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The Atmospheric Fate of C_3-C_6 Hydroxyalkyl Nitrates

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Rate coefficients for the reaction of OH radical with eleven C_3-C_6 hydroxyalkyl nitrates and with two C_4 hydroxy nitrates containing a double bond were determined at atmospheric pressure and 296 ± 2 K. The rate coefficients were measured in a photochemical reactor by the relative rate technique, employing solid-phase microextraction (SPME) coupled to gas chromatography (GC) for detection of the organic reactants. Hydroxyalkyl nitrates react faster than alkyl nitrates with the OH radical. The rate coefficients increase with increasing chain length and separation between the hydroxy and the nitrooxy groups. By including different loss processes such as photolysis, gas-phase reactions, and solubility, the tropospheric lifetime of C_3-C_6 hydroxyalkyl nitrates is estimated to range between 0.5 and 4.5 days. Due to their higher reactivity and solubility, hydroxyalkyl nitrates have a shorter atmospheric lifetime than alkyl nitrates.

Introduction

Organic nitrates are an important component of the tropospheric reactive odd nitrogen (NOy) budget. These reservoir species participate in the long-range transport and distribution of nitrogen oxides ($NOx = NO + NO_2$) to the remote troposphere.[1−5] Organic nitrates form during the atmospheric photodegradation of hydrocarbons in the presence of nitrogen oxides through reactions of peroxy alkyl radicals (RO_2) with NO. Initial oxidation of alkanes and alkenes produces peroxy radicals that further react with nitrogen oxides to produce alkyl nitrates.[1,6−8] Nitrate formation is a rather minor channel in the $RO_2 + NO$ reaction, increasing in importance with the increasing size of the RO_2 radical.[7,9] Ozone formation and distribution in remote areas are controlled by the distribution of the reactive nitrogen in the troposphere.[1,10−12] Because the formation of alkyl nitrates competes with the ozone production by sequestering both nitrogen oxides and organic radicals, a detailed understanding of alkyl nitrate abundance, formation, and loss mechanisms is needed.

Small alkyl nitrates (C_1-C_4) have been measured in the marine atmosphere.[5,13−15] It was recently suggested that alkyl nitrates may form in seawater in a photochemical mechanism analogous to the one occurring in the polluted atmosphere.[16] An additional potential source for alkyl nitrates is biomass burning.[17] Emissions of five C_1-C_4 alkyl nitrates from Australian savanna fires, with maximum alkyl nitrate mixing ratios ranging from 130 to 3300 pptv relative to local background levels (ranging from 0.3 to 5.4 pptv), have been reported.[17] Whereas alkyl nitrates are typically $<10\%$ of NOy within continental air masses,[10,18,19] they comprise a major component (20−80%) of NOy over the Pacific Ocean (∼50 pptv averaged alkyl nitrate sum)[20−22] and Greenland (∼34 pptv maximum in winter).[23] Alkyl nitrates have been detected over the Atlantic Ocean,[24] the Southern Ocean,[21] and the coastal Antarctic.[25,26]

Hydroxyalkyl nitrates, which are multifunctional organic nitrates, may comprise a large fraction of the nitrate reservoir species. They form during the atmospheric photodegradation of alkanes and alkenes via several different pathways. In addition to reactions of NO with peroxy radicals, some of the formation channels include isomerization processes.[9] The β-hydroxyalkyl nitrates form primarily during the oxidation of alkenes by OH radicals.[27−29] The yield of hydroxyalkyl nitrate formation increases with the size of the precursor alkene from 1% for ethene to 6% for 1-hexene.[27,29] δ-Hydroxyalkyl nitrates form via a 1,5-H shift of alkoxy radicals following the reactions of OH radical with long-chain ($\geq C_4$) *n*-alkanes.[9,30−33] Pathways leading to the formation of γ-hydroxyalkyl nitrates in the atmosphere could involve NO_3 reactions with unsaturated alcohols such as 2-methyl-3-buten-2-ol that form γ-hydroxyalkyl nitrates.[34] Isoprene nitrates form in high yield by OH insertion into one of isoprene's double bonds followed by reactions with O_2 and NO of the resulting radical.[8] Model calculations suggested that isoprene nitrates may be important sinks for NOx in rural environments.[3,4] However, field measurements in a low NOx environment suggest that isoprene nitrates' contribution to NOy may be lower.[35,36] Although the organic nitrate formation yield is small for short *n*-alkanes,[7] high emissions rates of their precursors in urban and rural environments can lead to significant production of the corresponding alkyl and hydroxyalkyl nitrates.

Some hydroxyalkyl nitrates have been measured in the atmosphere; C_2-C_4 β-hydroxyalkyl nitrates have been identified and estimated to account for ∼15% of the total atmospheric organic nitrates.[37,38] C_3-C_5 β-hydroxyalkyl nitrates in the low pptv range have been measured in marine air[39] at about 10% of their urban concentrations.[37,38] Nineteen different C_2-C_6 β-hydroxyalkyl nitrates have been identified in urban smog, and the sum levels of seven C_2-C_4 hydroxyalkyl nitrates ranged from 7.0 to 28 pptv in one study.[40] The mixing ratio sum of six C_2-C_4 hydroxyalkyl nitrates in Antarctica was in the range 0.2−1.1 pptv.[26] The large number of hydroxyalkyl nitrates that can form and the lack of standards for their identification have precluded their more detailed measurement.

Due to the role that hydroxyalkyl nitrates may play in transport of reactive nitrogen in the troposphere, a detailed understanding of their atmospheric removal pathways is needed for an accurate assessment of their overall atmospheric lifetime.

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The main atmospheric loss processes for hydroxyalkyl nitrates can be photolysis, gas-phase reactions with OH, Cl, and NO_3 radicals, and heterogeneous loss processes. Previous experiments have focused on the solubility of hydroxyalkyl nitrates in aqueous and organic phases.[28,41−43] While the kinetics of the gas-phase reactions of the hydroxyl radical (OH), the primary atmospheric oxidant, with alkyl mononitrates and alkyl dinitrates have been studied by several researchers,[11,44−46] little is known about the kinetics of the OH radical reaction with hydroxyalkyl nitrates. To our knowledge, only the reaction of the OH radical with a β-type hydroxy cyclopentyl nitrate has so far been studied.[47] In addition, the gas-phase kinetics of β-, γ-, and δ-hydroxyalkyl nitrates with Cl atoms have been reported.[48]

In this article we present a kinetic study of the rate coefficients for the gas-phase reactions of OH radical with a series of β-, γ-, and δ-hydroxyalkyl nitrates of atmospheric interest at atmospheric pressure and a temperature of 296 ± 2 K. This is the first time in which hydroxyalkyl nitrates containing a double bond were synthesized and investigated. These hydroxyalkyl nitrates are proxies to compounds that may form during the photochemical degradation of isoprene. We also investigate the reaction mechanisms involved by probing the effect of the hydroxyalkyl nitrates' chemical structure on their reactivity. With this new information, an overall estimation of hydroxyalkyl nitrates' atmospheric lifetime can be made. The experiments described here employ a relative rate technique, combined with solid-phase microextraction (SPME) sampling and analysis by GC equipped with an electron capture detector (ECD). The SPME technique is fast, sensitive, selective, solvent-free, and easy to use.[49,50] This method has only recently been applied to gas-phase kinetic studies.[51,52] For comparison reasons, we extend the experiment to other classes of organic nitrates, the alkyl dinitrates and alkyl mononitrates.

Experimental Section

Chemicals and Materials. The kinetic experiments were conducted using the following compounds. Hydroxyalkyl nitrates: 2-nitrooxy-1-propanol, 1-nitrooxy-2-propanol, 2-nitrooxy-1-butanol, 1-nitrooxy-2-butanol, 3-nitrooxy-1-butanol, 4-nitrooxy-2-butanol, 4-nitrooxy-1-butanol, 1-nitrooxy-2-butanol-3-ene, 4-nitrooxy-1-butanol-2-ene, 2-nitrooxy-1-pentanol, 1-nitrooxy-2-pentanol, 4-nitrooxy-1-pentanol, 5-nitrooxy-2-pentanol, and 6-nitrooxy-1-hexanol. Alkyl dinitrate: 1,4-butyl dinitrate. Alkyl nitrate: 1-pentyl nitrate. Reference compounds: 1-pentanol and 1-octanol. For simplicity, the nomenclature introduced by Schneider and Ballschmiter[53] for multifunctional nitrates will be used in this paper: $1OH2C_3$, $2OH1C_3$, $1OH2C_4$, $2OH1C_4$, $1OH3C_4$, $2OH4C_4$, $1OH4C_4$, 2OH1C4-3-ene, 1OH4C4-2-ene, $1OH2C_5$, $2OH1C_5$, $1OH4C_5$, $2OH5C_5$, $1OH6C_6$, $1,4C_4$, and $1C_5$, respectively. For clarification, Figure 1 shows the hydroxyalkyl nitrates and alkyl dinitrate and alkyl mononitrate studied and their shorthand notation.

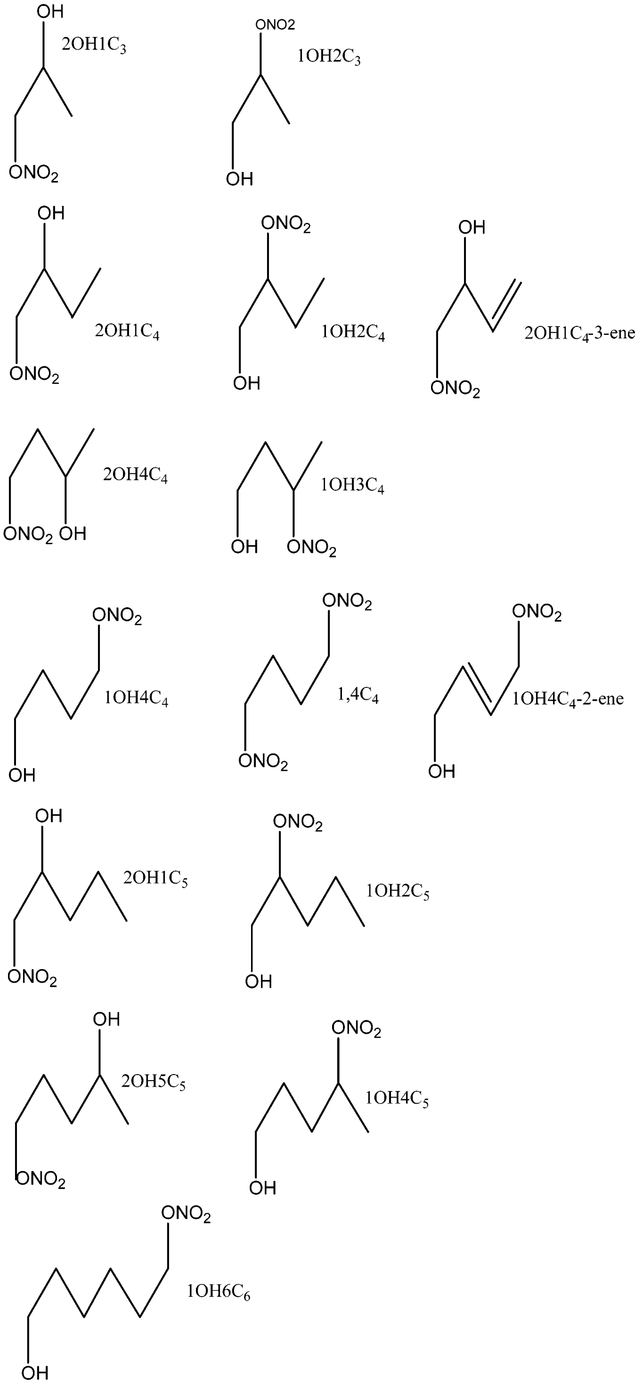

Figure 1. Structure of the studied compounds and their shorthand notation introduced by Schneider and Ballschmiter.[53] Note that $1OH4C_4$-2-ene is a mixture of both cis and trans isomers.

The hydroxyalkyl nitrates, including double-bond hydroxyalkyl nitrates, were all (except $1OH6C_6$) synthesized by selective nitration of the parent diols or epoxides. They were purified (>98%) and characterized according to the previously developed procedures.[41,54,55] $1OH6C_6$ was synthesized by nitration of (iodohexoxy)-*tert*-butyldimethylsilane by silver nitrate.[48] This reaction occurs via two steps: a replacement of the halogen atom by a nitrooxy group, while the *tert*-butyldimethylsilane tail blocks the hydroxy group. Following the nitration, the protecting group is removed by hydrolysis.

1,4-Butyl dinitrate and 1-pentyl nitrate were prepared via nitration of the parent 1,4-butanediol and 1-pentanol, respectively, by fuming HNO_3 and H_2SO_4 in dichloromethane.[56] 1-Octanol and 1-pentanol were respectively obtained from Fluka and Sigma-Aldrich. They were of chromatographic grade and were used without further purification.

The diluent gas used in the kinetic experiments was extra dry synthetic air (>99.999%). NO (>99.999%) was used without purification. Methyl nitrite and ethyl nitrite were prepared and stored as described by Atkinson et al.[57]

The SPME fiber used for sampling was Stableflex poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB, 65 μm coating thickness).[42] The fibers were conditioned inside the GC injector port for 30 min at 260 °C before use.

Reference Compounds. 1-Pentanol and 1-octanol were chosen as reference compounds since their rate coefficients for

OH reactions are well known. The rate coefficients of 1-pentanol and 1-octanol at 296 K are $k_{OH} = (1.12 \pm 0.15) \times 10^{-11}$ and $k_{OH} = (1.44 \pm 0.15) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively.[58,59] It was verified that these compounds do not photolyze or stick to the walls of the reaction chamber. No chromatographic interference between the retention times of these alcohols and the hydroxyalkyl nitrates was observed under the conditions employed.

Experimental Procedure. The experimental setup used in the present work has been described previously[48] and will be discussed briefly here. Kinetic experiments were carried out at 296 ± 2 K in 1 atm of synthetic air using a collapsible 100 L PVF-film (Tedlar) reaction chamber (SKC Inc.). The reaction bag was equipped with three inlets positioned at its upper, central, and lower sections. It was homogeneously surrounded by 20 UV fluorescent lamps (Philips TL 40W/05, $300 \leq \lambda \leq 460$ nm; $\lambda_{max} = 365$ nm). The irradiation time was controlled by a digital timer. An electric fan was positioned on top of the reactor chamber to maintain a uniform reaction temperature during irradiation periods.

Known amounts of the hydroxyalkyl nitrates and the reference compounds were injected as liquids through a septum into evacuated Pyrex bulbs. Methyl nitrite and NO were introduced into other evacuated Pyrex bulbs. The bulbs were then connected in series to the reaction chamber, at the upper and lower inlets, alternatively; to ensure good mixing, the reactants were flushed into the chamber by a stream of the bath gas. The reaction chamber was filled with synthetic air to 100 L. The reactants in the chamber were left in the dark to homogenize for ~30 min, prior to UV irradiation. Following the stabilization time, the chamber was irradiated for short periods (usually 30 s to 2 min) to produce OH radicals and initiate the reaction. Between each irradiation period, two SPME samples were taken.

OH radicals were generated by the photolysis of methyl nitrite or ethyl nitrite, at wavelengths > 300 nm, in the presence of NO.[57] The photolysis occurs via cleavage of the RO−NO bond:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \quad (1)$$

followed by subsequent reactions that produce the radicals:

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \quad (2)$$

$$HO_2 + NO \rightarrow NO_2 + OH \quad (3)$$

Excess NO was added to suppress the formation of ozone and of NO_3,[57] as well as to ensure that all the peroxy radicals produced reacted only with NO.

The typical initial concentrations of the reactant mixture were as follows (molecule cm^{-3}): hydroxyalkyl nitrates, dinitrate, and alkyl nitrate, $(2-6) \times 10^{13}$; methyl nitrite and ethyl nitrite, $(1-3) \times 10^{15}$; NO, $(4-9) \times 10^{14}$; and 1-pentanol and 1-octanol (the reference compounds), $(1-3) \times 10^{14}$. Following each experiment, the reaction chamber was cleaned by successive cycles of filling it with nitrogen (>99.999%) and pumping. The cycle was repeated until no nitrates were detected by SPME sampling.

Analytical Procedure. The decay of the organic nitrates due to reaction with OH radicals was monitored and quantitatively analyzed by a Varian Star 3800 GC, equipped with an electron capture detector (ECD). Data acquisition and processing was performed using the STAR software (Varian). Helium (99.999%) was used as the carrier gas at a flow rate of 1 cm^3 min^{-1}. Nitrogen (99.999%) was used as the makeup gas at a flow rate of 30 cm^3 min^{-1}. The ECD was kept at 300 °C. The injector was maintained at 200 °C. A DB5-MS capillary column was used for all experiments (30 m × 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific). The initial oven temperature was set to 80 °C for 2 min, ramped to 280 °C at a rate of 10 °C min^{-1}, and maintained at that temperature for 2 min. These conditions resulted in sharp and distinct peaks with no coelution problems, overlapping of the other reactants, nor products present in the reaction chamber.

Each compound's retention time was determined by direct injection of a liquid solution to the GC. Stock solutions of each compound in methanol were prepared. Typically, 5 mg was added to 1 mL of methanol, and the solutions were diluted in case of saturation of the detector response. The retention times were the same for the direct liquid and the SPME injections.

SPME Sampling Procedure. The gas-phase sampling using SPME allows for simultaneous sampling of both the hydroxyalkyl nitrates and the reference compounds. SPME sampling is a multiphase equilibration process that involves partitioning of the analyte between the gas phase and the SPME fiber. Traditionally, SPME sampling is considered complete when the analyte concentration has reached equilibrium between the gas phase and the fiber. However, to save time and make the sampling practical and rapid, it was found[60−63] that the sampling can take place prior to establishing equilibrium, provided that the SPME sampling conditions are held constant (temperature, sampling time, and the sample volume). Thus, such nonequilibrium conditions were employed in this study. Optimization and validation of the SPME sampling conditions were performed as has been described previously.[42]

For sampling, the SPME fiber was inserted into the reaction chamber, through a septum positioned at its center, to a constant depth of 1 cm. The fiber was exposed to the gas mixture for 30 s, which is less than the time required for reaching fiber−gas equilibrium (about 20 min). After sampling, the fiber was inserted into the GC injector for 30 s for thermal desorption, followed by chromatographic separation and quantification. Under these conditions, the SPME-GC response was linear with the concentration. No carryover was observed for any of the compounds upon a second injection, indicating a complete recovery from the fibers. The fiber was used immediately after desorption for the next sampling.

Measurement of the Rate Coefficients by the Relative Rate Method. The rate coefficients for the OH reactions were determined using a relative rate technique, which has been extensively described in the literature.[7,64,65] Briefly, the underlying principle of this method is to measure the decay rate of the selected hydroxyalkyl nitrate (HN) relative to a reference compound (1-pentanol and 1-octanol, alcohols, in this study (ROH)), whose OH radical reaction rate coefficient is known.

In the presence of OH radicals, the reactant hydroxyalkyl nitrate and the reference compound decay via reactions 3 and 4:

$$HN + OH \xrightarrow{k_{HN}} products \quad (3)$$

$$ROH + OH \xrightarrow{k_{ROH}} products \quad (4)$$

where k_{HN} and k_{ROH} are the rate coefficients for reactions 3 and 4, respectively. Provided that both reactants are removed solely by the reaction with OH radicals and that they do not re-form in the reaction chamber (see validation section), the following relation is obtained:

$$\ln\left(\frac{[HN]_0}{[HN]_t}\right) = \left(\frac{k_{HN}}{k_{ROH}}\right) \ln\left(\frac{[ROH]_0}{[ROH]_t}\right) \quad (I)$$

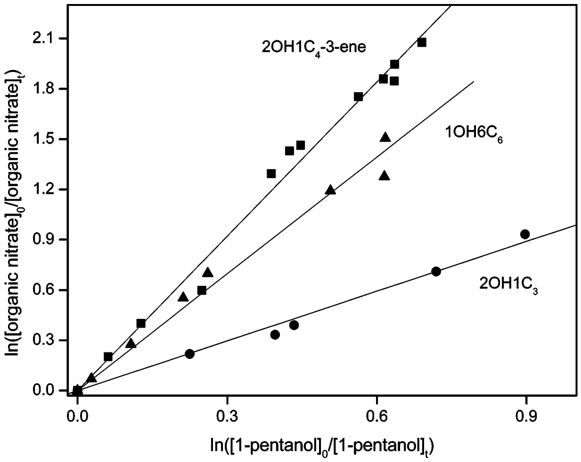

Figure 2. Relative rate plots for the gas-phase reactions of OH radicals with $2OH1C_3$, $1OH6C_6$, and $2OH1C_4$-3-ene at 296 ± 2 K and atmospheric pressure. 1-Pentanol is used as the reference compound.

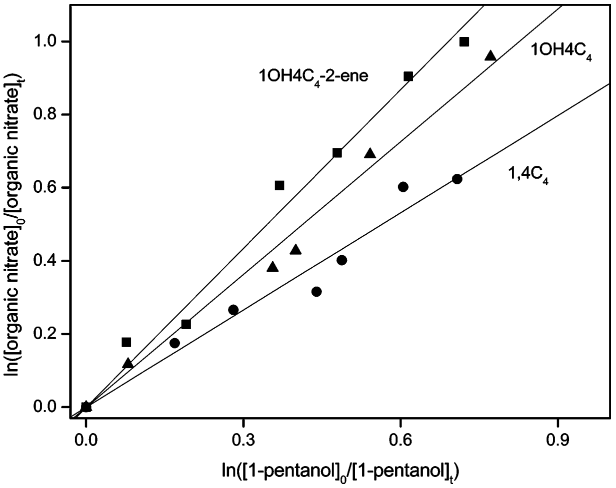

Figure 3. Relative rate plots for the gas-phase reactions of OH radicals with $1,4C_4$, $1OH4C_4$, and $1OH4C_4$-2-ene at 296 ± 2 K and atmospheric pressure. 1-Pentanol is used as the reference compound.

where $[HN]_0$ and $[ROH]_0$, and $[HN]_t$ and $[ROH]_t$, are the concentrations of the selected hydroxyalkyl nitrate and the reference compound at the beginning of the experiment and at time t, respectively. A plot of $\ln([HN]_0/[HN]_t)$ against $\ln([ROH]_0/[ROH]_t)$ yields a straight line with a slope equal to the ratio of the rate coefficients, k_{HN}/k_R, and with zero intercept. Given the known value of k_{ROH}, the value of k_{HN} may be calculated.

Results

The data obtained from the OH radical reactions with the hydroxyalkyl nitrates are plotted in accordance with eq I. Typical relative rate plots for $2OH1C_3$, $1OH6C_6$, and $2OH1C_4$-3-ene are shown in Figure 2 and for $1,4C_4$, $1OH4C_4$, and $1OH4C_4$-2-ene in Figure 3 (both figures use 1-pentanol as a reference compound). Very good linear correlations are obtained, with linear correlation coefficients (r) that are always higher than 0.98 for all compounds. The slopes of the plots were obtained by least-squares fit of the entire set of data. In all cases, the least-squares intercepts of the plots are within two standard deviations of zero. Each data point on the curves represents an inaccuracy of less than 20%. These errors result mostly from the precision of sampling and the manual injection.

TABLE 1: Measured (95% confidence level) and Calculated Rate Coefficients for the Reactions of OH Radical with C_3-C_6 Hydroxyalkyl Nitrates, Alkyl Nitrate, and Alkyl Dinitrate at 296 ± 2 K and Atmospheric Pressure[a]

compound[b]	k_{OH} ($\times 10^{-11}$) (measd)[c] (cm^3 molecule^{-1} s^{-1})	k_{OH} ($\times 10^{-11}$) (calcd)[d] (cm^3 molecule^{-1} s^{-1})	ratio
$1OH2C_3$	0.67 ± 0.13	1.27 ± 0.25	1.9
$2OH1C_3$	0.51 ± 0.10	2.07 ± 0.41	4.1
$1OH2C_4$	0.74 ± 0.15	1.28 ± 0.26	1.7
$2OH1C_4$	0.70 ± 0.14	4.22 ± 0.84	6.0
$1OH3C_4$	1.19 ± 0.46	4.08 ± 0.82	3.4
$2OH4C_4$	1.04 ± 0.40	7.73 ± 1.55	7.2
$1OH4C_4$	1.26 ± 0.25	6.73 ± 1.35	5.4
$1OH4C_4$-2-ene	2.20 ± 0.44	48.1 ± 9.62	21.9
$2OH1C_4$-3-ene	3.62 ± 0.72	43.4 ± 8.68	12.0
$2OH1C_5$	0.98 ± 0.19	5.93 ± 1.19	6.1
$1OH4C_5$	2.86 ± 0.57	6.81 ± 1.36	2.4
$2OH5C_5$	3.21 ± 0.64	10.7 ± 2.13	3.3
$1OH6C_6$	3.09 ± 0.61	9.56 ± 1.91	3.1
$1C_5$	0.49 ± 0.09	3.00 ± 0.60	6.3
$1,4C_4$	0.63 ± 0.13	0.55 ± 0.11	0.9

[a] Three to six experiments were performed for each compound. The values presented for the measured OH rate coefficients are averages of those experiments. [b] For simplicity, the nomenclature introduced by Schneider and Ballschmiter[53] for multifunctional nitrates is used in Table 2. [c] The rate coefficients, k_{OH}, are calculated according to eq I, using the following rate coefficients for the reference compounds: $k_{OH} = (1.12 \pm 0.15) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for 1-pentanol; $k_{OH} = (1.44 \pm 0.15) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for 1-octanol.[58] [d] Calculated according to the estimation method proposed by Kwok and Atkinson.[73]

The slopes of the relative rate plots have been placed on an absolute basis using the following rate coefficients for the reference compounds: $k_{OH} = (1.12 \pm 0.15) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for 1-pentanol; $k_{OH} = (1.44 \pm 0.15) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for 1-octanol.[58,59] The resulting values of k_{OH} for the hydroxyalkyl nitrates, alkyl nitrate, and dinitrate are presented in Table 1 and in a schematic form in Figure 4 together with literature values for the corresponding alkyl nitrates, alkanes, alkenes, alcohols, and alkyl dinitrates.[44−46,58,66−69] The errors quoted in Table 1 reflect the accuracy of the measurements and include statistical uncertainties of the averaged values and an additional 15% uncertainty to account for estimated overall uncertainties in the reference compounds' rate coefficients. The estimated overall errors of the rate coefficients of the compounds studied here are less than 20%.

As the ratios of the concentrations are used in the relative rate calculation (see eq I), peak areas are used directly instead of absolute concentrations. A linear relationship was observed between the amount of reactants extracted by the SPME fiber and their initial concentrations in the reaction chamber for all the compounds studied here. The linearity between the chromatographic response and the concentrations of the compounds was confirmed over 3 orders of magnitude.

Discussion

Validation of the Experimental System, Procedure, and Measurements. A series of control experiments were performed to verify that both the reactants and the reference compounds are removed solely by the reaction with OH radicals. Wall losses as well as dark reactions were found to be insignificant (~10^{-4} s^{-1} as compared to the measured reactive loss rates of ~10^2 s^{-1}) by allowing the reactants, reference compounds, and the OH radical precursors to stay in the dark in the reaction chamber for 2 h. In addition, it was confirmed that under the experimental conditions employed, the organic nitrates are photochemically stable. Secondary reactions were not significant, as is inferred by the good linearity of the relative rate plots and the fact that the fit lines pass through the origin (shown in Figures 1 and 2).

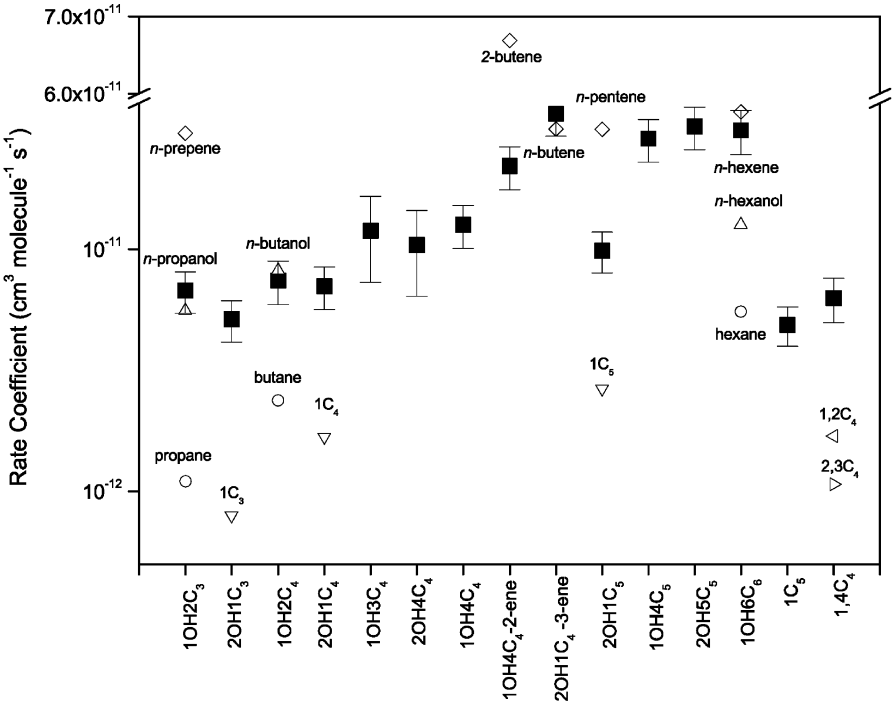

Figure 4. The OH radical rate coefficients for reactions with hydroxyalkyl nitrates, alkyl nitrate and dinitrate, and a comparison with the corresponding rate coefficients for alkyl nitrates, alkanes, alkenes, alcohols and alkyl dinitrates. Averaged values are taken in case of more than one literature value. Note the break in the Y-axis. Hydroxyalkyl nitrates, alkyl nitrate and dinitrate studied here (solid square); alkyl nitrates (down triangles); alkanes (open circles); alkenes (diamond); alcohols (top triangles); $2,3C_4$ alkyl dinitrate (right open triangles); $1,2C_4$ alkyl dinitrate (left open triangles).[44−46,58,66,67,69]

Finally, no coelution problems between the reactants, reference, and oxidation products are observed under the gas chromatography conditions employed.

The reproducibility of the measurements was excellent: variation between repeated SPME samplings was less than 10%. In general, uniform conditions were employed in all the experiments, as mentioned in the Experimental Section. It was verified that the rate coefficients obtained were independent of the initial concentrations of the reactants, which were varied over 3 orders of magnitude, the diluent gas (either dry air or nitrogen), the reference compounds, the light intensity (obtained by varying the number of the fluorescent lamps that were operated, although usually all 20 lamps were on for the experiments), and the photolysis time.

To our knowledge, this is the first study of OH radical reaction with straight chain hydroxyalkyl nitrates. The rate coefficient for the reaction of a β-type hydroxy cyclopentyl nitrate with OH was previously measured to be $k_{OH} = (3.82 \pm 0.19) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[47] A comparison with our observed values of k_{OH} for β-type C_3-C_5 hydroxyalkyl nitrates (Table 1) suggests that the rate coefficients for the straight hydroxyalkyl nitrates are higher but within the same order of magnitude. This might be explained by the higher availability to the OH radical attack of the H atoms attached to a straight alkyl chain than H atoms attached to a stressed alkyl ring structure.

Since the reactions of multifunctional organic nitrates with OH radicals have not yet been investigated, a comparison with literature values is not possible. Instead, we used two reference compounds (1-pentanol and 1-octanol) in each experiment as an intercalibration to validate our results. For each experiment the relative rate plots for the two reference compounds were plotted one against the other, providing their relative loss rate ($r > 0.99$). Their observed rate coefficients with the OH radical were compared to the literature values, and excellent agreement was found between them, indicating that the experimental system and procedure are valid and can be used to determine OH radical rate coefficients with the various hydroxyalkyl nitrates and dinitrate. In addition, the intercalibration check implies that choosing either of the references does not influence the results.

OH Radical Rate Coefficients. The primary reaction path of the electrophilic OH radical reaction with alkanes is believed to proceed via H atom abstraction from the C−H bonds.[59] The OH−alkenes reaction proceeds by OH addition to the double bond.[59,70,71] Due to the differences in the reaction mechanisms, a separate discussion regarding the relationship between the structure and the reactivity of the hydroxyalkyl nitrates will be devoted to the nitrates containing an alkene backbone.

The OH and ONO_2 groups have opposing effects on the rate coefficients of hydroxyalkyl nitrates with the OH radical, and therefore the two structural parameters that determine the reactivity are the length of the hydrocarbon chain and the separation between the hydroxy and the nitrooxy groups. In the following section we discuss the contribution of each of these structural elements to the overall reactivity of the hydroxyalkyl nitrates.

1. Effect of the OH Group. The hydroxy group significantly enhances the reactivity of hydroxyalkyl nitrates toward the OH radical, as compared to the corresponding alkyl nitrates and alkyl dinitrates. This is most vividly demonstrated for C_5 nitrates, as shown in Table 1 and Figure 4. The k_{OH} for the $2OH1C_5$ is $(9.86 \pm 1.96) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, which is higher than $(4.87 \pm 0.98) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, measured for 1-pentyl nitrate (Table 1 and Figure 4). The rate coefficient measured here for 1-pentyl nitrate ($(4.87 \pm 0.98) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) is higher than those previously measured by Nielsen et al.[44] and Becker and Wirtz:[45] $(3.3 \pm 0.30) \times 10^{-12}$ and $(2.5 \pm 0.09) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, respectively.

Moreover, k_{OH} for 2OH1C$_3$ is (5.13 ± 0.31) × 10^{-12} cm^3 molecule^{-1} s^{-1} (Table 1), as compared to k_{OH} for 1-propyl nitrate, which is (7.95 ± 0.80) × 10^{-13} cm^3 molecule^{-1} s^{-1}.[44] k_{OH} for 2OH1C$_4$ is (7.02 ± 0.14) × 10^{-12} cm^3 molecule^{-1} s^{-1}, whereas k_{OH} for 1-butyl nitrate is (1.68 ± 0.13) × 10^{-12} cm^3 molecule^{-1} s^{-1} .[44]

This trend is similar to the one observed for OH−alcohol reactions. Nelson et al.[58] observed that alcohols are more reactive than the corresponding alkanes due to lowering of the C−H bond dissociation energies for a carbon bound to a hydroxy group by about 4−5 kcal mol^{-1}, thus facilitating the hydrogen abstraction.[58] This tendency is also similar to the one observed for the reactions of OH radical with small alcohols, which is explained by the more labile hydrogen atom in the α position relative to the OH group.[58,59] However, since most of the reaction proceeds via H atom abstraction from the C−H bond, the effect for alcohols is expected to decrease for larger alcohols.[58,59] Accordingly, k_{OH} for 1-propanol is (5.57 ± 0.46) × 10^{-12} cm^3 molecule^{-1} s^{-1},[58] whereas k_{OH} for *n*-propane is (1.10 ± 0.07) × 10^{-12} cm^3 molecule^{-1} s^{-1}.[66−68] k_{OH} for 1-butanol is (8.18 ± 0.45) × 10^{-12} cm^3 molecule^{-1} s^{-1},[58] whereas k_{OH} for *n*-butane is (2.37 ± 0.07) × 10^{-12} cm^3 molecule^{-1} s^{-1}.[66−68] k_{OH} for 1-hexanol is (1.26 ± 0.18) × 10^{-11} cm^3 molecule^{-1} s^{-1},[58] whereas k_{OH} for *n*-hexane is × (5.52 ± 0.09) × 10^{-12} cm^3 molecule^{-1} s^{-1} [67] (see Figure 4).

2. Effect of the Nitrooxy Group. The presence of the nitrooxy group decreases the OH radical reactivity of the hydroxyalkyl nitrates relative to the corresponding unsubstituted alkanes. This behavior is attributed to the nitrooxy group's strong electron-withdrawing nature that exhibits long-range electronic effects to the extent that might influence the reactivity of C−H bonds that are not directly adjacent.[72] Within the C$_4$ organic nitrates, the OH radical reactivity toward 1,4C$_4$ (alkyl dinitrate) is the lowest due to the presence of a second nitrooxy group. It is about 50% lower than the OH atom reactivity toward the corresponding 1OH4C$_4$ hydroxyalkyl nitrates (see Figures 3 and 4). The OH rate coefficients for reactions with other dinitrates are also slow:[46] (1.69 ± 0.32) × 10^{-12} and (1.07 ± 0.26) × 10^{-12} cm^3 molecule^{-1} s^{-1} for 1,2C$_4$ and 2,3C$_4$ alkyl dinitrate, respectively (see Figure 4). The rate coefficient for the 1,4C$_4$ is higher ((6.28 ± 0.13) × 10^{-12} cm^3 molecule^{-1} s^{-1}), probably due to a larger separation between the bulky nitrooxy groups, in line with the observed trend for hydroxyalkyl nitrates (see below).

3. Effect of Chain Length. For the same separation between the hydroxy and the nitrooxy groups, there is an increase in the OH radical reactivity with the increase in the alkyl chain length. This trend is apparent in Table 1 and in Figure 4; the addition of CH$_2$ groups to the alkyl chain enhances the overall reactivity because of lowering of the C−H bond dissociation energies. Hence, the rate coefficients of β-hydroxyalkyl nitrates increase in the order C$_3$ β-hydroxyalkyl nitrate (1OH2C$_3$; 2OH1C$_3$) < C$_4$ β-hydroxyalkyl nitrate (1OH2C$_4$; 2OH1C$_4$) < C$_5$ β-hydroxyalkyl nitrate (1OH2C$_5$; 2OH1C$_5$). For δ-hydroxyalkyl nitrates, C$_4$ (1OH4C$_4$) < C$_5$ (1OH4C$_5$; 2OH5C$_5$).

4. Effect of Separation between the OH and Nitrooxy Groups. For hydroxyalkyl nitrates with the same chain length, the rate coefficients increase with increasing separation between the hydroxy and the nitrooxy groups. This effect is attributed to the decreasing effect of the nitrooxy group that at close separations overwhelms the enhancement effect of the hydroxy group. Therefore, the rate coefficients for the OH radical toward C$_4$ hydroxyalkyl nitrate decrease in the order δ-hydroxyalkyl nitrate (1OH4C$_4$) > γ-hydroxyalkyl nitrate (1OH3C$_4$; 2OH4C$_4$) > β-hydroxyalkyl nitrate (1OH2C$_4$; 2OH1C$_4$). 1OH6C$_6$, the longest hydroxyalkyl nitrate studied here, has the largest separation between the two functional groups and the highest rate coefficient (except of 2OH5C$_5$). This suggests that the long 1OH6C$_6$ can bend or even form a cyclic configuration of the six membered alkyl chain. Such a configuration could slow the OH radical reaction (see Figure 1 and Table 1). However, calculations of the structure of hydroxyalkyl nitrates should be performed before such conclusions can be drawn. Finally, there is little difference between the OH radical reactivity toward the two isomers (for example, 1OH2C$_4$ and 2OH1C$_4$) of the hydroxyalkyl nitrates.

5. Reaction of Hydroxynalkyl Nitrates Containing Double Bonds. In general, OH−alkene reactions are very fast.[71] OH addition to a double bond is fast, and the OH and ONO2 groups play a limited role in determining the reaction rate coefficients. As can be seen from Figures 2 and 3 and Table 1, OH radicals are highly reactive toward the hydroxyalkyl nitrates containing a double bond. We observe that the rate coefficient for 2OH1C$_4$-3-ene is higher than that of 1OH4C$_4$-2-ene. We suggest that the higher reactivity of 2OH1C$_4$-3-ene can be attributed to a double bond that is not hindered by the functional groups, and therefore this species reacts faster. In addition, in 2OH1C$_4$-3-ene the double bond is further away from the ONO$_2$ group. The comparison of the C$_4$ hydroxyalkyl nitrates containing a double bond to alkenes (Figure 4) reveals that the OH radical rate coefficient of 2OH1C$_4$-3-ene is similar to that of the corresponding 1-butene.[58] These rate coefficients are also similar to those of C$_3$−C$_6$ *n*-alkenes (∼3 × 10^{-11} cm^3 molecule^{-1} s^{-1})[58] (Figure 4). The OH radical rate coefficient of 1OH4C$_4$-2-ene is lower than that of the corresponding 2-butene (in cm^3 molecule^{-1} s^{-1}): (2.2 ± 0.44) × 10^{-11} and (6.69 ± 0.53) × 10^{-11}, respectively.

The rate coefficients measured in this study can be compared with those predicted using the structure−reactivity estimation method proposed by Kwok and Atkinson.[73] As shown in Table 1, the calculated rate coefficients for hydroxyalkyl nitrates are overestimated by factors ranging between 2 and 21 compared with the measured ones. A similar mismatch between the experimentally derived and the structure−reactivity calculated OH radical rate coefficients for organic nitrates was also observed by Neeb.[72] The shortcoming of the estimation methods for this class of compounds probably results from the opposing effects that the nitrooxy and OH groups have on the reactivity and the lack of previous experimental data on this class of compounds.

To summarize, the differences between the rate coefficients for OH reactions with the various hydroxyalkyl nitrates are not very large, but they show distinct structure-dependence behavior.

Atmospheric Implications

The main atmospheric sinks of the hydroxyalkyl nitrates are assumed to be gas-phase reactions with OH, Cl, and NO$_3$ radicals, photolysis, and heterogeneous loss processes: partitioning into organic aerosols and wet deposition. Reactions with the NO$_3$ radical are considered slow loss processes for the hydroxyalkyl nitrates.[1,71]

Photolysis. The photolysis of the hydroxyalkyl nitrates is estimated to be a slow reaction on the basis of a few available measurements of absorption cross sections for alkyl nitrates,[74−78] for (nitrooxy)ethanol,[75] and for hydroxy cyclopentyl nitrate.[47] Hydroxy cycloapentyl nitrate has no absorption in the atmospheric actinic region,[47] and the cross section of (nitrooxy)-ethanol is approximately a factor of 3 lower than that of methyl

TABLE 2: Henry's Law Coefficients (*H*), Wet Deposition Rate Coefficients (k_{wd}), Octanol−Air Partition Coefficients (k_{OA}), Rate Coefficients for the Reactions of Cl Atoms (k_{Cl}) and OH Radicals (k_{OH}), the Corresponding Lifetimes (τ_{wd}, τ_{Cl}, and τ_{OH}, respectively), and the Overall Global Daily Tropospheric Lifetimes (τ) for Various C$_3$−C$_6$ Hydroxyalkyl Nitrates

compound[a]	H ($\times 10^3$)[b] (Matm^{-1})	k_{wd} ($\times 10^{-6}$)[c] (s^{-1})	τ_{wd} (days)	K_{OA}[d] ($\times 10^4$)	k_{Cl} (10^{-10})[e] (cm^3 molecule^{-1} s^{-1})	τ_{Cl} (days)	k_{OH} (10^{-11})[e] (cm^3 molecule^{-1} s^{-1})	τ_{OH} (days)	τ_{total}[f] (days)
1OH2C$_3$					0.42	275.6	0.67	3.4	3.4
2OH1C$_3$					0.45	257.2	0.51	4.5	4.4
1OH2C$_4$	8.9	1.70	6.8		0.98	118.1	0.74	3.1	1.1
2OH1C$_4$	9.0	1.70	6.8	68	0.87	133.0	0.70	3.3	1.1
1OH3C$_4$	14.0	2.40	4.8		1.39	83.3	1.19	1.9	1.1
2OH4C$_4$	13.6	2.40	4.8	170	1.40	82.7	1.04	2.2	1.1
1OH4C$_4$	29.0	4.00	2.9	810	1.82	63.6	1.26	1.8	1.2
1OH4C$_4$-2-ene							2.20	1.0	1.1
2OH1C$_4$-3-ene							3.62	0.6	0.6
2OH1C$_5$					1.25	92.6	0.98	2.4	2.3
1OH4C$_5$	20.5	3.20	3.6		1.56	74.2	2.86	0.8	0.6
2OH5C$_5$	36.7	4.50	2.6	340	2.05	56.5	3.21	0.7	0.6
1OH6C$_6$					2.44	47.4	3.09	0.8	0.7

[a] For simplicity, the nomenclature introduced by Schneider and Ballschmiter[53] for multifunctional nitrates is used in the table. [b] The Henry's law coefficient, *H*, is defined as $H = ([X]/P_x)$, where [X] is the aqueous phase concentration (molar) and P_x is the partial pressure (atm). [c] The first-order removal constant by wet deposition, k_{wd}, is given by[82] $k_{wd} = (R_r E e^{(-z/Z_x)}/Z_x[(HRT)^{-1} + L_{wc}))$ where R_r is the assumed annual rainfall rate (1 m yr^{-1}), *E* is an enhancement factor due to droplet evaporation (assumed to be 1.33[82]), *z* is a characteristic height for clouds (assumed to be 3.5 km), Z_x is the scale height for the species (assumed to be 2.2 km[82]), L_{wc} is the dimensionless liquid water content of the cloud (4.2×10^{-7}), and *H* is the Henry's law constant. [d] K_{OA} is the octanol−air partition coefficient: $K_{OA} = (C_O/C_A)$ where C_O and C_A are the concentrations of the organic matter in octanol and in air, respectively. K_{OA} is dimensionless.[42] [e] k_{Cl} and k_{OH} are calculated according to eq I (see Experimental Section). [f] Tropospheric lifetimes for hydroxyalkyl nitrates were calculated using the relationship $\tau_{total} = (k_{wd} + k_{Cl}[Cl] + k_{OH}[OH])^{-1}$; assuming Cl concentration of $\sim 10^3$ atom cm^{-3} [71,83,84] and OH concentration of 5×10^5 radical cm^{-3}.[71,85]

nitrate at 300 nm.[75] Assuming that saturated hydroxyalkyl nitrates have lower photolysis rate coefficients than the alkyl nitrates ($J \approx 1 \times 10^{-6}$ s^{-1}, 30° N, summer, overhead ozone abundance of 305 DU for a U.S. standard atmosphere[77]) and have the same quantum yield (unity), the photolytic lifetime of small hydroxyalkyl nitrates is estimated to be about 12 days. With increasing chain length, the photolytic lifetime may be a little shorter, as is the trend for alkyl nitrates. Consequently, photolysis is probably an insignificant removal pathway for the hydroxyalkyl nitrates.

Solubility. Since hydroxyalkyl nitrates contain the polar OH group, they can efficiently partition into liquid water and organic aerosol. Using the previously measured Henry's law coefficients (*H*) of C$_3$−C$_6$ hydroxyalkyl nitrates,[28,41] the wet deposition rate coefficients (k_{wd}) and the corresponding lifetimes (τ_{wd}) have been estimated and are presented in Table 2. The high solubility in water implies that hydroxyalkyl nitrates would significantly dissolve in atmospheric cloud water. They can also dissolve in fog droplets. Wet deposition also represents a net sink. The wet deposition lifetime for hydroxyalkyl nitrates is 2−7 days, depending on the species (Table 2). This is in contrast to alkyl nitrates, where heterogeneous processes are not expected to play a significant role in their atmospheric removal.[1,28,47]

Hydroxyalkyl nitrates, which have intermediate volatility,[79] can be removed from the atmosphere by incorporation into aerosols with high organic content, which are expected to be found in rural and urban environments. Their octanol−air partition coefficients (K_{OA})[42] (see Table 2) suggest that a substantial fraction of the longer chain hydroxyalkyl nitrates may reside in the organic aerosols, especially at low temperatures and high aerosol loading.

Reactions with Cl Atoms. Reactions of hydroxyalkyl nitrates with Cl atoms, although fast, may not be globally important.[48] Since the global tropospheric concentration of Cl atoms is much lower than within the marine boundary layer ($\sim 10^2$ to 10^5 atom cm^{-3} [71,80,81]), the lifetime due to reaction of hydroxyalkyl nitrates with Cl atoms is in the range of 47 days for 1OH6C$_6$ to 276 days for 1OH2C$_3$ (taking an average Cl concentration of $\sim 10^3$ atom cm^{-3}). Even so, gas-phase reactions of hydroxyalkyl nitrates with Cl atoms may be a significant loss process, mainly for the larger hydroxyalkyl nitrates, in particular in the marine boundary layer, at peak concentration of Cl atoms.

Reactions with the OH Radical. A comparison of the gas-phase rate coefficients of the hydroxyalkyl nitrates with Cl atoms[48] and OH radicals (current work) reveals that the former reaction is faster than the later reaction by a factor of ∼10. However, since the atmospheric abundance of OH radicals is at least 2 orders of magnitude greater than that of chlorine atoms, the removal of hydroxyalkyl nitrates in the troposphere will be dominated by the reaction with OH radicals. On the basis of the rate coefficients determined in this study, the atmospheric lifetimes of the investigated hydroxyalkyl nitrates, with respect to their removal by reaction with OH radicals, are derived assuming an ambient 24 h average OH concentration of 5×10^5 radicals cm^{-3}.[71] These calculations are presented in Table 2. The estimated tropospheric lifetimes of the hydroxyalkyl nitrates, with respect to their removal via reaction with OH radicals, are in the range of 0.7 day for 2OH5C$_5$ to 4.5 days for 2OH1C$_3$ (Table 2). 1-Pentyl nitrate and 1,4C$_4$ dinitrate lifetimes are in the range of the less reactive hydroxyalkyl nitrates: 4.7 and 3.7 days, respectively. It should be pointed out that the actual tropospheric lifetimes may be slightly longer than those calculated here since the OH radical rate coefficients at the typical tropospheric temperature of 277 K are expected to be smaller than those at 296 K for reactions of saturated compounds. The OH radical rate coefficients measured and the corresponding lifetimes derived from them (see Table 2) demonstrate that gas-phase reaction with OH radicals is globally the major loss process for the short ($<$C$_6$) hydroxyalkyl nitrates.

Conclusions. The overall global daily atmospheric lifetimes of the hydroxyalkyl nitrates due to heterogeneous loss processes and gas-phase reactions are estimated to be in the range of a few hours to a few days (Table 2). It is found that the dominant atmospheric loss process for the hydroxyalkyl nitrates is the gas-phase reaction with the OH radical. Partition into cloud droplets and organic aerosols may also be significant at times. Our laboratory studies on the atmospheric fate of hydroxyalkyl nitrates show that the presence of the OH group has two significant effects on hydroxyalkyl nitrates' atmospheric lifetime: it increases their solubility in water and enables them to react faster with the OH radical compared with the corresponding alkyl nitrates or dinitrates. This implies that hydroxyalkyl nitrates will be removed faster from the atmosphere due to reaction with the OH radical and by wet deposition than alkyl nitrates. As a result, hydroxyalkyl nitrates will be less efficient for long-range transport of nitrogen oxides in the troposphere, compared with alkyl nitrates and dinitrates.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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