A Quantitative Examination of the Detection Sensitivities of Proton-Transfer Reaction Mass Spectrometry for Gaseous 2-Propanol and Acetic Acid

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The detection sensitivities of proton-transfer reaction mass spectrometry for isobaric 2-propanol and acetic acid were examined systematically at five different kinetic energies. The detection sensitivity for acetic acid was in good agreement with the sensitivities calculated from the experimentally and theoretically obtained rate constants for the reaction of H_3O^+ with acetic acid. However, the detection sensitivity for 2-propanol was quite small compared with the calculated values. In deuterium-labeling studies, the formation of H_2DO^+ ions at m/z 20 in the reaction of H_3O^+ with $(CD_3)_2CHOH$ was clearly observed, whereas the formation of H_2DO^+ was not observed in the reaction of H_3O^+ with $CD_3C(O)OH$. We concluded that the difference between the experimental and calculated detection sensitivities for 2-propanol was attributed to a reaction channel that reproduced H_3O^+ ion during the reaction of H_3O^+ with 2-propanol.

Proton-transfer reaction mass spectrometry (PTR-MS), which allows online detection of volatile organic compounds (VOCs) at trace levels in air,[1–3] is currently used in many areas of research, such as atmospheric chemistry, plant physiology and ecology, medical research, and food research.[4] Proton transfer is a type of chemical ionization that enables soft ionization of chemical species that have a proton affinity higher than that of the reagent species (i.e., water):

$$H_3O^+ + VOC \rightarrow VOC{\cdot}H^+ + H_2O \tag{1a}$$

Unlike gas chromatography, PTR-MS does not require any sample treatment such as drying or preconcentration, and therefore quantitative measurements of even oxygenated VOCs are possible.

Another property of PTR-MS is that the concentration of a detected VOC can be calculated from the following kinetic relationship, because the ionization reaction is an ion–molecule reaction:[1]

$$[VOC] \approx \frac{i(VOC{\cdot}H^+)}{k \cdot t \cdot i(H_3O^+)} \tag{2}$$

where $i(H_3O^+)$ and $i(VOC{\cdot}H^+)$ represent the count rates of the reagent ion, H_3O^+, and the product ion, $VOC{\cdot}H^+$, respectively; k represents the rate constant for the proton-transfer reaction; and t represents the reaction time. This property is useful for some VOCs, the calibration of which is difficult. The reaction time, which is typically 10^{-4} s, can be determined from the H_3O^+ drift velocity and the length of the drift tube.[5] The rate constants usually range between 1.5×10^{-9} and 4×10^{-9} $cm^3\,molecule^{-1}\,s^{-1}$, which are identical to collision limiting values.[1] The rate constants can be obtained experimentally, for example, by means of selected ion flow tube mass spectrometry,[6] which supplies thermal rate constants, while they can be also derived theoretically.[7] The agreement between the theoretical and experimental rate constants is within 25% in most cases.[4]

For fragile VOCs at ionization, $i(VOC{\cdot}H^+)$ in eq 2 should be replaced with the sum of the count rates of the protonated molecule and any fragment ions:

$$H_3O^+ + VOC \rightarrow fragment^+ + \text{other products} \tag{1b}$$

$$[VOC] \approx \frac{i(VOC{\cdot}H^+) + \sum i(fragment^+)}{k \cdot t \cdot i(H_3O^+)} \tag{3}$$

Recently, we investigated the detection sensitivity of PTR-MS for ethanol.[8] The experimental detection sensitivity obtained from count rates for protonated ethanol was substantially lower than the value calculated from the reported rate constant for the reaction of H_3O^+ with ethanol and the reaction time. Even when the count rates for fragments ions such as $C_2H_5^+$ and CH_2OH^+ were taken into consideration, the experimental total detection sensitivity for ethanol was still inconsistent with the calculated value. Then, a deuterium-labeling study revealed the reproduction of H_3O^+, by detecting H_2DO^+ formed in the reactions of H_3O^+ with deuterium-labeled ethanols. However, approximately 80% of the overall H_3O^+ + ethanol reaction was unidentified and it was not confirmed whether the calculated detection sensitivity is in agreement with the total detection sensitivity summing the detection sensitivities of all reaction channels, in the case of ethanol.

2-Propanol, $(CH_3)_2CHOH$, and acetic acid, $CH_3C(O)OH$, are isobaric compounds and both have an OH group in common. The rate constant of the $H_3O^+ + (CH_3)_2CHOH$ reaction is similar to that of the $H_3O^+ + CH_3C(O)OH$ reaction (ca. $3 \times 10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$):[1,9,10]

$$H_3O^+ + (CH_3)_2CHOH \rightarrow products \tag{4}$$

$$H_3O^+ + CH_3C(O)OH \rightarrow products \tag{5}$$

In addition, the proton affinity of 2-propanol ($793\,kJ\,mol^{-1}$) is

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Table 1. Detection Sensitivities/ncps ppbv^{-1} for Each Reaction Channel, E/N Ratios, and Reaction Times for the $H_3O^+ + (CH_3)_2CHOH$ Reaction[a)]

(E/N)/Td[b)]	102	111	120	129	139
Reaction time/µs	122	111	102	94	86
Reaction (4a)	0.05 ± 0.01	0.02 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
Reaction (4b)	7.48 ± 0.84	6.12 ± 0.75	4.25 ± 0.39	2.45 ± 0.23	1.34 ± 0.12
Reaction (4c)	0.32 ± 0.04	0.93 ± 0.11	1.92 ± 0.21	2.68 ± 0.26	2.53 ± 0.26
Total	7.85 ± 0.84	7.07 ± 0.76	6.18 ± 0.44	5.14 ± 0.35	3.88 ± 0.29

a) Error limits represent 95% confidence levels determined by t-test. b) Unit of E/N is Townsend (Td) and $1\,\mathrm{Td} = 10^{-17}\,\mathrm{cm^2\,V\,molecule^{-1}}$.

close to that of acetic acid (784 kJ mol^{-1}). In the present work, we systematically investigated the detection sensitivities of PTR-MS for 2-propanol and acetic acid. In spite of the similar properties between 2-propanol and acetic acid, we found that the total detection sensitivity for 2-propanol was quite lower than the calculated value, like in the case of ethanol, whereas the total detection sensitivity for acetic acid was in good agreement with the calculated value. Deuterium-labeling studies were then performed and it was concluded that the difference between the experimental and calculated detection sensitivities for 2-propanol was attributed to a reaction channel that reproduced H_3O^+ observed only in reaction (4).

Results and Discussion

Detection Sensitivity for 2-Propanol. Previous studies of the detection of 2-propanol by PTR-MS[11–13] have shown that fragment ions at m/z 43 ($C_3H_7^+$) and 41 ($C_3H_5^+$) are significantly observed compared with the protonated molecule:

$$H_3O^+ + (CH_3)_2CHOH \rightarrow (CH_3)_2CHOH{\cdot}H^+ + H_2O \qquad \Delta H_r^\circ = -102\,\mathrm{kJ\,mol^{-1}} \quad (4a)$$

$$H_3O^+ + (CH_3)_2CHOH \rightarrow C_3H_7^+ + 2H_2O \qquad \Delta H_r^\circ = +10\,\mathrm{kJ\,mol^{-1}} \quad (4b)$$

$$H_3O^+ + (CH_3)_2CHOH \rightarrow C_3H_5^+ + H_2 + 2H_2O \qquad \Delta H_r^\circ = +138\,\mathrm{kJ\,mol^{-1}} \quad (4c)$$

Therefore, in the present work, we measured the ion signals at m/z 61 ($(CH_3)_2CHOH{\cdot}H^+$), 43 ($C_3H_7^+$), and 41 ($C_3H_5^+$). The detection sensitivities determined from these ion signals at five different E/N ratios are summarized in Table 1, where E is the electric field strength (V cm^{-1}) and N is the buffer gas number density (molecule cm^{-3}).

The detection sensitivity for each ion X was defined as the signal intensity of the ion normalized to a H_3O^+ intensity of 10^6 counts per second (cps) when 1 part per billion by volume (ppbv) of the target compound was present in the sample, and the unit for the sensitivity is normalized cps (ncps) ppbv^{-1}. The sum of the detection sensitivities for the three channels represents the total detection sensitivity for 2-propanol (S_{exp}) experimentally determined by PTR-MS at each E/N ratio:

$$S_{\mathrm{exp}}/\mathrm{ncps\,ppbv^{-1}} = \frac{\sum_{\mathrm{X}} i(\mathrm{X})}{i(H_3O^+)\cdot[\mathrm{VOC}]/\mathrm{ppbv}} \times 10^6 \quad (6)$$

where X = $(CH_3)_2CHOH{\cdot}H^+$, $C_3H_7^+$, and $C_3H_5^+$. The calculated detection sensitivity (S_{calc}) can be derived from the rate constant, the reaction time, and eq 3:

$$S_{\mathrm{calc}}/\mathrm{ncps\,ppbv^{-1}} = k \cdot t \times 10^6 \cdot (4.71 \times 10^7) \quad (7)$$

In eq 7, the number density of the sample at 1 ppbv under the the drift tube conditions of 2.1 mbar and 50 °C is 4.71×10^7 molecule cm^{-3}. In Table 1, the reaction times are also listed. Reaction time decreased with increasing E/N because of an increase of the H_3O^+ drift velocity.[5]

As reported previously,[11–13] the branching ratio for channel (4a) was negligibly small even at $E/N = 102$ Townsend (Td), and the branching ratio for channel (4b) was larger than that of the other two channels at the lower E/N ratios (102, 111, and 120 Td). At the higher E/N ratios (129 and 139 Td), the branching ratio for channel (4c) was the largest. In Figure 1, the total detection sensitivity derived from the sum of the values for channels (4a)–(4c) at each E/N ratio is plotted against reaction time. A positive relationship between total detection sensitivity and reaction time was observed. This result is consistent with the relationship in eq 7, which indicates that the total detection sensitivity should be proportional to the reaction time and should intercept the origin.

In Figure 1, the detection sensitivities calculated from the experimentally obtained rate constants for reaction (4) ($2.7 \times 10^{-9}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ from Spanel and Smith[9] and $2.8 \times 10^{-9}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ from Lindinger et al.[1]) are shown as a solid line and a dashed line, respectively. Errors indicated in dark and light gray are the errors in the detection sensitivities, which arise from the typical errors in the rate constants (±20%[14] and ±30%,[1] respectively). The reported theoretically calculated rate constants for reaction (4)[1,7,9] are 2.8, 2.47, and $2.7 \times 10^{-9}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$, and these values are consistent with the experimentally obtained rate constants. When the error limits were taken into consideration, the total detection sensitivity for 2-propanol was quite small compared with the calculated detection sensitivities, which suggests the presence of unidentified channel(s) in reaction (4).

Detection Sensitivity for Acetic Acid. In previous work, a fragment ion at m/z 43 ($CH_3C(O)^+$) was observed in addition to protonated molecules in the detection of acetic acid by PTR-MS:[1,11]

$$H_3O^+ + CH_3C(O)OH \rightarrow CH_3C(O)OH{\cdot}H^+ + H_2O \qquad \Delta H_r^\circ = -93\,\mathrm{kJ\,mol^{-1}} \quad (5a)$$

$$H_3O^+ + CH_3C(O)OH \rightarrow CH_3C(O)^+ + 2H_2O \qquad \Delta H_r^\circ = +13\,\mathrm{kJ\,mol^{-1}} \quad (5b)$$

Therefore, in the present work, we measured the ion signals at m/z 61 ($CH_3C(O)OH{\cdot}H^+$) and 43 ($CH_3C(O)^+$). The detection sensitivities determined from each ion signal at five different

Table 2. Detection Sensitivities/ncps ppbv^{-1} for Each Reaction Channel and E/N Ratios for the $H_3O^+ + CH_3C(O)OH$ Reaction[a)]

(E/N)/Td	102	111	120	129	139
Reaction (5a)	12.4 ± 0.74	11.0 ± 0.66	9.54 ± 0.57	8.38 ± 0.50	7.20 ± 0.43
Reaction (5b)	1.34 ± 0.08	1.31 ± 0.08	1.32 ± 0.08	1.46 ± 0.09	1.89 ± 0.11
Total	13.7 ± 0.7	12.3 ± 0.7	10.9 ± 0.6	9.84 ± 0.51	9.09 ± 0.44

a) Error limits were estimated from the errors in the calibration of the Permeater and include the errors in the diffusion coefficient for acetic acid and in the flow rate.

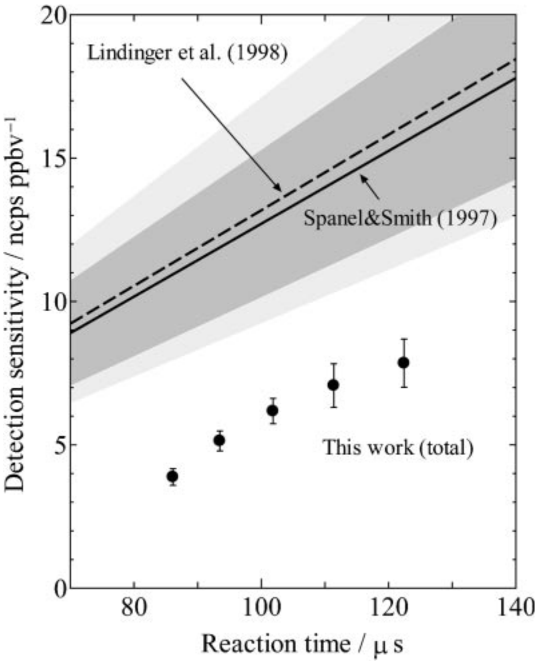

Figure 1. Plots of the total detection sensitivity derived from the sum of the values for channels (4a)–(4c) of the $H_3O^+ + (CH_3)_2CHOH$ reaction against reaction time. The solid and dashed lines show detection sensitivities calculated from experimentally obtained rate constants for reaction (4). Errors indicated in dark and light gray are the errors in the detection sensitivities, which arise from the errors in the rate constants from Spanel and Smith (1997) and Lindinger et al. (1998), respectively.

E/N ratios, as well as the total detection sensitivity for acetic acid, are summarized in Table 2. The branching ratio for channel (5a) was larger than that of the other channel over the entire range of E/N ratios. The relationship between the total detection sensitivity derived from the sum of the values for channels (5a) and (5b) at each E/N ratio and reaction time was linear (Figure 2).

In Figure 2, the detection sensitivity calculated from the experimentally obtained rate constant for reaction (5) ($(3.0 \pm 0.9) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} from Mackay et al.[10] and Lindinger et al.[1]) is shown as a solid line with error limits (gray area). The theoretically obtained rate constants for reaction (5)[1,7,15] are 2.7, 2.27, and 2.6×10^{-9} cm^3 molecule^{-1} s^{-1}, and these values were consistent with the experimentally obtained rate constants. In addition, the total detection sensitivity derived from the sum of the values for channels (5a) and (5b) was in good agreement with the calculated detection sensitivity.

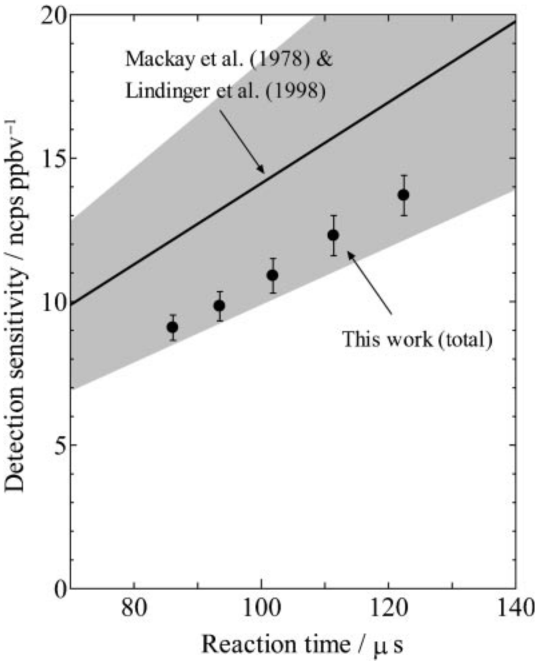

Figure 2. Same as Figure 1, except that the plot is for reaction (5).

Reproduction of H_3O^+. As shown in Figure 1, the total detection sensitivity for 2-propanol was approximately half of the calculated detection sensitivity. We suspected that a reaction channel that reproduced H_3O^+ (reaction (4d)) may have contributed, as is the case for ethanol:[8]

$$H_3O^+ + (CH_3)_2CHOH \rightarrow H_3O^+ + C_3H_6 + H_2O \qquad \Delta H_r^\circ = +51\,\mathrm{kJ\,mol^{-1}} \quad (4d)$$

To verify the presence of channel (4d), we examined the formation of H_2DO^+ ions at m/z 20 in reactions of H_3O^+ with deuterium-labeled 2-propanols ($(CD_3)_2CHOH$ and $(CH_3)_2CDOH$). In contrast to reaction (4), the total detection sensitivity for reaction (5) was in good agreement with the calculated value (Figure 2), which suggests the absence of any additional channels for reaction (5). As a reference, the same experiment was performed for the reaction of H_3O^+ with deuterium-labeled acetic acid ($CD_3C(O)OH$) in order to confirm the absence of a reaction channel that reproduced H_3O^+ for reaction (5).

Figure 3a shows the ion signal of a fragment ion, $(CD_3)_2CH^+$, at m/z 49 (M49) and the ion signal of H_2DO^+ at m/z 20 (M20) before and after the introduction of the

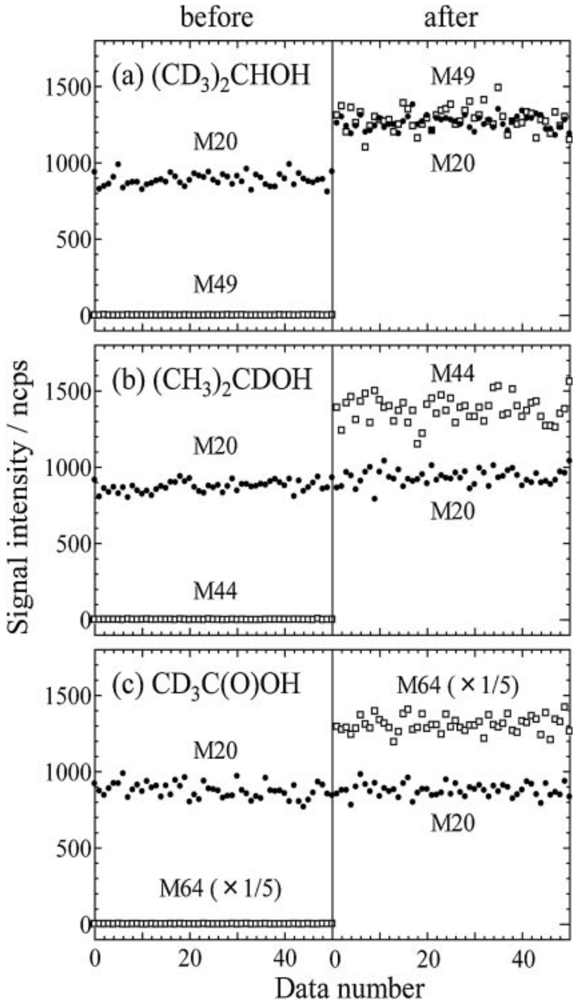

Figure 3. Ion signals of propyl radical ions and H_2DO^+ before and after the introduction of (a) $(CD_3)_2CHOH$ and (b) $(CH_3)_2CDOH$ at $E/N = 139$ Td, (c) ion signals of protonated acetic acid and H_2DO^+ before and after the introduction of $CD_3C(O)OH$ at $E/N = 139$ Td. M20: H_2DO^+, M49: $(CD_3)_2CH^+$, M44: $(CH_3)_2CD^+$, and M64: $CD_3C(O)OH{\cdot}H^+$.

$(CD_3)_2CHOH$ sample at $E/N = 139$ Td. After the sample was introduced, not only did the ion signals of $(CD_3)_2CH^+$ increase, but the ion signal at m/z 20 (M20) also increased, from 887 ± 81 to 1260 ± 93 ncps (Error limits represent 2σ). The background ion signals at m/z 20 were relatively high because of the ion signals from H_2DO^+ and $H_3{}^{17}O^+$, the intensities of which are 0.015% and 0.038% of the intensity of H_3O^+, respectively. Previously, we reported that the extent of H/D exchange between H_3O^+ and ethylbenzene-d_{10} was too small to be observed by PTR-MS.[16] Similarly, the formation of H_2DO^+ was unlikely to have resulted from H/D exchange between H_3O^+ and $(CD_3)_2CHOH$, and instead resulted from the reaction of H_3O^+ with $(CD_3)_2CHOH$. The formation of H_2DO^+ probably proceeds via two steps: (i) A proton transfer occurs to produce protonated $(CD_3)_2CHOH$, in which the proton attaches to an O atom in $(CD_3)_2CHOH$ (reaction (8)). Then, (ii) an H_2DO^+ elimination occurs (reaction (9a)), which competes with an H_2O elimination to produce $(CD_3)_2CH^+$.

$$H_3O^+ + (CD_3)_2CHOH \rightarrow (CD_3)_2CHOH{\cdot}H^+ + H_2O \quad (8)$$

$$(CD_3)_2CHOH{\cdot}H^+ \rightarrow H_2DO^+ + CD_2CHCD_3 \quad (9a)$$

$$(CD_3)_2CHOH{\cdot}H^+ \rightarrow (CD_3)_2CH^+ + H_2O \quad (9b)$$

Similarly, the ion signals of the fragment ion $(CH_3)_2CD^+$ at m/z 44 (M44) and of H_2DO^+ at m/z 20 (M20) before and after the introduction of the $(CH_3)_2CDOH$ sample at $E/N = 139$ Td are shown in Figure 3b. The ion signal of $(CH_3)_2CD^+$ increased after the addition of the sample gas, whereas no significant increase in the ion signal at m/z 20 was observed: 873 ± 71 ncps before compared to 933 ± 99 ncps after:

$$H_3O^+ + (CH_3)_2CDOH \rightarrow (CH_3)_2CDOH{\cdot}H^+ + H_2O \quad (10)$$

$$(CH_3)_2CDOH{\cdot}H^+ \rightarrow H_2DO^+ + C_3H_6 \quad (11a)$$

$$(CH_3)_2CDOH{\cdot}H^+ \rightarrow (CH_3)_2CD^+ + H_2O \quad (11b)$$

This difference likely reflects the fact that abstraction of an H atom from the 1- and 3-positions of protonated 2-propanol to form an H_3O^+ ion is easier than abstraction of an H atom from the 2-position. A similar result was obtained in the fragmentation of protonated ethylbenzene[16] and protonated ethanol.[8]

In contrast to the reaction of the deuterium-labeled 2-propanols, the reaction of H_3O^+ with $CD_3C(O)OH$ did not produce H_2DO^+ even at $E/N = 139$ Td (875 ± 99 ncps before compared to 877 ± 84 ncps after), as shown in Figure 3c. The ion signals of the protonated $CD_3C(O)OH$ at m/z 64 (M64) increased after the introduction of the $CD_3C(O)OH$ sample. Thus, the absence of any additional channels was confirmed for reaction (5). This is consistent with the fact that the total detection sensitivity for reaction (5) was in good agreement with the calculated value.

In conclusion, the reproduction of H_3O^+ in reaction (4) caused the difference between the detection sensitivities of 2-propanol and acetic acid even though the rate constant for reaction (4) is similar to that for reaction (5). As discussed in the previous paper,[8] the branching ratio for channel (4d) determined from the H_2DO^+ signals is possibly underestimated owing to loss processes of H_2DO^+ ions. Therefore, we cannot precisely determine the branching ratio for channel (4d) experimentally. However, since the calculated detection sensitivity was in agreement with the total detection sensitivity summing the detection sensitivities of all reaction channels in the case of acetic acid and product ions other than $(CH_3)_2CHOH{\cdot}H^+$, $C_3H_7{}^+$, and $C_3H_5{}^+$ were not observed in the H_3O^+ + 2-propanol reaction, the unidentified channel for reaction (4) was concluded to be the channel that reproduced H_3O^+ ion (channel (4d)).

Experimental

We used a commercially available PTR-MS instrument (Ionicon Analytik).[1–3,8] Briefly, H_3O^+ ions were produced from a pure water vapor flow of 7.5 standard cubic centimeters per minute (sccm) in a hollow cathode discharge ion source. The sample was introduced into the drift tube, and the drift tube pressure was held at 2.1 mbar. Temperatures of the sampling inlet and the drift tube were held at 80 and 50 °C, respectively. 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, $H_3O^+\cdot(H_2O)_n$ ($n = 1, 2, \ldots$). In the drift tube, trace gases such as VOCs in the sample air were ionized by proton-transfer reactions. 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 quadrupole mass spectrometer was calibrated by the manufacturer.

$(CH_3)_2CHOH$ at mixing ratios of 20–120 ppbv was produced by dynamic dilution of the standard gas (10.55 ppm) with air. A standard gas mixture of $CH_3C(O)OH$/air at 1 ppm by volume (ppmv) was produced with a diffusion tube (Permeater, PD-1B, Gastec). The diffusion coefficient of $CH_3C(O)OH$ was determined in the present study. For the deuterium-labeling study, the Permeater was used to produce the standard gases at 1 ppmv. Ion signals were obtained in multi-ion detection mode at five field strengths of the drift tube, E/N (102, 111, 120, 129, and 139 Td. The count rate of H_3O^+, calculated from the count rate at m/z 21 ($H_3{}^{18}O^+$) multiplied by 500, was $(3–5) \times 10^6$ cps. The ratios of the ion intensity of $H_3O^+\cdot H_2O$ (m/z 37) to that of H_3O^+ were 0.01 at $E/N = 102$ Td and 0.0002 at $E/N = 139$ Td, and the ratio of the ion intensity of $O_2{}^+$ (m/z 32) to that of H_3O^+ was 0.01.

The stated purities and the suppliers of gases and chemicals used were as follows: air, >99.99995% (Japan Fine Products); 2-propanol ($(CH_3)_2CHOH)/N_2$, 10.55 ppm (ppm) (Sumitomo Seika Chemicals); isopropyl-1,1,1,3,3,3-d_6 alcohol, 99.8 atom %D ($(CD_3)_2CHOH$; C/D/N isotopes); isopropyl-2-d_1 alcohol, 99.4 atom %D ($(CH_3)_2CDOH$; C/D/N isotopes); acetic acid, >99.99% (Sigma-Aldrich); and acetic 2,2,2-d_3 acid, 99.5 atom %D ($CD_3C(O)OH$; C/D/N isotopes).

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