

Functional group analysis of gas-phase oxidation products of α -pinene using HR-CID-MS: The effects of oxidants

*Daisuke Fukuyama¹, Kanako Sekimoto¹

1. Yokohama City University

Introduction

Forests emit large quantities of monoterpenes ($C_{10}H_{16}$), especially α -pinene, into the atmosphere. It can be converted to multifunctional highly oxygenated molecules (HOM) by ozone (O_3), hydroxyl radicals, and NO_3 radicals. The resulting oxidation products are significantly involved in secondary organic aerosols (SOA) formation that affect the Earth's radiation balance [Ehn et al., *Nature*, 2014]. In addition, structural analysis of oxidation products of monoterpene is important in atmospheric chemistry because SOA production efficiency strongly depends on functional groups of oxidation products [Atkinson et al., *Atmos. Environ.*, 1995].

There have been many reports on the estimated structures of the oxidation products of α -pinene using mass spectrometry, but most of these analyses have used "nominal mass". Therefore, it has been difficult to distinguish oxidation products with the same nominal mass but different elemental compositions (e.g., $C_9H_{14}O_3$ and $C_{10}H_{18}O_2$ with nominal mass 170), the detailed analysis has hardly been done.

In this study, we investigated the functional groups of the unknown oxidation products of α -pinene by using an atmospheric pressure corona discharge ionization mass spectrometry (APCDI-MS) which is similar to atmospheric pressure chemical ionization mass spectrometry (APCI-MS) [Sekimoto et al., *Eur. Phys. J. D.*, 2010] and high-resolution collision-induced dissociation (HR-CID) method.

Results and Discussion

In this study, standard products of α -pinene oxidation products were measured before the analysis of actual oxidation products for investigating the relationship between functional groups and dissociated neutral species from oxidation products by CID. As an example, the results of a CID experiment for pinonic acid are shown in Figure 1. When the deprotonated molecules of pinonic acid were dissociated, the most dominant CO_2 loss, medium intensity for the neutral loss of C_2H_2O and minor neutral loss of H_2O were detected. These losses were derived from the respective functional groups, CO_2 loss corresponding to the carboxyl group, H_2O loss to the hydroxy group within the carboxyl group, and C_2H_2O loss corresponding to the acetyl group. Other standards were measured under the same conditions, and a relationship was found between the functional group and the neutral loss (Figure 2).

Based on Figure 2, the functional groups of the actual unknown oxidation products of α -pinene were analyzed qualitatively. In this presentation, the discussion focuses on $[C_{10}H_{16}O_4-H]^-$ at m/z 199 under the different oxidation conditions. The losses of neutral species suggesting the presence of functional groups and their percentages were different under the three oxidation conditions (Figure 3). The loss of C_2H_2O , suggesting the presence of acetyl groups, was detected under conditions where O_3 was the oxidant, however, it was not detected under the other conditions. On the other hand, the loss of H_2O_2 was not detected, suggesting the presence of peroxy groups under this condition. It was found that O_3 is likely to form oxidation products with acetyl groups and unlikely to form oxidation products with peroxy groups.

Keywords: Monoterpene, Oxidation reaction, Functional group, HR-CID-MS

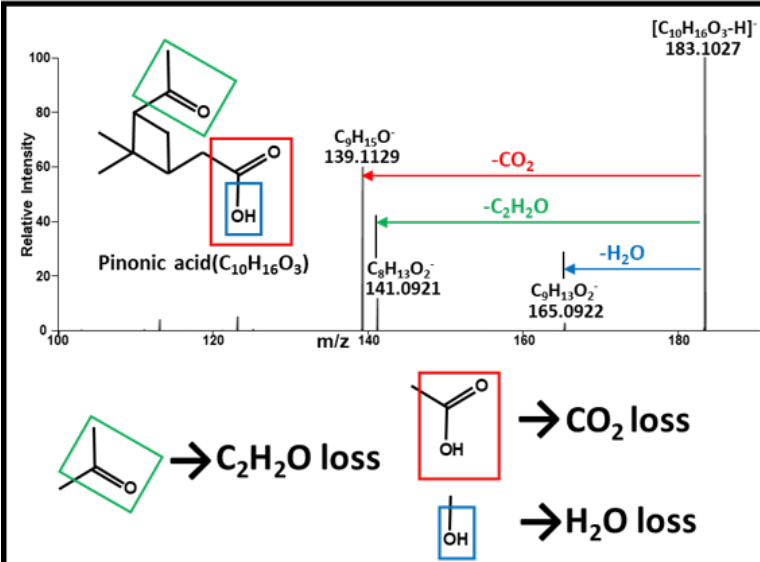


Figure 1 CID spectrum of deprotonated molecule of pinonic acid $[C_{10}H_{16}O_3-H]^-$.

Functional group		Neutral loss
R-COOH	R-COOH	HCOOH(CO+H ₂ O)
	R-COO ⁻	CO ₂
R-CHO	R-CHO	CO
	R-C=O	-
R-OH	R-OH	H ₂ O
	R-O ⁻	-
R-COCH ₃	R-COCH ₃	C ₂ H ₂ O
	R-CO ⁻ CH ₂	-
R-OOH	R-OOH	H ₂ O ₂
	R-OO ⁻	-
R-CO-R'	R-CO-R	CO
	R=CO ⁻ -R'	-

Figure 2 Relationship between the functional group and the neutral loss by CID.

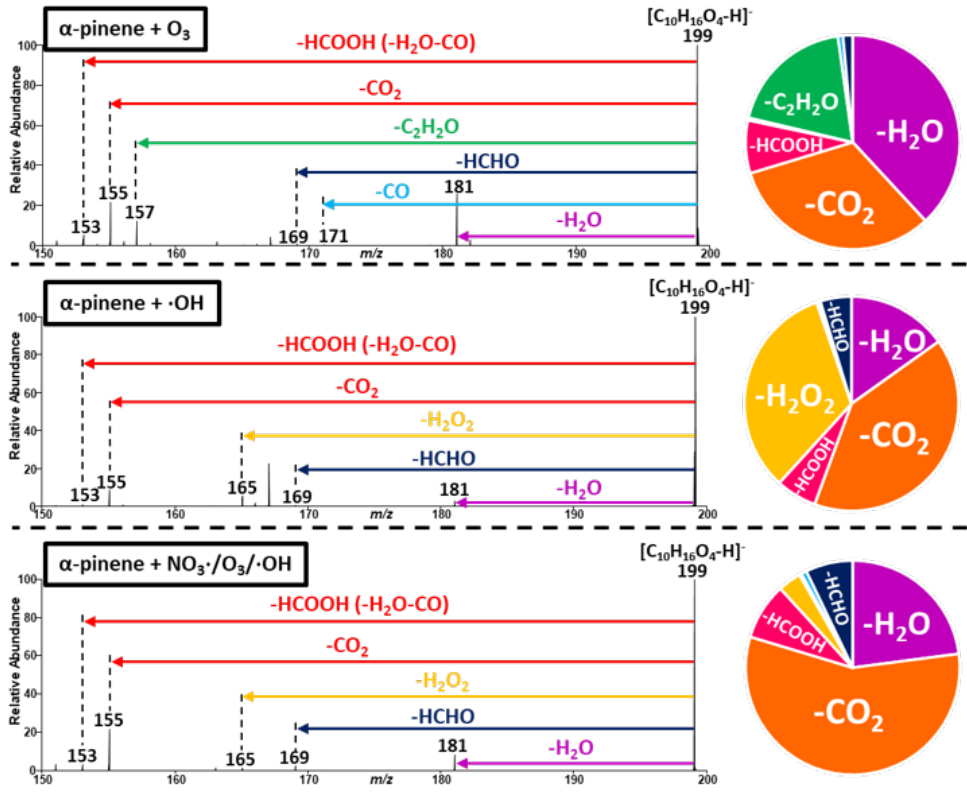


Figure 3 CID spectra of deprotonated molecules of oxidation products of α -pinene $[C_{10}H_{16}O_4-H]^-$ under the different oxidation conditions and the ratio of the ion intensity of losses of neutral species.