Negative Ion Chemical Ionization Mass Spectra of C_1–C_6 *n*-Alkyl Nitrates

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Negative ion chemical ionization mass spectra were examined for C_1–C_6 *n*-alkyl nitrates. In contrast to peroxyacyl nitrates, NO_3^- ions were minor fragments. Major fragment ions were found to be NO_2^-, and $[RO - H_2]^-$, alkoxy counterparts from which two hydrogen atoms were eliminated. Relative intensity of the two fragment ions largely depends on the speciation, and the $[RO - H_2]^-/NO_2^-$ ratio increases with the increasing carbon number.

Alkyl nitrates ($RONO_2$) are produced in sequential oxidation processes of non-methane hydrocarbons (NMHCs) in the presence of nitrogen oxides (NO_x) in air. They are formed in the reaction of alkyl peroxy radicals (RO_2) with nitric oxide (NO), followed by rearrangement of nitroxy group. This reaction acts as a sink of NO_x and RO_2, and hence contributes to terminate photochemical ozone (O_3) formation. $RONO_2$ are transported in the long-range due to their relatively long atmospheric lifetime (days–weeks), and redistribute NO_x in remote regions.[1] Since $RONO_2$ are present in the atmosphere only on the order of parts per trillion per volume (pptv) levels, accurate and precise measurements require challenging instrumentation.

Gas chromatography/electron capture detection (GC/ECD) has often been used to measure $RONO_2$ because of its high sensitivity to large electron affinity (EA) compounds.[2–5] However, ECD is sensitive to other trace gases including peroxyacyl nitrates (PANs, $RC(O)OONO_2$) and halogenated hydrocarbons in the atmosphere.[6] Accordingly well-designed separation of interfering compounds by GC columns is needed to identify and quantify $RONO_2$ in air samples.[7]

Negative ion chemical ionization mass spectrometry (NI-CIMS) is potentially a powerful technique to detect organic nitrates at trace levels, as it is not only sensitive to high EA compounds but also more selective than ECD with the selected ion monitoring detection. Indeed GC/NI-CIMS was used to measure $RONO_2$ in the atmosphere.[8,9] Our previous paper reported that methyl and *i*-propyl nitrates showed large NO_2^- (mass-to-charge ratio, $m/z = 46$) fragments, while PANs produced both NO_2^- and NO_3^- ($m/z = 62$) fragments.[10] Similar fragmentation patterns in the NICI mass spectra of $RONO_2$ were reported in other studies.[8,9] However, there is little quantitative information, including dependence on carbon chain length and/or isomeric structures of $RONO_2$, which may facilitate more sensitive and selective detection of $RONO_2$ with GC/NI-CIMS. We report here fragmentation patterns in the NICI mass spectra of C_1–C_6 *n*-$RONO_2$ in a systematic manner.

Methyl and ethyl nitrates were synthesized by the reaction of methanol and ethanol, respectively, with a mixture of concentrated nitric acid and sulfuric acid (1:1).[11,12] Propyl, butyl, pentyl, and hexyl nitrates were synthesized by the reaction of alkyl bromides with silver nitrate dissolved in acetonitrile.[13] All chemicals used for the syntheses were reagent grade (Wako Pure Chemical Industries, and Kanto Chemical). A portion of liquid $RONO_2$ ($\approx 10\,\mu L$) was vaporized and diluted with ultra-high pure nitrogen (purity $\approx 99.9995\%$, Nippon Sanso) to the ambient pressure in a 1-L vacuum glass bottle. These procedures resulted in $RONO_2$ concentrations of 10–100 parts per million by volume (ppmv). The NICI scheme used in this study was based on electron attachment ionization with methane (CH_4) as a reagent gas, and the instrument used is a Hewlett Packard model 5890/5989A. Detailed description of the analytical setup has been published elsewhere.[10]

Figure 1 shows NICI mass spectra of C_1–C_6 *n*-$RONO_2$. It is apparent that NO_2^- fragments are common for all homologues,

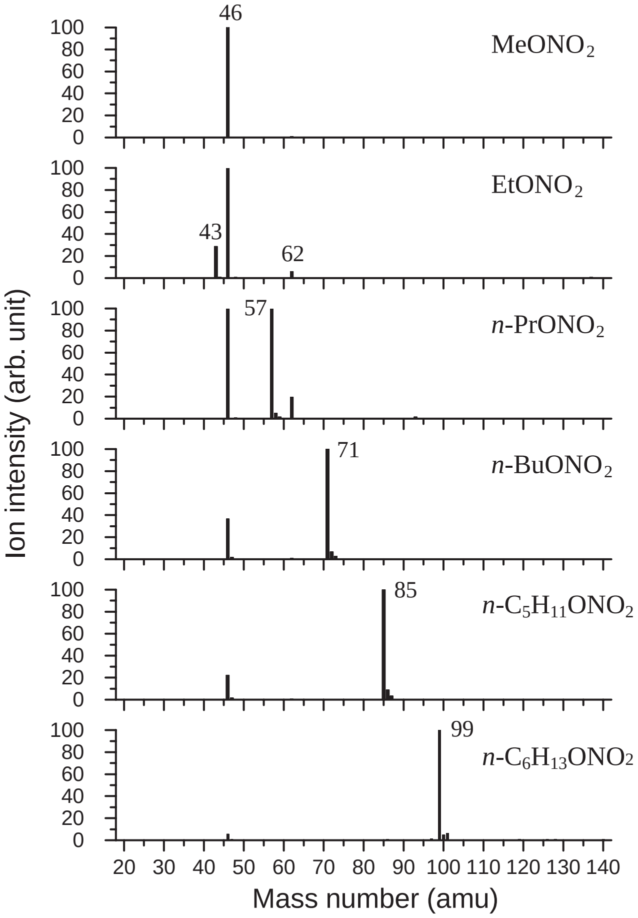

Figure 1. Negative ion chemical ionization mass spectra of C_1–C_6 *n*-alkyl nitrates. The mass spectra were obtained in the scan mode with a range of 10–150 amu. Ion intensity is normalized to adjust the maximum intensity mass number as 100%.

while their intensity largely varies depending on compounds. The relative intensity decreases with the increasing carbon number. It is also found that NO_3^- ions are very minor fragments. They are usually negligible ($<1\%$) except for ethyl and *n*-propyl nitrate showing approximately 6 and 20% abundances against NO_2^-. This fragmentation pattern is very different from that of PANs, which shows stronger intensity at NO_3^- than at NO_2^-.[10] The differences in the fragmentation patterns of $RONO_2 + e^-$ reactions from those of $PAN + e^-$ reactions would be related to the differences in reaction enthalpies giving NO_2^- and NO_3^- fragments, which are comparable in case of $RONO_2$, and much more exothermic for NO_3^- than NO_2^- channel in case of PANs.[14]

Also clearly visible is that C_2–C_6 *n*-$RONO_2$ produce fragment ions whose mass numbers are dependent on the compounds. The mass number of these fragment ions are expressed as $m/z = 43 + (n - 2) \times 14$, where n denotes the carbon number of C_2–C_6 *n*-$RONO_2$. These fragments were considered to be $[RO - H_2]^-$ ions, which are formed via elimination of two hydrogen atoms. The formation of $[RO - H_2]^-$ ions was also observed in $RONO + e^-$ reactions,[15] suggesting the elimination of molecular hydrogen from activated RO^- (RO^{-*}) as a mechanism producing $[RO - H_2]^-$ (e.g., Eqs 1 and 2).[16]

$$CH_3CH_2ONO + e^- \rightarrow (CH_3CH_2O^-)^* + NO, \qquad (1)$$

$$(CH_3CH_2O^-)^* \rightarrow CH_2CHO^- + H_2. \qquad (2)$$

However, RO^- ions, which were observed as primary fragments in the electron attachment reactions to RONO,[15] were not found in the NICI mass spectra of *n*-$RONO_2$. Hence, $[RO - H_2]^-$ ions from *n*-$RONO_2$ might be formed by different reaction mechanisms.

Figure 1 shows another interesting feature; i.e., as the carbon number increases, the relative intensity of NO_2^- decreases, and that of $[RO - H_2]^-$ increases accordingly. Relative abundance of $[RO - H_2]^-$ against NO_2^- as a function of the carbon number of *n*-$RONO_2$ is illustrated in Figure 2. The $[RO - H_2]^-/([RO - H_2]^- + NO_2^-)$ ratio systematically increases as the carbon number increases. The ratio is only ≈ 0.22 for ethyl nitrate, but as high as ≈ 0.95 for *n*-hexyl nitrate.

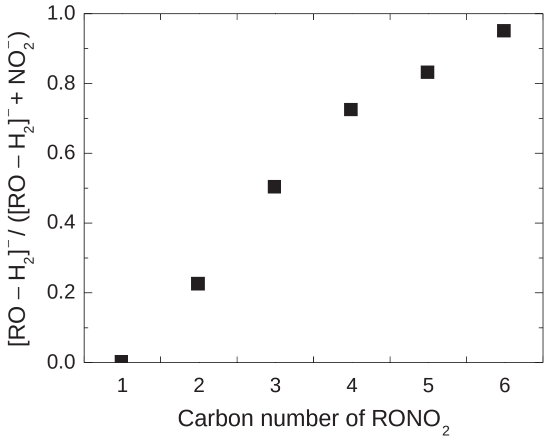

Figure 2. Dependence of the $[RO - H_2]^-/([RO - H_2]^- + NO_2^-)$ ratio on the carbon number of C_1–C_6 *n*-alkyl nitrates. Symbol size denotes a standard deviation of 5 measurements.

To summarize, the following fragmentation patterns are possible for the NICI scheme applied in this study:

$$\begin{aligned} RONO_2 + e^- &\rightarrow R + ONO_2^-, && (3)\\ &\rightarrow RO^- + NO_2, && (4)\\ &\rightarrow RO + NO_2^-, && (5)\\ &\rightarrow [RO - H_2]^- + \text{other products}. && (6) \end{aligned}$$

Eqs 3 and 4 are minor paths as described in detail above. Eqs 5 and 6 are major pathways, and likely compete with each other. Theoretical calculations are desired to better explain the mechanisms of the fragmentation patterns of *n*-$RONO_2$ observed in this study.

These findings would have a potential importance to improve overall signal-to-noise ratio (high signal and/or low noise) and selectivity by choosing appropriate fragment ions for the measurements of $RONO_2$ in ambient air.

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