ion signals of protonated ethanol and H_2DO^+ before and after the introduction of ethanols at $E/N = 108$ Td. (a) C_2H_5OH, (b) CD_3CH_2OH, and (c) CH_3CD_2OH.

The count rate of the reagent ion, H_3O^+, calculated from the count rate at m/z 21 ($H_3{}^{18}O^+$) multiplied by 500, was in the range $(5–10) \times 10^6$ cps. The ratios of the ion intensity of $H_3O^{+\bullet}H_2O$ (m/z 37) to that of H_3O^+ were 0.016 at $E/N = 108$ Td and 0.00014 at $E/N = 162$ Td, while the ratio of the ion intensity of $O_2{}^+$ (m/z 32) to that of H_3O^+ was 0.02–0.03. The ion count rates of the product ions totaled $(4–16) \times 10^2$ ncps normalized to an H_3O^+ intensity of 10^6 cps, which is within the linear dynamic range of the PTR-MS instrument.

The stated purities of gases and chemicals used were as follows: air, >99.99995% (Japan Fine Products); methanol/N_2, 10.8 parts per million (ppm) (Takachiho); ethanol/N_2, 9.56 ppm (Takachiho); ethanol, >99.5% (C_2H_5OH; Kanto Kagaku); ethyl-2,2,2-d_3 alcohol, 99 at.% D (CD_3CH_2OH; Isotec); and ethyl-1,1-d_2 alcohol, 98 at.% D (CH_3CD_2OH; Isotec).

3. Results and discussion

Fig. 1(a) shows the ion signals of protonated ethanol, $C_2H_5OH{}^\bullet H^+$, at m/z 47 (M47) and of H_2DO^+ at m/z 20 (M20) before and after the introduction of the C_2H_5OH sample at $E/N = 108$ Td. As expected, the ion signals of the protonated ethanol increased with ethanol as the sample gas, while the ion signals at m/z 20 did not change. The background ion signals at m/z 20 were relatively high because of the ion signals from H_2DO^+ and $H_3{}^{17}O^+$, which intensities are 0.015% and 0.038% of that of H_3O^+, respectively. Fig. 1(b) and (c) show results from the same experiments, but with CD_3CH_2OH

Table 1
Normalized signal intensities (ncps) of product ions in reactions of H_3O^+ with ethanols[a].

E/*N* (Td)	108	119	130	140	151	162
C_2H_5OH						
M47 ($C_2H_5OH{\bullet}H^+$)	1076 ± 10	498 ± 6	246 ± 4	138 ± 3	79 ± 3	54 ± 2
M29 ($C_2H_5^+$)	35 ± 2	34 ± 2	–[b]	–[b]	–[b]	–[b]
M31 (CH_2OH^+)	27 ± 2	25 ± 2	22 ± 2	19 ± 2	18 ± 2	18 ± 2
M19 (H_3O^+)[c]	–	–	–	–	–	–
CD_3CH_2OH						
M50 ($CD_3CH_2OH{\bullet}H^+$)	1135 ± 8	536 ± 7	262 ± 4	145 ± 3	84 ± 2	57 ± 2
M32 ($CD_3CH_2^+$)[d]	–	–	–	–	–	–
M31 (CH_2OH^+)	48 ± 2	49 ± 2	47 ± 3	39 ± 3	36 ± 3	30 ± 3
M20 (H_2DO^+)	353 ± 15	411 ± 15	429 ± 18	439 ± 19	435 ± 20	413 ± 20
CH_3CD_2OH						
M49 ($CH_3CD_2OH{\bullet}H^+$)	703 ± 12	315 ± 3	157 ± 3	86 ± 2	51 ± 2	34 ± 2
M31 ($CH_3CD_2^+$)	5 ± 2	7 ± 2	9 ± 2	9 ± 2	10 ± 2	8 ± 2
M33 (CD_2OH^+)	21 ± 2	16 ± 2	16 ± 2	13 ± 2	13 ± 2	11 ± 3
M20 (H_2DO^+)	91 ± 11	115 ± 14	125 ± 14	128 ± 15	111 ± 17	121 ± 18

[a] Error limits were calculated by propagation of the errors on the ion counts and indicate only the precision. The errors on the ion counts were derived from 95% confidence levels by a *t*-test.

[b] Background signals at *m*/*z* 29 increased significantly as the *E*/*N* ratio increased.

[c] Ion signals are overlapped with those of the primary ions of H_3O^+.

[d] Ion signals are overlapped with those of O_2^+ primarily generated in the ion source.

and CH_3CD_2OH, respectively. In both cases, enhancement of the ion signals at *m*/*z* 20 (M20) was observed, as well as an increase of the ion signals of protonated ethanols at *m*/*z* 50 for CD_3CH_2OH (M50) and *m*/*z* 49 for CH_3CD_2OH (M49), respectively. Previously, we reported that the extent of an H/D exchange between H_3O^+ and ethylbenzene-d_{10} was too small to be observed by PTR-MS [17]. Similarly, the formation of H_2DO^+ is unlikely to result from the H/D exchange between H_3O^+ and deuterium-labeled ethanols, but instead results from the reaction of H_3O^+ with deuterium-labeled ethanols:

$$H_3O^+ + CD_3CH_2OH \rightarrow C_2H_2D_2 + H_2DO^+ + H_2O \tag{3}$$

$$H_3O^+ + CH_3CD_2OH \rightarrow C_2H_3D + H_2DO^+ + H_2O \tag{4}$$

Since the formation of H_2DO^+ is observed for deuterium-labeled ethanols in both the 1-position and the 2-position, the reaction (2d) consists of two channels, i.e., it reproduces H_3O^+ with an H atom at the 1-position (reaction ($2d_\alpha$)) and with an H atom at the 2-position (reaction ($2d_\beta$)):

$$H_3O^+ + CH_\beta H_\beta H_\beta CH_\alpha H_\alpha OH \rightarrow C_2H_\alpha H_\beta H_\beta H_\beta + H_2H_\alpha O^+ + H_2O \tag{$2d_\alpha$}$$

$$H_3O^+ + CH_\beta H_\beta H_\beta CH_\alpha H_\alpha OH \rightarrow C_2H_\alpha H_\alpha H_\beta H_\beta + H_2H_\beta O^+ + H_2O \tag{$2d_\beta$}$$

By comparing Fig. 1(b) and (c), it can be seen that the degree of formation of H_2DO^+ with a D atom at the 1-position seems to be smaller than that of the formation of H_2DO^+ with a D atom at the 2-position.

The signal intensities of product ions in the reactions of H_3O^+ with ethanol and deuterium-labeled ethanols at six different *E*/*N* conditions are tabulated in Table 1. At *E*/*N* = 108 Td, a small number of ion signals at *m*/*z* 29 and *m*/*z* 31, corresponding to those from $C_2H_5^+$ and CH_2OH^+ ions, respectively, were observed in addition to the ion signals of the protonated C_2H_5OH at *m*/*z* 47 in the case of C_2H_5OH. As the *E*/*N* ratio increased, the ion signals of the protonated C_2H_5OH drastically decreased. A similar decrease of ion signals of protonated ethanols with an increasing *E*/*N* ratio was observed for both CD_3CH_2OH and CH_3CD_2OH. However, the ion signals of the fragment ion, CH_2OH^+, in the reaction with C_2H_5OH did not increase with an increase in the *E*/*N* ratio in the case of C_2H_5OH. Similarly, an increase of the ion signals of CH_2OH^+ and CD_2OH^+ in the cases of CD_3CH_2OH and CH_3CD_2OH, respectively, was not observed with an increasing *E*/*N* ratio. In regard to the channel that produces the ethyl radical cation, we obtained the dependence of ion signals from $CH_3CD_2^+$ on the *E*/*N* ratio without any interference only in the case of CH_3CD_2OH. The ion signals of $CH_3CD_2^+$ did not increase strongly with an increasing *E*/*N* ratio. On the other hand, it was observed that the ion signals of H_2DO^+ produced in reactions (3) and (4) increased with an increasing *E*/*N* ratio.

We examined branching ratios between (2a)–(2d), as shown in Table 2 along with the reaction times calculated according

Table 2
Detection sensitivities (ncps/ppbv) at each channel and the *E*/*N* ratios in the $H_3O^+ + C_2H_5OH$ reaction[a].

E/*N* (Td) Reaction time (μs)	108 113	119 103	130 94	140 87	151 81	162 76
Reaction (2a)[b]	1.6 ± 0.1	0.74 ± 0.10	0.37 ± 0.04	0.20 ± 0.03	0.12 ± 0.01	0.08 ± 0.01
Reaction (2b)[c]	0.01 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01
Reaction (2c)[b]	0.05 ± 0.04	0.05 ± 0.04	0.05 ± 0.05	0.04 ± 0.04	0.04 ± 0.03	0.03 ± 0.02
Reaction ($2d_\alpha$)[c,d]	0.34 ± 0.05	0.44 ± 0.08	0.47 ± 0.11	0.49 ± 0.09	0.41 ± 0.07	0.46 ± 0.09
Reaction ($2d_\beta$)[e,d]	0.81 ± 0.07	0.92 ± 0.13	0.97 ± 0.06	1.00 ± 0.14	0.99 ± 0.09	0.95 ± 0.13
Unidentified[f]	9.6	9.1	8.4	7.8	7.3	6.7

[a] Error limits were calculated by propagation of the errors on the ion counts.

[b] Averaged data of protonated non-deuterium-labeled and deuterium-labeled ethanols.

[c] Based on the data for CH_3CD_2OH.

[d] A multiplication factor for the isotope effect that favors H migration over D migration was included.

[e] Based on the data for CD_3CH_2OH.

[f] See text.

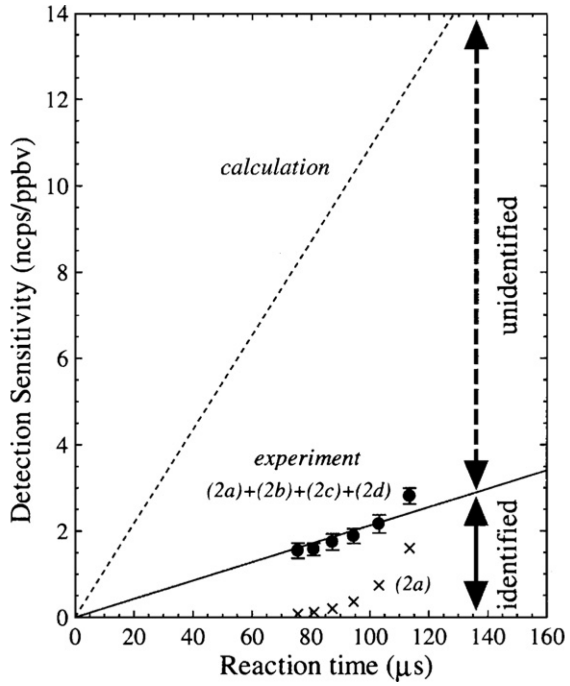

Fig. 2. Plots of the total detection sensitivity derived by the sum of the values in reactions (2a)–(2d) (filled circles) as well as the detection sensitivity only for reaction (2a) (crosses) in the $H_3O^+ + C_2H_5OH$ reaction vs. reaction time (µs). The dashed line is a fit by the function $y = ax$ of the total detection sensitivity data. The solid line shows the detection sensitivity calculated by using the rate constant for reaction (2).

to Hanson et al. [19]. In the table, the detection sensitivities (ncps/ppbv) at each reaction channel and the E/N ratios are summarized. As mentioned earlier, the detection sensitivity of reaction (2a) at $E/N = 108$ Td was determined to be 1.6 ± 0.1 ncps/ppbv in our laboratory. For values in reaction (2a), the dependence of the signals of protonated ethanol on the E/N ratio was taken from the averaged values of protonated non-deuterium-labeled and deuterium-labeled ethanols at each E/N ratio. The values for reactions (2b) and ($2d_\alpha$) were estimated based on the data for CH_3CD_2OH, while those for reaction ($2d_\beta$) were estimated based on the data for CD_3CH_2OH. In addition, a previously determined [17] multiplication factor for the isotope effect that favors H migration over D migration, 1.63 ± 0.04, was included in the derivation of the values for reactions ($2d_\alpha$) and ($2d_\beta$). The values for reaction (2c) were estimated from the averaged value of protonated non-deuterium-labeled and deuterium-labeled ethanols.

As seen in Table 2, the reaction (2d) is apparently significant among the fragmentation processes (2b)–(2d). Even at $E/N = 108$ Td, the branching ratio of reaction (2d) was comparable to that of reaction (2a), which produces protonated ethanol. At $E/N = 162$ Td, the branching ratio of reaction (2d) was more than 90%. In regards to the ratio between reaction ($2d_\alpha$) and ($2d_\beta$), the branching ratio of reaction ($2d_\beta$) was almost twice that of reaction ($2d_\alpha$) and it was independent of the E/N ratio. This likely reflects the fact that an abstraction of an H atom at the 2-position of protonated ethanol to form an H_3O^+ ion is easier than an abstraction of an H atom at the 1-position. A similar result was obtained in the fragmentation process of protonated ethylbenzene [17].

We also explored the reason why the detection sensitivity of ethanol (1.6 ± 0.1 ncps/ppbv) is low compared with that of methanol (10.6 ± 0.4 ncps/ppbv) (Inomata et al., 2009). In Fig. 2, the total detection sensitivity at each E/N ratio derived from the sum of the values in reactions (2a)–(2d) as well as the detection sensitivity for reaction (2a) are plotted against the reaction time. Generally, the count rates of $VOC^\bullet H^+$ ions, $i(VOC^\bullet H^+)$, can be calculated from:

$$i(VOC^\bullet H^+) = i(H_3O^+)(1 - \exp(-k[VOC]t) \approx i(H_3O^+)k[VOC]t, \qquad (5)$$

where t is the reaction time and k is the reaction rate constant. According to this, the data in Fig. 2 should be fit linearly and forced to intercept zero. The correlation coefficient (r^2) was 0.81 and the slope was 0.021 (ncps ppbv^{-1} µs^{-1}). However, the slope was found to be quite small compared with the calculated value (0.109 (ncps ppbv^{-1} µs^{-1}) = 10^6 (ncps) · 2.7×10^{-9} (cm^3 molecule^{-1} s^{-1}) · 2.6868×10^{19} (molecule cm^{-3}) · [273.15 (K)/(273.15 + 105) (K)] · [2.1 (mbar)/1013.25 (mbar)] · 10^{-9}(ppbv^{-1})·10^{-6}(µs^{-1})) obtained using the reported k value [7]. The unidentified channel(s) was also listed in Table 2, suggesting that approximately 80% of the overall H_3O^+ + ethanol reaction was unidentified.

We should note that the branching ratio of reaction (2d) is underestimated due to loss processes of H_2DO^+ ions in the experiments with CD_3CH_2OH and CH_3CD_2OH. A possible loss process is H/D exchange between H_2DO^+ and H_2O because of a large amount of H_2O in the drift tube:

$$H_2DO^+ + H_2O \rightarrow H_3O^+ + HDO \qquad (6)$$

The rate constant for the reaction (6) was reported to be 7.3×10^{-10} cm^3 molecule^{-1} s^{-1} [20]. Since the concentration of water vapor in the drift tube was expected to be approximately 10 mmol/mol [15], the loss rate of H_2DO^+ by the reaction (6) is about 3×10^5 s^{-1} (=7.3×10^{-10}(cm^3 molecule^{-1} s^{-1})·4×10^{16} (molecule cm^{-3}) · 10 (mmol/mol)). On the other hand, the production rate of H_2DO^+ by the reactions (3) and (4) is at most 10^2 s^{-1} (=2.7×10^{-9} (cm^3 molecule^{-1} s^{-1}) · 4×10^{16} (molecule cm^{-3}) · 1 (ppmv)). This suggests that H_2DO^+ quickly reaches in the steady state. Therefore, the observed ion count of H_2DO^+ became low and the branching ratio of reaction (2d) may be underestimated. Thus, since the present results give a lower limit of the branching ratio of reaction (2d), the reproduction of the H_3O^+ ions was found to be significant in the detection of ethanol by PTR-MS. The low detection sensitivity of ethanol by PTR-MS likely results from the reaction channel (2d).

References

[1] J. de Gouw, C. Warneke, Mass Spectrom. Rev. 26 (2007) 223.

[2] C.A.M. Brenninkmeijer, P. Crutzen, F. Boumard, T. Dauer, B. Dix, R. Ebinghaus, D. Filippi, H. Fischer, H. Franke, U. Frieβ, J. Heintzenberg, F. Helleis, M. Hermann, H.H. Kock, C. Koeppel, J. Lelieveld, M. Leuenberger, B.G. Martinsson, S. Miemczyk, H.P. Moret, H.N. Nguyen, P. Nyfeler, D. Oram, D. O'Sullivan, S. Penkett, U. Platt, M. Pupek, M. Ramonet, B. Randa, M. Reichelt, T.S. Rhee, J. Rohwer, K. Rosenfeld, D. Scharffe, H. Schlager, U. Schumann, F. Slemr, D. Sprung, P. Stock, R. Thaler, F. Valentino, P. van Velthoven, A. Waibel, A. Wandel, K. Waschitschek, A. Wiedensohler, I. Xueref-Remy, A. Zahn, U. Zech, H. Ziereis, Atmos. Chem. Phys. 7 (2007) 4953.

[3] T.G. Karl, T.J. Christian, R.J. Yokelson, P. Artaxo, W.M. Hao, A. Guenther, Atmos. Chem. Phys. 7 (2007) 5883.

[4] J. Lelieveld, T.M. Butler, J.N. Crowley, T.J. Dillon, H. Fischer, L. Ganzeveld, H. Harder, M.G. Lawrence, M. Martinez, D. Taraborrelli, J. Wiiliams, Nature 452 (2008) 737.

[5] J.A. de Gouw, P.D. Goldan, C. Warneke, W.C. Kuster, J.M. Roberts, M. Marchewka, S.B. Bertman, A.A.P. Pszenny, W.C. Keene, J. Geophys. Res. 108 (2003) 4682.

[6] J. de Gouw, C. Warneke, R. Holzinger, T. Klüpfel, J. Williams, Int. J. Mass Spectrom. 239 (2004) 129.

[7] P. Spanel, D. Smith, Int. J. Mass Spectrom. Ion Process. 167/168 (1997) 375.

[8] T. Karl, T. Jobson, W.C. Kuster, E. Williams, J. Stutz, R. Shetter, S.R. Hall, P. Goldan, F. Fehsenfeld, W. Lindinger, J. Geophys. Res. 108 (2003) 4508.

[9] K.P. Wyche, R.S. Blake, A.M. Ellis, P.S. Monks, T. Brauers, R. Koppmann, E.C. Apel, Atmos. Chem. Phys. 7 (2007) 609.

[10] C. Warneke, J.A. de Gouw, W.C. Kuster, P.D. Goldan, R. Fall, Environ. Sci. Technol. 37 (2003) 2494.

[11] E.C. Apel, T. Brauers, R. Koppmann, B. Bandowe, J. Boßmeyer, C. Holzke, R. Tillmann, A. Wahner, R. Wegener, A. Brunner, M. Jocher, T. Ruuskanen, C. Spirig, D. Steigner, R. Steinbrecher, E. Gomez Alvarez, K. Müller, J.P. Burrows, G. Schade, S.J. Solomon, A. Ladstätter-Weißenmayer, P. Simmonds, D. Young, J.R. Hopkins, A.C. Lewis, G. Legreid, S. Reimann, A. Hansel, A. Wisthaler, R.S. Blake, A.M. Ellis, P.S. Monks, K.P. Wyche, J. Geophys. Res. 113 (2008) D20307.

[12] E. Boscaini, T. Mikoviny, A. Wisthaler, E. von Hartungen, T.D. Märk, Int. J. Mass Spectrom. 239 (2005) 215.

[13] L. Keck, C. Hoeschen, U. Oeh, Int. J. Mass Spectrom. 270 (2008) 156.
[14] R.S. Blake, K.P. Wyche, A.M. Ellis, P.S. Monks, Int. J. Mass Spectrom. 254 (2006) 85.
[15] S. Inomata, H. Tanimoto, S. Kameyama, U. Tsunigai, H. Irie, Y. Kanaya, Z. Wang, Atmos. Chem. Phys. 8 (2008) 273.
[16] S.C. Smith, M.J. McEwan, K. Giles, D. Smith, N.G. Adams, Int. J. Mass Spectrom. Ion Process. 96 (1990) 77.
[17] S. Kameyama, S. Inomata, H. Tanimoto, Int. J. Mass Spectrom. 276 (2008) 49.
[18] W. Lindinger, A. Hansel, A. Jordan, Int. J. Mass Spectrom. Ion Process. 173 (1998) 191.
[19] D.R. Hanson, J. Greenberg, B.E. Henry, E. Kosciuch, Int. J. Mass Spectrom. 223–224 (2003) 507.
[20] D. Smith, N.G. Adams, M.J. Henchman, J. Chem. Phys. 72 (1980) 4951.