

# Henry's Law Constants of Some $\beta$ -, $\gamma$ -, and $\delta$ -Hydroxy Alkyl Nitrates of Atmospheric Interest

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Organic nitrates form via the photodegradation of hydrocarbons in the troposphere in the presence of NO and NO<sub>2</sub>. This process competes with the chemical cycle leading to ozone production since it sequesters both nitrogen oxides and organic radicals. Hydroxy nitrates form via the atmospheric reactions of alkanes and alkenes and are thought to be an important nitrogen oxides reservoir. In this study, new synthetic methods to produce  $\beta$ -,  $\gamma$ -, and  $\delta$ -hydroxy nitrates of atmospheric interest were developed. NMR and IR spectroscopies were used to characterize these compounds. Henry's law coefficients of C<sub>4</sub> and C<sub>5</sub> hydroxy nitrates at 291 ± 2 K were measured using a dynamic equilibrium system. The solubility decreases with the organic chain length and increases with increasing distance between the nitrooxy and hydroxy groups. Due to their large Henry's law coefficients these species will partition into droplets in the presence of clouds and fogs. Measurements of the OH reaction and photolysis rate coefficients are needed for an accurate assessment of the atmospheric lifetimes of these compounds.

## Introduction

It has been well established that together with transport from the stratosphere, photochemistry is the most important source of ozone in the lower troposphere (1–5). Global background levels of tropospheric ozone have increased over the past three decades (5) showing large regional differences during the last two decades (6). Because of its strong correlation with air quality, a detailed understanding of tropospheric ozone formation is needed. Tropospheric ozone is produced via a complex series of photochemical reactions, in which volatile organic compounds (VOC) are consumed (7), and nitrogen oxides act as catalysts (8). While VOC can be emitted by both anthropogenic and biogenic sources, the majority of NO and NO<sub>2</sub> (=NO<sub>x</sub>) is a byproduct of anthropogenic activity. Though NO<sub>x</sub> has a short atmospheric lifetime, some byproducts of the ozone formation cycle, such as alkyl nitrates, are longer lived. Long-range transport of these species to regions remote from the original pollution source and their subsequent decomposition to give NO<sub>x</sub> will influence regional and global tropospheric ozone production.

Formation of ozone in the troposphere involves reactions of organic peroxy radicals and NO:



However, a fraction of this reaction proceeds via organic nitrate formation



The yield of nitrate formation is a function of the hydrocarbon chain length. For primary alkanes, it varies from 8% for *n*-butane to 33% for *n*-octane (9). Reaction 2 is a radical recombination step leading to NO<sub>x</sub> sequestration in stable compounds and therefore terminates the ozone production cycle as opposed to reaction 1. Organic nitrates could have an impact on the global NO<sub>x</sub> distribution since some of these species are long-lived and can undergo long-range transport (10). Alkyl nitrates can be used as a measure of air mass age (11, 12), and measurements of PAN-type compounds may be used to differentiate between anthropogenic and natural sources of trace gases in an air mass (13). It has been postulated that organic nitrates might constitute the unidentified fraction of reactive nitrogen in atmospheric measurements (14).

The photochemical degradation of anthropogenic and natural hydrocarbons can lead to the formation of organic nitrates that contain more than one functional group, one example being the hydroxy nitrates. Several pathways for their formation exist. For example,  $\beta$ -alkoxy radicals that form in the OH initiated degradation of alkenes are the precursors for  $\beta$ -hydroxy nitrates (15, 16). The yield of  $\beta$ -hydroxy nitrates from alkene reactions increases with the size of the precursor alkene, although it is lower than alkyl nitrates formation from reactions of alkanes of similar size (15). Another mechanism for hydroxy nitrates formation is via alkoxy radicals produced in the OH-initiated photochemical degradation of alkanes. These alkoxy radicals can react with O<sub>2</sub>, unimolecularly decompose, or isomerize via an H shift involving five- and six-membered ring transition states (17–21). Alkoxy radical isomerization in the OH radical initiated reactions of C<sub>4</sub>–C<sub>8</sub> *n*-alkanes and of alkenes has recently been demonstrated (18–22). The ratio between the isomerization and reaction with O<sub>2</sub> is dependent on the chain length and varies between 0.04 for the *n*-butane to 50 for the *n*-octane. The 1,5-H shift of the alkoxy radicals can lead to the formation of  $\delta$ -hydroxy nitrates. Eberhard et al. (20) showed that the 1,4-H shift is insignificant, probably because the five-membered ring intermediate is not as stable as the six-membered transition state of the 1,5-H shift. Therefore, it is most likely that  $\gamma$ -hydroxy nitrates do not form via this pathway. In Figure 1 the reactions of the 1-butyl alkoxy radical, including the pathway leading to 4-nitrooxy-1-butanol (a  $\delta$ -hydroxy nitrate), is shown. Although the ratio for nitrate formation is small for short *n*-alkanes (9), their high flux in the urban atmosphere may result in high mixing ratios for the corresponding nitrates.

Pathways leading to the formation of  $\gamma$ -hydroxy nitrates in the atmosphere are not well-known. One mechanism involves reactions of unsaturated alcohols with the nitrate radical. For example, the reaction of 2-methyl-3-butene-2-ol (a recently identified emission from vegetation (23, 24)) with NO<sub>3</sub> leads to the formation of various multifunctional nitrates in total yield of ~50% (25). One of the degradation pathways results in formation of a nitrate with hydroxy and nitrooxy groups in a  $\gamma$  position.

Although there is a general understanding that hydroxy nitrates form in the atmosphere, not many observations exist (26–28). Detection of hydroxy nitrates is difficult due to their low vapor pressure and high solubility. Their identification is also hard due to the lack of readily available standards (16,

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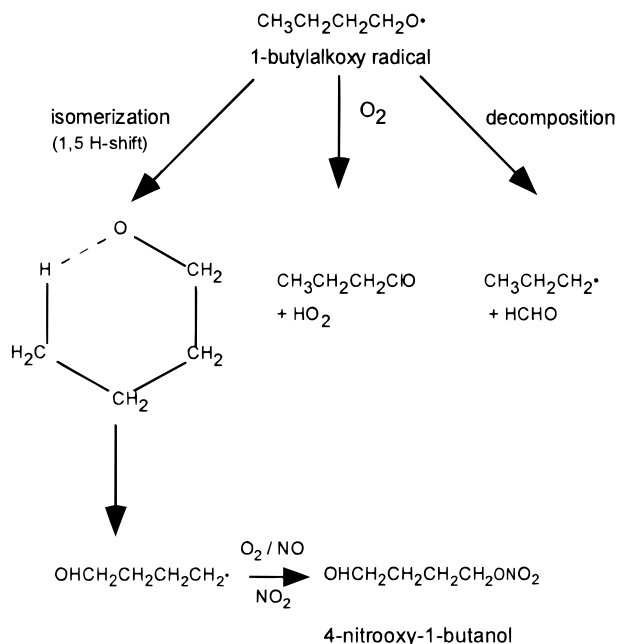


FIGURE 1. Possible degradation pathways of the 1-butylalkoxy radical: reaction with  $\text{O}_2$ , decomposition and isomerization. Isomerization leads to 4-nitrooxy-1-butanol formation (a  $\delta$ -hydroxy nitrate).

29). Recent measurements in ambient air showed that many of the hydroxy nitrates that are expected to form in the atmosphere indeed exist (27, 28). As synthetic procedures for production of  $\beta$ -hydroxy nitrates exist, most of the work reported so far has concentrated on their detection. However, there are no reports on the detection of  $\gamma$ - and  $\delta$ -hydroxy nitrates, presumably due to lack of standards for these compounds.

It is evident that one of the challenges in hydroxy nitrates research is obtaining pure samples that can be used for laboratory chemical kinetics and photochemical studies as well as standards for field measurements. Previously,  $\beta$ -hydroxy nitrates were synthesized by nitration of epoxides (30) and, to a lesser extent, using nitration by  $\text{N}_2\text{O}_5$  (29, 31), and by reactions of hydroxy halides with silver nitrate (28). These techniques are mainly limited to production of  $\beta$ -substituted compounds and result in high yields of the dinitrates in addition to the hydroxy nitrates. So far, techniques to produce and identify  $\gamma$ - and  $\delta$ -hydroxy nitrates were not available. In this study, we developed new synthetic methods to produce and purify  $\beta$ -,  $\gamma$ -, and  $\delta$ -hydroxy nitrates. With these techniques, the position of the hydroxyl group relative to the nitroxy group can be systematically varied from the  $\beta$  to the  $\gamma$  and  $\delta$  positions. We also provide information about the NMR, IR, and GC detection and identification of these compounds. A series of these compounds provides an opportunity to study systematically the structure–reactivity relationship for hydroxy nitrates and to obtain standards for field measurements.

The physical properties of the hydroxy nitrates depend on their structure. Since it is expected that  $\delta$ -hydroxy nitrates form in the atmosphere, it is important to include estimates for their atmospheric fate in models of urban and forested environments. To account correctly for  $\delta$ -hydroxy nitrates partitioning in clouds and aqueous solutions, we have measured, for the first time, the solubility of the three smallest  $\delta$ -alkyl hydroxy nitrates expected to be present in the atmosphere: 4-nitrooxy-1-butanol, 5-nitrooxy-2-pentanol, and 4-nitrooxy-1-pentanol.

## Experimental Section

**1. Synthesis of Hydroxy Nitrates.** We developed two new methods to synthesize  $\text{C}_4$  and  $\text{C}_5$  hydroxy nitrates, where the position of the OH group relative to the nitroxy group was systematically varied from the  $\beta$  to the  $\gamma$  and  $\delta$  positions. Both methods employ diols as the starting reagents for the synthesis. The basic principle underlying these techniques is the use of mild nitration reactions that differentiate between two unequivalent OH groups in the reagent diol. The techniques are not limited to  $\text{C}_4$  and  $\text{C}_5$  molecules and can be extended to larger compounds. Pure samples (>99%) of the following hydroxy nitrates were obtained: 1-nitrooxy-2-butanol, 2-nitrooxy-1-butanol, 4-nitrooxy-2-butanol, 3-nitrooxy-1-butanol, 4-nitrooxy-1-butanol, 5-nitrooxy-2-pentanol, and 4-nitrooxy-1-pentanol (2OH1C<sub>4</sub>, 1OH2C<sub>4</sub>, 2OH4C<sub>4</sub>, 1OH3C<sub>4</sub>, 1OH4C<sub>4</sub>, 2OH5C<sub>5</sub>, and 1OH4C<sub>5</sub>, using the nomenclature suggested by Schneider et al. (32)).

The synthetic procedures applied in this study are modifications of several techniques (33, 34) and therefore are described in detail.

**Method 1.** Nitration by zinc nitrate (33): 6 g of zinc nitrate hexahydrate was dissolved in 50 mL of extra dry acetonitrile. Twenty millimoles of the appropriate butanediol was added, followed by addition of 4 g (20 mmol) of DCC (dicyclohexyl carbodiimide). The reaction mixture was kept cold using an ice–water bath. It was then warmed and stirred at room-temperature overnight. The white precipitate was filtered, and the solvent was evaporated under vacuum. The hydroxy nitrates present in the solution were isolated by flash chromatography on silica gel 60 (230–400 mesh) using a mixture of ethyl acetate and hexane (2:3 ratio) as the eluent. This technique was employed for preparation of all hydroxy nitrates discussed in this work

**Method 2.** One-pot nitration using reactions with  $\text{Ph}_3\text{P-I}_2$ -imidazole followed by silver nitrate (34): 10.5 g (40 mmol) of triphenylphosphine was dissolved in 70 mL of extra dry acetonitrile. Imidazole (2.78 g, 40 mmol) was added followed by 10.14 g (40 mmol) of iodine addition. The mixture was cooled in an ice–water bath until the reagents completely dissolved. Following, 3.6 mL (40 mmol) of 1,3-butanediol was added, and the mixture was stirred for 3 h at room temperature. Finally, 20.4 g (120 mmol) of silver nitrate were added, and the reaction mixture was stirred at room-temperature overnight. The precipitate (silver iodide, yellow) was filtered, and the solvent was evaporated under vacuum. The hydroxy nitrates were isolated by flash chromatography on silica gel 60 (230–400 mesh) using a mixture of ethyl acetate and hexane (2:3 ratio) as the eluent. This technique was used for the preparation of 2OH4C<sub>4</sub>, 1OH2C<sub>4</sub>, and 2OH1C<sub>4</sub>.

**Method 3.** For comparison with previous studies,  $\beta$ -hydroxy nitrates (1OH2C<sub>4</sub> and 2OH1C<sub>4</sub>) were also prepared by nitration of 1,2-epoxybutane by fuming  $\text{HNO}_3$  in methylene chloride (30, 35).

Flash chromatography was extensively used for separating and obtaining pure samples. To simplify the detection of nitrates, we developed a simple and easy to use nitrate-sensitive technique to detect the presence of nitrates in each fraction exiting the chromatography column using thin-layer chromatography (TLC, silica gel 60 F<sub>254</sub> aluminum sheets with ethyl acetate and hexane as the solvent). The presence of the nitrates in each eluted fraction was easily monitored by observing the brown spots that appeared after spraying the TLC plate with a solution of 1-% diphenylamine in 95% ethanol and exposing it to UV or sunlight. The technique was sensitive enough to resolve different isomers. Nitrate-containing fractions were further analyzed by NMR.

All the reagents (including the reagent diols) used for the synthesis and chromatography were obtained from com-

mercial sources (at analytical grade) and were used without further purification.

$^1\text{H}$ ,  $^{13}\text{C}$  NMR, and IR spectroscopies of the pure compounds were used for the identification of the new hydroxy nitrates. The  $^1\text{H}$  NMR spectra were recorded with a 250 MHz spectrometer, and  $^{13}\text{C}$  NMR spectra were recorded with a 400 MHz spectrometer (Bruker) using  $\text{CDCl}_3$  as the solvent. In addition, the hydroxy nitrates were analyzed by gas chromatography (see below).

**2. Measurement of Henry's Law Constants. Methodology.** Henry's law constants were determined for the hydroxy nitrates synthesized in this study using a dynamic equilibrium system (16, 36). Briefly, nitrogen (99.99%) passed through a microporous PTFE membrane tube (80 cm  $\times$  0.6 cm i.d. length, GoreTex, W. L. Gore and Associates) at a known flow rate (200 or 300  $\text{cm}^3/\text{min}$ ). The tube was immersed in  $\sim 0.5$  L of a dilute aqueous solution of the compound under study ( $10^{-3}$  M). Phase equilibrium for the dissolved nitrate was achieved at the gas/water interface along the tube. Gas-phase hydroxy nitrates, at equilibrium concentrations, were collected on a charcoal trap (150-mg activated charcoal tube, Supelco Inc.). By using two charcoal traps in series, it was verified that all the hydroxy nitrates were adsorbed onto the first trap. To find the optimal operating conditions, at which the system was at equilibrium, several measurements of the Henry's law coefficients were conducted at flow rates ranging from 100 to 400  $\text{cm}^3/\text{min}$  at a constant temperature. The Henry's law coefficients were the same for that range of flows. Therefore, the working flow rates were chosen to be 200 or 300  $\text{cm}^3/\text{min}$ . For each experiment, up to  $\sim 16$  h were needed to concentrate the hydroxy nitrates on the trap.

**Solvent Extraction.** After sampling, the compounds were extracted by passing 5 mL of methanol through the charcoal trap.  $4\text{OH}2\text{C}_4$  and  $1\text{OH}3\text{C}_4$  could be immediately analyzed, while the rest of the hydroxy nitrates required additional preconcentration. The methanol was evaporated using nitrogen flow, and the remaining hydroxy nitrates were dissolved in 0.2 mL of methanol and injected into the GC.

**GC Analysis.** The extracts from the charcoal traps were analyzed using a GC (Varian 3800) equipped with an electron capture detector (ECD) and a 30-m, 0.25-mm inner diameter DB-5MS (J&W Scientific) capillary column. The column was kept at 80  $^\circ\text{C}$  for 2 min and was then brought to a final temperature of 280  $^\circ\text{C}$  at a rate of 10  $^\circ\text{C}/\text{min}$ .  $\text{N}_2$  was used as the makeup gas (29  $\text{cm}^3/\text{min}$ ) in the ECD, and He was used as the carrier gas (1  $\text{cm}^3/\text{min}$  – flow in the column and 20  $\text{cm}^3/\text{min}$  in the split vent). The injector and detector temperatures were 300  $^\circ\text{C}$ . It was verified (by the peaks shape and integral) that the compounds did not thermally dissociate in the injector. These conditions yielded the best separation and peak shapes that allowed reliable integration of peak areas. Injection volumes were always 0.5  $\mu\text{L}$ . Isomers were easily separated by this technique as can be seen in Figure 3. Separation of  $1\text{OH}2\text{C}_4$  and the  $2\text{OH}4\text{C}_4$ , however, could not be achieved using this method; therefore they could not be analyzed simultaneously.

**Calibration by Standards.** To quantitatively determine the gas-phase concentration of hydroxy nitrates, calibration curves were prepared, based on standards prepared under conditions resembling the sampling conditions. Known amounts of the nitrate were placed in a small tube connected to a charcoal trap. The tube was heated to 200  $^\circ\text{C}$  in a sand bath for  $\sim 2$  h until the compound completely evaporated and was adsorbed by the trap. The trap was then solvent-extracted and analyzed using the same procedure as above. The experiment was repeated for different concentrations, and a curve of concentration versus GC peak areas was plotted. This procedure was repeated for all the compounds. The calibration curves were linear in the concentration range

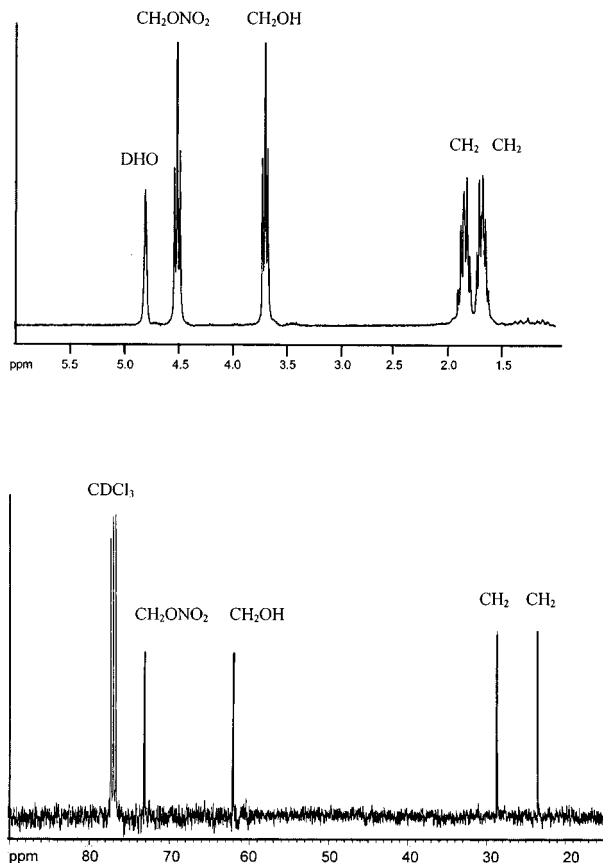


FIGURE 2.  $^1\text{H}$  (top) and  $^{13}\text{C}$  NMR (bottom) spectra of  $10\text{H}4\text{C}_4$ . The peak assignments are also given in Table 1.

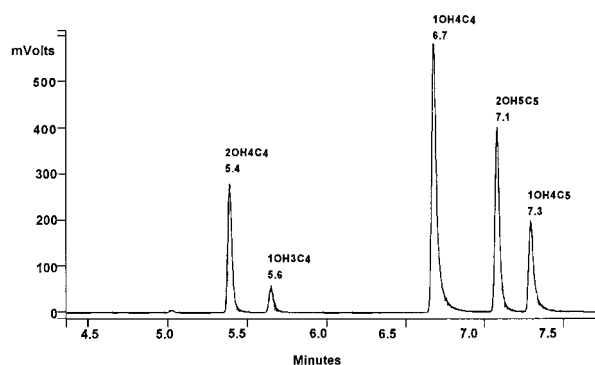


FIGURE 3. The GC chromatogram of a mixture of five hydroxy nitrates. Isomers are clearly separated enabling quantitative analysis of these compounds.

used in this study, with correlation coefficients larger than 0.95.

## Results and Discussion

**1. Synthesis of Hydroxy Nitrates.** Two new methods were used for the synthesis of the hydroxy nitrates. Method 1 enables a mild nitration of primary and secondary alcohols, while tertiary alcohols are unreactive (33). As such, the method is selective. This method was developed for alcohols, and we applied it for selective nitration of diols. Due to the mild nitration, Method 1 provides a good tool for nitration of a single hydroxy group when the hydroxy groups are not equivalent. Although it does not distinguish between primary and secondary hydroxy groups, it provides a general technique that can be applied to a wide spectrum of compounds (33). For the diols used in this study, this reaction produces

both isomers but not at a 1:1 ratio. Compared to nitration of 1,2-epoxibutane (Method 3), it was easier to separate them from the other reaction products and reagents. In the synthesis of 1OH4C<sub>4</sub>, it was very difficult to avoid formation of the dinitrate, since the two hydroxy groups in the parent 1,4-diol are equivalent. Therefore, extra care was taken to control the conditions and concentrations employed and to use the stoichiometric ratio of the reactants to reduce the possibility of double nitration. This method was used for the synthesis of the  $\delta$ -hydroxy nitrates: 1OH4C<sub>4</sub> as well as of 1OH4C<sub>5</sub> and 2OH5C<sub>5</sub> (in a 1:3 ratio). Only Method 1 enabled 1OH4C<sub>4</sub> synthesis. The nitration of 1,3- and 1,2-butandiol by this method produces a low-yield mixture of the two isomers, with the nitration of the primary hydroxy group being dominant.

Method 2 provides a good tool for selective nitration when the two OH groups in the reagent diol are not equivalent. The reaction proceeds via the formation of an iodide compound that can be easily nitrated by silver nitrate.



In this technique, nitration of primary OH groups of an alcohol is easier than nitration of secondary groups (34); thus, this is a selective technique. Using this method, 2OH4C<sub>4</sub> was synthesized with ~50% yield. As expected, the substitution on the primary hydroxy group was the predominant nitration site (~65%). Unexpectedly, though, using the same conditions, the nitration of 1,2-butanediol led to formation of 1OH2C<sub>4</sub> predominately with ~20% yield, and nitration of 1,4-pentanediol did not produce the  $\delta$ -hydroxy nitrate but only the dinitrate. Therefore, it is not always easy to predict with this method which hydroxy group will be predominantly nitrated.

Nitration of epoxides using Method 3 leads to a 1:1 mixture of the two isomers, (estimated by GC analysis) with a yield of ~70%. However, the other reaction products are not easily separated from the hydroxy nitrates.

The mild nitration techniques presented here provide tools for synthesis of more complex multifunctional nitrates. Such nitrates are expected to form in the atmosphere from the degradation of various natural hydrocarbons, such as the isoprene nitrates. For example, we applied Method 1 to synthesize the 4-nitrooxy-3-hydroxy-1-butene from 1-butene-3,4-diol without affecting the double bond.

**NMR Assignment.** There is little information available in the literature about the NMR characterization of hydroxy nitrates. We used the NMR spectra of the parent diols combined with the data presented by Muthuramu et al. (30) to identify the synthesized hydroxy nitrates and to assign the spectra to the specific structures. <sup>13</sup>C and <sup>1</sup>H NMR spectra of 1OH4C<sub>4</sub> are shown in Figure 2, and the peak assignments are given in Table 1 (including the <sup>13</sup>C NMR). In general, the chemical shifts of protons near the nitrate group are large compared to similar oxygenated compounds. This is attributed to the electron withdrawing character of the nitrooxy group. The chemical shift of the proton adjacent to the hydroxy group does not change upon nitration of the other hydroxy group in the parent diol. It can also be seen in Table 1 that the chemical shift due to the nitrooxy group is smaller when it is located on the terminal carbon atom. The hydroxyl proton signal was also observed as a broad peak, which disappeared when D<sub>2</sub>O was used. In the chiral hydroxy nitrates, complex splitting patterns were observed, due to the numerous interactions caused by the asymmetric center, which make the protons unequivalent.

**IR Identification.** Additional evidence for the existence of hydroxy nitrates was obtained by infrared spectroscopy

TABLE 1. <sup>1</sup>H NMR and <sup>13</sup>C NMR Assignment for the Hydroxy Nitrates Synthesized in This Study<sup>a</sup>

compound	<sup>1</sup> H chemical shift (ppm)	<sup>13</sup> C chemical shift (ppm)
1OH2C <sub>4</sub>	1.02 (t, <i>J</i> = 7.5), CH <sub>3</sub>	9.39, CH <sub>3</sub>
	1.73, CH <sub>2</sub>	22.2, CH <sub>2</sub>
	5.07 (m), CHONO <sub>2</sub>	85.97, CHONO <sub>2</sub>
	3.72–3.88 (dq), CH <sub>2</sub> OH	62.09, CH <sub>2</sub> OH
2OH1C <sub>4</sub>	0.99 (t, <i>J</i> = 7.5), CH <sub>3</sub>	9.75, CH <sub>3</sub>
	1.55, CH <sub>2</sub>	26.31, CH <sub>2</sub>
	3.87 (m), CHOH	69.57, CHOH
	4.3–4.5 (dq), CH <sub>2</sub> ONO <sub>2</sub>	76.37, CH <sub>2</sub> ONO <sub>2</sub>
1OH3C <sub>4</sub>	1.42 (t, <i>J</i> = 6.3), CH <sub>3</sub>	18.67 (t, <i>J</i> = 6.3), CH <sub>3</sub>
	5.32 (m), CHONO <sub>2</sub>	78.53 (m), CHONO <sub>2</sub>
	1.88 (m), CH <sub>2</sub>	36.65 (m), CH <sub>2</sub>
	3.76 (m), CH <sub>2</sub> OH	58.42 (m), CH <sub>2</sub> OH
2OH4C <sub>4</sub>	1.26 (d, <i>J</i> = 6.2), CH <sub>3</sub>	23.87, CH <sub>3</sub>
	3.97 (m), CHOH	64.55, CHOH
	1.84 (m), CH <sub>2</sub>	35.70, CH <sub>2</sub>
	4.61 (m), CH <sub>2</sub> ONO <sub>2</sub>	70.48, CH <sub>2</sub> ONO <sub>2</sub>
1OH4C <sub>4</sub>	3.71 (t, <i>J</i> = 6.0), CH <sub>2</sub> OH	61.98, CH <sub>2</sub> OH
	1.71 (m), CH <sub>2</sub>	23.44, CH <sub>2</sub>
	1.82 (m), CH <sub>2</sub>	28.61, CH <sub>2</sub>
	4.51 (m), CH <sub>2</sub> ONO <sub>2</sub>	73.09, CH <sub>2</sub> ONO <sub>2</sub>
1OH4C <sub>5</sub>	1.37 (d, <i>J</i> = 6.3), CH <sub>3</sub>	18.38, CH <sub>3</sub>
	5.12 (m), CHONO <sub>2</sub>	81.10, CHONO <sub>2</sub>
	1.7–1.9, CH <sub>2</sub>	30.42, CH <sub>2</sub>
	3.66, (m) CH <sub>2</sub> OH	28.02, CH <sub>2</sub>
2OH5C <sub>5</sub>	1.21 (d, <i>J</i> = 6.3), CH <sub>3</sub>	23.18, CH <sub>3</sub>
	3.84 (m), CHOH	67.31, CHOH
	1.7–1.9, CH <sub>2</sub>	23.62, CH <sub>2</sub>
	4.48, (m) CH <sub>2</sub> ONO <sub>2</sub>	34.84, CH <sub>2</sub>
		73.29, CH <sub>2</sub> ONO <sub>2</sub>

<sup>a</sup> The results are reported in ppm relative to tetramethylsilane. All NMR spectra were taken with CDCl<sub>3</sub> as a solvent: m, multiplet; t, triplet; dq, doublet quartet; *J* is the splitting in Hz.

TABLE 2. Infrared Spectra of a Few Hydroxy Nitrates Synthesized in This Study (cm<sup>-1</sup>)

	O–N stretch	–NO <sub>2</sub> symmetric stretch	–NO <sub>2</sub> asymmetric stretch	hydroxy group
2OH1C <sub>4</sub>	859.7	1276.6	1634.0	3600
1OH2C <sub>4</sub>	859.6	1276.6	1625.5	3608
2OH4C <sub>4</sub>	868.1	1285.1	1632.7	3617
1OH4C <sub>4</sub>	865.8	1281.5	1630	3617

by detection of both nitrooxy and hydroxyl groups. The results and assignment of these measurements are given in Table 2.

**GC Detection.** All hydroxy nitrates synthesized in this study were detected and identified using conventional GC methods. Both an ECD and FID were employed for quantitative detection. The ECD was found to be more accurate due to its higher sensitivity to the nitrooxy group and its insensitivity to the solvent used. For the  $\beta$ -,  $\gamma$ -, and  $\delta$ -hydroxy nitrates, isomers containing a terminal ONO<sub>2</sub> group always eluted before those with the nitrooxy group inside the chain (see Figure 3 and Table 3). The good separation between the nitrates allowed reliable integration of the peak areas.

**2. Solubility Measurements.** The air/water partition is one of the main atmospheric heterogeneous loss processes of hydroxy nitrates; therefore Henry's law coefficients were determined for the synthesized compounds. The Henry's law coefficient is defined as  $H = [X]/P_x$ , where [X] is the aqueous phase concentration (Molar) and  $P_x$  is the partial pressure (atm).

The Henry's law coefficients of all the hydroxy nitrates synthesized in this study were determined at  $291 \pm 2$  K and are presented in Table 3. The Henry's law coefficients of

TABLE 3. Measured Henry's Law Coefficients for Hydroxy Nitrates Synthesized in This Study at  $291 \pm 2$  K. the Error Bars Represent the Standard Deviation ( $1\sigma$ ) from the Average of 4–6 Measurements

compound	MW (AMU)	retention time (min)	H (M/atm)	lit. value ( $1\theta$ )
2OH1C <sub>4</sub>	135	5.15	9000 ± 2700	12 400 ± 4500
1OH2C <sub>4</sub>	135	5.45	8900 ± 2400	13 100 ± 7500
2OH4C <sub>4</sub>	135	5.30	13 600 ± 1300	
1OH3C <sub>4</sub>	135	5.60	14 000 ± 4400	
1OH4C <sub>4</sub>	135	6.80	29 000 ± 5400	
2OH5C <sub>5</sub>	149	7.05	36 700 ± 2000	
1OH4C <sub>5</sub>	149	7.20	20 500 ± 4600	

1OH2C<sub>4</sub> and 2OH1C<sub>4</sub> measured here are in agreement with those calculated based on  $\Delta H_{\text{sol}}$  and  $\Delta S_{\text{sol}}$  measured by Shepson et al. (16) within the combined errors.

The errors in the Henry's law coefficient measurement result mainly from the manual injection of the sample to the GC, from the evaporation procedure used, from incomplete recovery from the traps, and from wall losses on the tubing. To check for the recovery efficiency from the charcoal traps, an additional amount of solvent was passed through the trap after the extraction of the nitrates and injected to the GC. Within the experimental signal-to-noise (1:30), no signal was observed from the second injection, implying that only a negligible amount of the nitrates may exist in the second extract. Wall losses can occur in the dynamic equilibrium system itself. To minimize the error due to this process, the apparatus was extensively washed with water after each experiment, and blank samples were injected to check that there are no remains in the tubing. It is also assumed that the hydroxy nitrates adsorb to the walls of the apparatus mainly via their functional groups. Therefore no correlation between the wall loss and chain length is expected. Finally, some error may result from the calibration curves themselves. All the Henry's law coefficients given in Table 3 are an average of 4–6 measurements. The quoted error represents 1 SD.

As was shown for dinitrates (37) and for  $\beta$ -hydroxy nitrates (16, 28), the presence of a second polar group increases the nitrate's solubility in water, with respect to the alkyl nitrates of comparable size. The solubility of hydroxy nitrates in water is affected by their chemical structure; it decreases with increasing length of the hydrocarbon chain and increases with increasing the distance between the two functional groups. This behavior can be understood by the availability of the hydroxy group to hydrogen bonding with the surrounding water molecules, since it is less hindered by the nitrooxy group. In addition, the distribution of two polar functional groups along the hydrocarbon chain effectively reduces the length of the hydrophobic part of the molecule.

There is little difference between the solubility of the two isomers of each species. The reasons for the large differences in the solubility constants of 1OH4C<sub>5</sub> and 2OH5C<sub>5</sub> are not currently known. Based on the analogy with diols and dinitrates we expect the solubility of both to be lower than that of 1OH4C<sub>4</sub>, as is observed for 1OH4C<sub>5</sub>. Such unexplained behavior was also observed for some hydroxy nitrates and dinitrates (16, 29, 37).

**Atmospheric Implications.** The presence of the hydroxy group enhances the solubility of the hydroxy nitrates compared to alkyl nitrates of comparable size by a few orders of magnitude. It is therefore expected that they will partition into clouds and fog droplets and that wet deposition may be an efficient mechanism for nitrogen oxides removal from the troposphere. This is in contrast to alkyl nitrates, where heterogeneous processes are not expected to play a significant role in their atmospheric processing. The fraction of a specific

compound dissolved in typical cloudwater droplets,  $f_x$ , can be calculated using eq I:

$$f_x = \frac{L_{wc}}{(HRT)^{-1} + L_{wc}} \quad (\text{I})$$

where  $L_{wc}$  is the dimensionless liquid water content,  $R$  is the gas constant, and  $T$  is the temperature (K). The liquid water content was taken to be  $L = 4.2 \times 10^{-7}$  (cm<sup>3</sup> of liquid H<sub>2</sub>O/cm<sup>3</sup> air) typical of a cloud (38). The solubility constants at temperatures other than 291 K (at which they were measured in this study) are calculated assuming  $\Delta H^{\circ} = -79$  kJ/mol for the solvation energy (16). This is an average value which was measured for C<sub>4</sub> $\beta$ -hydroxy nitrates (16).  $H$  was calculated by eq II

$$H(T) = H_{291} e^{-\Delta H^{\circ}/R(1/T - 1/291)} \quad (\text{II})$$

At  $T = 283$  K (typical of cumulus clouds), 20–50% of the C<sub>4</sub> hydroxy nitrates are dissolved in cloudwater assuming only physical solubility. The  $f_x$  values for 291 and 283 K are shown in Table 4. Note that the fraction  $f_x$  is determined both by the solubility and the liquid water content of the cloud. In general, the  $\gamma$ - and  $\delta$ -nitrooxy butanols are more soluble in liquid water compared to the  $\beta$ -nitrooxy butanols, due to the larger distance between the hydroxy and the nitrooxy groups. Our results also show that isomers have similar solubility, and therefore models can treat these isomers with the same solubility.

The large fraction of dissolution calculated above implies that wet deposition may be an efficient mechanism for the removal of hydroxy nitrates from the atmosphere in wet environments. It is possible to estimate the removal rate of hydroxy nitrates by assuming a first-order loss mechanism. The first-order removal constant by wet deposition,  $k_{wd}$ , is given by (39)

$$k_{wd} = \frac{R_r E e^{(-z/Z_x)}}{Z_x [(HRT)^{-1} + L_{wc}} \quad (\text{III})$$

where  $R_r$  is the assumed annual rainfall rate (1 m/yr),  $E$  is an enhancement factor due to droplet evaporation (assumed to be 1.33 (39)),  $z$  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) (39),  $L_{wc}$  is the dimensionless liquid water content of the cloud ( $4.2 \times 10^{-7}$ ), and  $H$  is the Henry's law constant. The annual rainfall varies considerably from one environment to another, but the assumptions made here enable estimating the time scale of this removal process. Based on these assumptions, the wet deposition lifetime for hydroxy nitrates is 2–7 days, depending on the species (Table 4).

The high yield of hydroxy nitrates formation by isoprene and terpene oxidation implies that the efficient removal of nitrogen oxides from the atmosphere by deposition of multifunctional nitrates, such as those studied here, may be an important mechanism for nitrogen deposition in forest environments (40, 41). The higher efficiency of wet deposition of  $\gamma$ - and  $\delta$ -hydroxy nitrates calls for a thorough examination of their production yields in the photochemical degradation of alkanes, alcohols, and naturally emitted compounds.

It is difficult to quantify the other loss mechanisms of hydroxy nitrates from the atmosphere. Unfortunately, there are no measurements of the rate coefficients for reactions of the OH radical with hydroxy nitrates. Recent measurements of the OH reaction with alkyl nitrates indicate that the reaction proceeds by hydrogen atom abstraction (10, 42). The temperature-dependent rate coefficient of ethyl nitrate follows a two-exponential form which reflects the contribution of

TABLE 4. Calculated Henry's Law Coefficient at 283 K and of the Wet Deposition Rate Coefficient at 283 K<sup>a</sup>

compound	H (291 K) (M atm <sup>-1</sup> )	H (283 K) (M atm <sup>-1</sup> )	f <sub>x</sub> (291 K)	f <sub>x</sub> (283 K)	k <sub>wd</sub> (s <sup>-1</sup> )	k <sub>OH</sub> (cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	estimated lifetime without washout (days)
2OH1C <sub>4</sub>	9.00 × 10 <sup>3</sup>	2.27 × 10 <sup>4</sup>	0.08	0.18	1.7 × 10 <sup>-6</sup>	3.0 × 10 <sup>-12</sup>	4.6
1OH2C <sub>4</sub>	8.90 × 10 <sup>3</sup>	2.24 × 10 <sup>4</sup>	0.08	0.18	1.7 × 10 <sup>-6</sup>	1.3 × 10 <sup>-12</sup>	7.0
2OH4C <sub>4</sub>	1.36 × 10 <sup>4</sup>	3.43 × 10 <sup>4</sup>	0.12	0.25	2.4 × 10 <sup>-6</sup>	8.5 × 10 <sup>-12</sup>	2.2
1OH3C <sub>4</sub>	1.40 × 10 <sup>4</sup>	3.53 × 10 <sup>4</sup>	0.12	0.26	2.4 × 10 <sup>-6</sup>	4.5 × 10 <sup>-12</sup>	3.6
1OH4C <sub>4</sub>	2.90 × 10 <sup>4</sup>	7.31 × 10 <sup>4</sup>	0.22	0.42	4.0 × 10 <sup>-6</sup>	5.8 × 10 <sup>-12</sup>	3.0
2OH5C <sub>5</sub>	3.67 × 10 <sup>4</sup>	9.25 × 10 <sup>4</sup>	0.26	0.47	4.5 × 10 <sup>-6</sup>	9.1 × 10 <sup>-12</sup>	2.1
1OH4C <sub>5</sub>	2.05 × 10 <sup>4</sup>	5.17 × 10 <sup>4</sup>	0.17	0.33	3.2 × 10 <sup>-6</sup>	5.7 × 10 <sup>-12</sup>	3.0

<sup>a</sup> Assuming an annual rainfall of 1 m/year. Also shown are calculated rate coefficients for the reaction with the OH radical based on the estimation method of Kwok and Atkinson (45). The loss rate due to reaction with OH is calculated assuming a daytime OH concentration of 10<sup>6</sup> cm<sup>-3</sup>. The photolysis rate coefficients are assumed to be 1 × 10<sup>-6</sup> s<sup>-1</sup>.

primary and secondary H atom abstraction (10). In the reaction of 2-propyl nitrate with OH, the contribution of the tertiary H atom becomes more significant at lower temperatures, leading to a smaller temperature dependence. The recent room-temperature measurements as well as the temperature-dependent rate coefficients (10, 42, 43) are substantially different than those measured previously (44). The hydroxy nitrates studied here contain more than two different hydrogen atoms. In contrast to alkyl nitrates, where the O–NO<sub>2</sub> group slows the H atom abstraction, the hydroxy group is expected to accelerate it. Therefore, it is difficult to estimate the rate coefficients for reactions of hydroxy nitrates with the OH radical based solely on alkyl nitrates reactivity. Using the structure–reactivity estimation method of Kwok and Atkinson (45), the rate coefficients of hydroxy nitrates with the OH radical can also be estimated and are shown in Table 4. Assuming a daytime OH concentration of 1 × 10<sup>6</sup> cm<sup>-3</sup>, the lifetimes of the compounds range from 2.5 to 14 days (see Table 4). The presence of the OH group, and the larger distance from the nitrooxy group especially in  $\gamma$ - and  $\delta$ -hydroxy nitrates, accelerates the reaction with OH compared with the alkyl nitrates. These estimates suggest that the structure of hydroxy nitrates will have a large effect on its reactivity and therefore on the lifetime of a given species.

Absorption cross-sections for alkyl nitrates have been measured in a few studies (46–50). To the best of our knowledge, only one measurement exists for  $\beta$ -hydroxy nitrate, that of (nitrooxy)ethanol (47). Roberts and Fajar (47) found that (nitrooxy)ethanol has a cross-section approximately a factor of 3 lower than that of methyl nitrate at 300 nm. Assuming that saturated hydroxy nitrates have lower photolysis rate coefficients than the alkyl nitrates ( $J \approx 1 \times 10^{-6} \text{ s}^{-1}$ , 30°N, summer, overhead ozone abundance of 305 DU for a US standard atmosphere (49)) and have the same quantum yield (unity), the photolytic lifetime of small hydroxy nitrates is estimated to be on the order of 12 days. With increasing chain length, the photolytic lifetime may be shorter, as is the trend for alkyl nitrates.

The overall atmospheric lifetime of hydroxy nitrates due to photolysis and OH reaction is therefore estimated to be 2–7 days. Due to efficient washout by rain, the lifetime may be shorter in heavy rains, and these additional processes may be rendered unimportant. In drier environments, photolysis and reaction with the OH radical are expected to be the main loss mechanism of hydroxy nitrates. While photolysis is the main loss mechanism for alkyl nitrates (49), the OH reactions of hydroxy nitrates will be more significant due to the enhancement of the reactivity caused by the presence of the hydroxy group and due to the lower photolysis rates. Since these compounds are fairly nonvolatile and soluble, dry deposition by aerosol particles and ground and vegetation surfaces is also possible and would serve to reduce their atmospheric lifetime. Knowledge of the appropriate parameters of hydroxy nitrates photochemical reactions (such

as rate coefficients, absorption cross sections, quantum yields) is necessary to calculate the atmospheric lifetime of these species. The lifetime estimated here (> 2 days) implies that these compounds may be important NO<sub>x</sub> reservoir species and can survive long range transport in the troposphere, especially in dry environments.

Although it is expected that the ambient concentrations of hydroxy nitrates will decrease during rainy periods, hydroxy nitrates have still been detected during rain events (28). This observation has led to the suggestion that their concentration is not greatly influenced by wet deposition (28). Alternatively, it may be an indication of the high flux of hydroxy nitrates into the atmosphere, especially in urban areas, which can sustain detectable amounts even in wet environments. This observation is challenging and requires additional field measurements under different conditions.

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